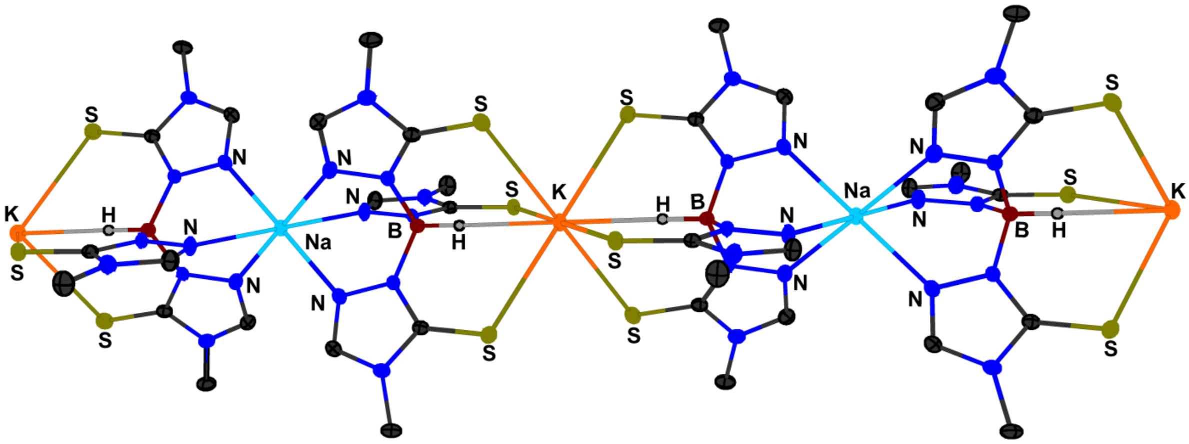
Boron-centred soft ligands and their complexes with Na, K, Bi(III) and Pb(II) ions - An approach towards inexpensive luminescent materials



Muhammad Imran

-2014-

Boron-centred soft ligands and their complexes with Na, K, Bi(III) and Pb(II) ions - An approach towards inexpensive luminescent materials

Dissertation
zur Erlangung des
naturwissenschaftlichen Doktorgrades (Dr. rer. nat.)
der Fakultät für Chemie
der Universität Bielefeld

vorgelegt von

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Chakwal, Pakistan

-2014-

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Date of PhD defense: February 14th, 2014
Date of award of PhD degree: February 14th, 2014

This research work was carried out from October 2010 to October 2013 under the supervision of Prof. Dr. Norbert W. Mitzel, Professor of Inorganic and Structural Chemistry, Faculty of Chemistry, Bielefeld University, Germany

My research supervisor

Prof. Dr. Norbert W. Mitzel

I am deeply obliged for providing me a place in your laboratory, motivating me towards heavy metals (bismuth and lead) chemistry, training me to improve my scientific interpretation and writing skills.

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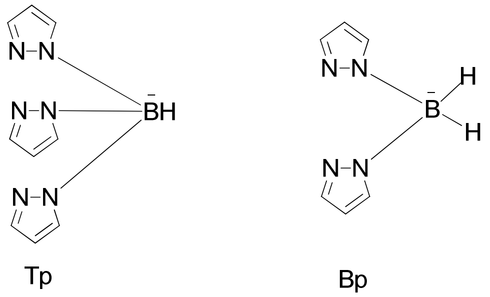
Chapter-1

Introduction and background

1.1. Boron-centred ligands

Trofimenko in 1966 reported a versatile class of ligands having pyrazole units attached to the central boron atom and represented by the general formulae $[H_nB(pz)_m]^-$ (n = 0 – 3, m = 1 – 4, pz = pyrazole unit). These ligands are referred as poly(pyrazolyl)borates or Trofimenko ligands.[1] Two main types of these ligands are tri- and di-substituted boron-centred ligands with general formulae $HB(pz)_3$ and $H_2B(pz)_2$, respectively (Scheme 1.1)



Scheme 1.1. Tri- and di-substituted boron-centred ligands based on pyrazole units.

Later on similar ligands involving other heterocyclic units (imidazole, triazole etc.) have been introduced. Therefore instead of poly(pyrazolyl)borate, the general term boron-centred ligands is more appropriate for their description. During the present work described in this thesis, we have used different heterocycles bearing soft donor atoms to produce similar ligands, therefore we employ the term boron-centred soft ligands.

As earlier reported, the tri-substituted poly(pyrazolyl)borate ligands (Tp) exert their coordination to metal atosms through nitrogen atoms from two pyrazole rings while the third pyrazole unit coordinates like the sting of a scorpion (Figure 1.1). Due to this analogy, these ligands were also named as scorpionate ligands.[2-5] But the term scorpionate ligand has also its limitation and can only be used when such ligands coordinate in tridentate manner in accordance with the analogy of a scorpion.

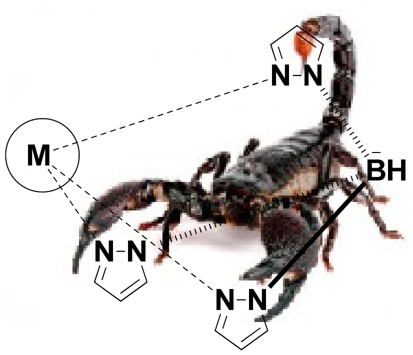


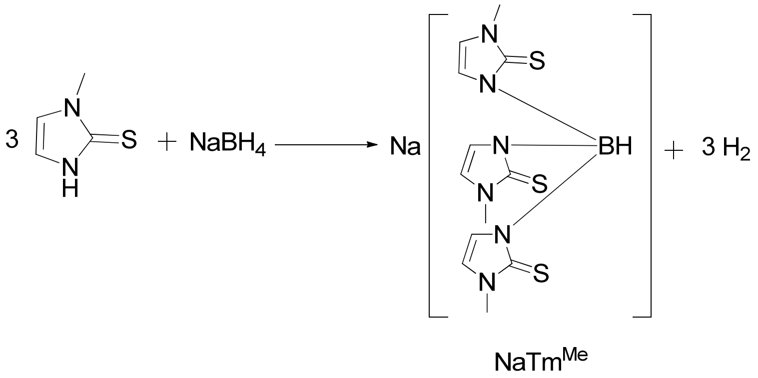
Figure 1.1. Pyrazol-based scorpionate ligand.[6]

A large number of modifications at the 3 and 5 position of the pyrazolyl ring as well as at the central boron atom have been described. Boron has been replaced by carbon,[7-10] phosphorus,[11-13] gallium and indium,[14] aluminium, tin and germanium,[15] nitrogen[16,17] and silicon.[18,19] Inspite of several modifications, the most widely used class of these ligands is boron-centred tris(pyrazolyl)borate derivatives.[1] The coordination chemistry of these ligands with a wide range of metals have been explored.[3,20-32] Major areas other than structure and reactivity, where these tri-substituted boron-centred ligands (hydridotris(pyrazolyl)borates) have been widely studied are catalysis[33] and bio-inorganic chemistry.[34,35] In bio-inorganic chemistry successful models of zinc[31,36-39] and copper[40,41] containing proteins using these tri-substituted systems have been developed.

1.2. Boron-centred soft ligands

1.2.1. Tri-substituted boron-centred soft ligands

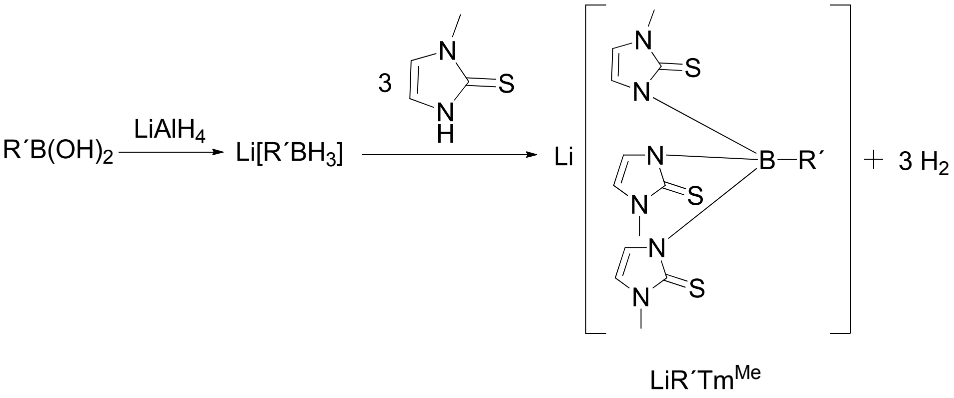
The well-known Tp-based ligand systems (described above) possess hard donor sites. Reglinski et al. reported the first soft analogue known as sodium hydrotris(methimazolyl)borate [NaTm^{Me}].[42] [Tm^{Me}]$^-$ was *in-situ* produced by reacting methimazole with sodium borohydride via Trofimenko's protocol and was isolated in the form of [NaTm^{Me}].[42] Later on, [Tm^{Me}]$^-$ was also isolated in the form of lithium and potassium salts.[43-47]



Scheme 1.2. Synthesis of sodium hydrotris(methimazolyl)borate (NaTm^{Me}).

The synthesis of NaTm^{Me} was also attempted by some researchers in high boiling solvents. However the resulting products were di-substituted species [Bm]$^-$ instead of [Tm^{Me}]$^-$.[26,44,48,49] While discussing NaTm^{Me} as soft analogue, it is necessary to mention here, tris(methylthioalkyl)borates (RTt$^-$) reported by Riordan et al. in 1994.[50] They reacted an excess of $LiCH_2SCH_3$ with $BF_3 \cdot Et_2O$ in THF at –78 °C to produce tris(methylthioalkyl)borate (RTt$^-$) followed by its precipitation as Bu_4N(RTt) salt. Tris(methylthioalkyl)borate was also reported by these authors as soft analogue of poly(pyrazoly)borates but it contains no heterocyclic sulphur donor units.

Large numbers of modifications were done on NaTm^{Me} to introduce more boron-centred soft ligands. For instance, several derivatives of NaTm^{Me} were prepared by the replacement of an *N*-methyl group with other alkyl/aryl groups like Et,[51] *t*-Bu,[52,53] Cy,[54] Ph,[44] *p*-tolyl,[55,56] *o*-tolyl,[54] mesityl[52] etc. A further variant of the replacement of the *N*-methyl group by Santos et al. was placing a biologically active group (piperazine) at the 5-position of the heterocycle to produce Na[H_2B(Tim^{Me,pip})$_2$]$_3$.[57] The same group further altered [Tm^{Me}]$^-$ ligand by replacing B–H unit with other groups as illustrated in Scheme 1.3.



Scheme 1.3. Synthesis of LiR´Tm^{Me} (R´ = Me, Ph).

1.2.2. Boron-centred soft vs hard donor ligands

Boron centred soft ligands are considered to be advantageous over their hard analogues pyrazolylborates. These ligands not only stabilize low-valent, electron-rich metals ions,[58,59] but also increase their susceptibility for oxidation thus giving rise to metal complexes with unusual oxidation states. The soft ligands exert weaker field strengths compared to hard ligands as established in the examples of [Fe(Tm^{Me})$_2$][60] (Tm = hydrotris(methimazolyl)borate) and [FeTp^{Me})$_2$].[61] Moreover, these ligands have twisting and flexibility capabilities to accommodate metal ions of larger ionic radii and show variable coordination modes such as monodentate (κ^1-*S*), bidentate (κ^2-*S*,*S* or κ^2-*S*,*H*) and tridentate (κ^3-*S*,*S*,*S* or κ^3-*S*,*S*,*H*).[62,63]

1.2.3. Janus scorpionates

Janus scorpionates are another category of tri-substituted boron-centred soft ligands. Silva et al. in 2006[64] and 2008[65] have synthesized first and second generation Janus scorpionate ligands via Trofimenko`s protocol. Their name “Janus” was derived from Roman mythology: the god of gates and doors, Janus has a two-faced figure.[64,65] These are also closely related to Bailey’s[66] and Marchiò’s ambidentate thioxotriazolylborate[67] and are also known as hybrid of Trofimenko’s tris(pyrazolyl)borate[1] and Reglinski’s tris(mercaptoimidazolyl)borate.[42] The characteristic feature of these ligands is the placement of a boron-hydride moiety (B–H) towards the soft side defined by the three sulphur atoms (Figure 1.2). Silva et al. pointed out that “this placement restricts the repulsions between the lone pairs of electrons at the thione donor sites and the π-electrons of the attached ring”.[64,65]

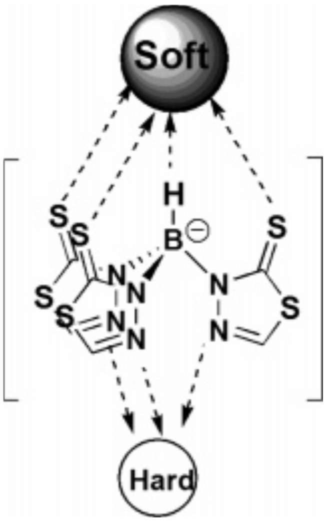
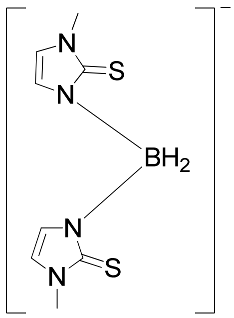


Figure 1.2. Typical coordination behaviour of a Janus scorpionate ligand.[64]

1.2.4. Di-substituted boron-centred soft ligands

Di-substituted boron-centred soft ligands are generally characterized by the presence of BH_2 unit. Most of them have been synthesized by refluxing the heterocycles and MBH_4 in 2:1 ratio in suitable solvents like tetrahydrofuran, toluene etc. Hydrobis(methimazolyl)borate $[Bm]^-$ (Scheme 1.4), a di-substituted boron-centred soft ligand[68] is considered to be the first soft congener of dihydrobis(pyrazolyl)borate (Bp).[1] Bm is capable of providing bidentate or tridentate coordination modes via its thione donor units and agostic hydrogen bonding.[26] Some other notable examples of di-substituted boron-centred soft ligands include dihydrobis(2-thiopyridone)borate (Bmp),[69] dihydrobis(thioxotriazolyl)borate(Bt),[70,71] dihydrobis(1-methyl-5-thiotetrazolyl)-borate (Btt^{Me}).[72] Among these, hydrobis(methimazolyl)borate $[Bm]^-$ is the most commonly used.[68] It finds applications for radiopharmaceuticals as well as in bio-inorganic chemistry. In contrast to their tri-substituted boron-centred soft ligands, these ligands have the ability to establish B–H···M interactions, resulting in some cases the formation of metalloboranes.[72–75]



Bm

Scheme 1.4. Constitution of hydrobis(methimazolyl)borate $[Bm]^-$.

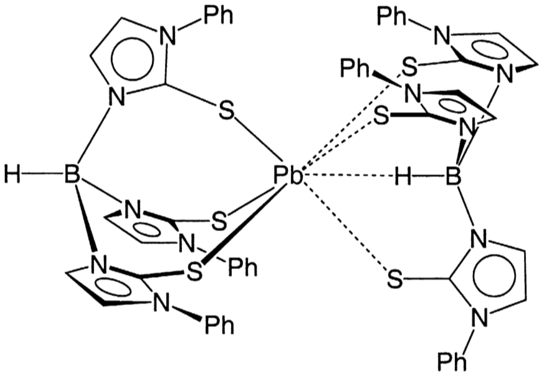
1.3. Chemistry of bismuth with boron-centred soft ligands

An accessible approach through literature and a search through crystal structure data bases reveals no bismuth complex with hydrotris(pyrazolyl)borate(Tp), earlier reported by Trofimenko in 1966. Reger in his review stated that the p block element complexes with Tp ligands are somewhat thermally unstable and extremely moisture sensitive, therefore their synthesis is difficult.[76] However, after first report on hydrotris(methimazolyl)borate (Tm^{Me}) in 1996, few bismuth complexes have been prepared and well characterized. A year-wise brief description of these complexes is described below. Spicer et al. (1999)[77] has reported the bismuth complex $[Bi(Tm^{Me})_2]^+$ (Tm^{Me} = hydrotris(methimazolyl)borate) which is remarkably stable and possesses octahedral geometry with a ligand motif (κ^3-*S,S,S*). Reglinski et al. (1999)[78] has obtained a dimeric complex $[(Tm)BiCl(\mu\text{-}Cl)]_2$ by the treatment of $BiCl_3$ with 3 eq of NaTm. The complex has distorted octahedral geometry. In the same effort, they also reacted $BiCl_3$ with 2 eq of NaTm followed by the addition of NaTp (sodium hydrotris(pyrazoly)borate) and have reported an unusual salt $[(Tm)_2Bi][(Tp)_2Na]$. Bailey et al. (2001) has reported a bismuth complex $[Bi(Tt)_2]Cl$ by the treatment of bismuth trichloride with sodium hydridotris(thioxotriazolyl)borate (NaTt). The complex is octahedral with the usual coordination mode of the ligand (κ^3- *S,S,S*). Furthermore the lone pair on the bismuth atom is stereochemically almost inactive.[66] Marchiò et al. (2003)[79] have prepared $[Bi(Tr^{Et,Me})_2]NO_3$ ($Tr^{Et,Me}$ = hydrotris(4-ethyl-3-methyl-5-thioxo-1,2,4-triazolyl)borate) with a similar coordinative situation as found in $[Bi(Tt)_2]Cl$.[66] A year later in 2004, Marchiò et al.[80] reported another bismuth complex $[Bi(Tr^{Ph,Me})_2]NO_3$

($Tr^{Ph,Me}$ = hydrotris(1,4-dihydro-3-methyl-4-phenyl-5-thioxo-1,2,4-triazolyl)borate) with a similar coordinative situation as found in $[Bi(Tr^{Et,Me})_2]NO_3$[79] and $[Bi(Tt)_2]Cl$.[66] Shimada et al. (2004)[81] communicated the preparation of a trinuclear organo-bismuth complex $[(Me_2Bi)_3(Tm^{tBu})_2]^+[Me_2BiCl_2]^-$ (Tm^{tBu}, hydrotris(2-mercapto-1-*tert*-butylimidazolyl)borate) by reacting $[Na(Tm^{tBu})]$ with Me_2BiCl in 1:1 ratio. In their same study, a parallel effort of the reaction between $BiCl_3$ and $[Na(Tm^{tBu})]$ in 1:1 ratio afforded a bridged complex $[Bi(Tm^{tBu})Cl(\mu\text{-}Cl)]_2$. Both the bismuth complexes $[(Me_2Bi)_3(Tm^{tBu})_2]^+[Me_2BiCl_2]^-$ and $[Bi(Tm^{tBu})Cl(\mu\text{-}Cl)]_2$ are air stable. Shu et al. (2005)[82] prepared $Bi[HB(Tim^{Ph})_3](NO_3)_2$ (Tim^{Ph} = hydro[tris(3-phenyl-2-thioimidazol-1-yl)]borate) which exhibits a distorted pentagonal pyramidal geometry defined by three sulfur atoms of $[Tim^{Ph}]^-$ and three oxygen atoms, stemming from mono- and bi-dentate nitrate ligands. Spicer et al. (2006)[83] carried out reactions of BiX_3 (X = I^-, NO_3^-) with $NaTm^{Me}$ resulting in two complexes $[Bi(\kappa^3\text{-}Tm^{Me})(\kappa^1\text{-}Tm^{Me})I]$ and $[Bi(Tm^{Me})_2]NO_3$ respectively. The latter contains a regular S_6 coordination sphere (ligand mode κ^3-*S,S,S*) and a stereochemically inactive lone pair on the bismuth atom.

1.4 Chemistry of lead with boron-centred soft ligands

During the last few decades, the coordination chemistry of lead(II) with hetero donor ligands remained an active area of research due to their interesting modes of bonding. A wide range of coordination numbers (1 – 12) for Pb(II) in such complexes has been reported.[84] Lead(II) complexes have not only bio-relevant importance but have also been employed as precursors for bulk or nanostructured PbS and PbSe materials for optoelectronics.[85] It has been reported that the 6s electron pair and several other factors such as the hard or soft nature of ligands, attractive or repulsive forces etc. affect the geometries around lead(II) centres.[86] Despite great efforts in the field of coordination chemistry of Pb(II) with S donor ligands in the past, rational design and tuning of the ligand structure to satisfy the coordination preferences and requirements of a Pb(II) atom remains still a challenging task. To the best of our knowledge, only two complexes of lead with boron-centred soft ligands have been reported in literature. Parkin et al. (2000) reported two lead complexes $[(Tm^{Ph})_2Pb]$[87] and $[Tm^{Ph}Pb]ClO_4$[88] by reacting together $[Tm^{Ph}]Li$ and $Pb(ClO_4)_2$ in 2:1 and 1:1 ratio, respectively. The molecular structure of $[(Tm^{Ph})_2Pb]$[87] features unusual coordination mode (κ^4- *H,S,S,S*) for one of the $[Tm^{Ph}]^-$ ligand (Scheme 1.5). In the latter complex $[Tm^{Ph}Pb]ClO_4$,[88] $[Tm^{Ph}]^-$ coordinates in an usual trigonal manner to the Pb ion.



Scheme 1.5. Structure of $[(Tm^{Ph})_2Pb]$.[87]

1.5. Photo-physical studies of main group metal complexes

Luminescence, is a complex phenomenon that involves ‘‘spontaneous emission of radiation from an electronically or vibrationally excited species not in thermal equilibrium with its environment’’.[89] Excitation is possible in a number of different ways, for instance, from chemical or electrode reactions, by high energy radiation etc. However, the basic principle is same, i.e. after absorbing a photon, an electron moves from the ground to an excited state and then comes back to the ground state which results in the emission of a photon. ‘‘There are two main types of luminescence (a) fluorescence that describes the direct re-emission of absorbed light and (b) phosphorescence which describes delayed emission including processes like intersystem crossing’’.[90]

The search for luminescent metal complexes especially those which can emit in the whole visible region remains an active area of research.[91] Some mixed-ligand complexes involving 2,2′-bipyridine and 1,10-phenanthroline have been prepared in this direction because of their favorable absorption and excited state properties.[92] Among two types of metal-centred (MC) or charge transfer (CT) transitions in main group metal complexes, metal-centred (MC) is most likely observed in main group metals (s–p-transitions).[90,93] It has been observed that for a clear display of MC luminescence, the best candidates are compounds containing s^2 ions such as lead(II) or bismuth(III). Generally, s^2-metal cations can feature MC (metal-centred) sp transitions and – if ligands with low-lying HOMOs are bonded – also LMCTs.[94-96] Mitzel et al.[97] in a recent publication on the basis of td-dft calculations pointed out, that the lowest energy excited states of Ph_3Bi are lying close to each other and one has to expect a mixture of different transitions in this energy range. Among luminescent bismuth complexes, an important example in the literature is the 2D coordination polymer $Bi(pydc)_2(H_3O)(H_2O)_{0.83}$ ($pydc^{2-}$ = pyridine-2,5-dicarboxylate). This coordination polymer shows a broad emission at 481 nm (blue emission), while the free ligand H_2pydc shows an emission at 518 nm. It has been argued that the emission in this coordination polymer are LMCT and/or s–p transitions. Similar conclusions have also been drawn from related literature.[90,98] Inspite of strong spin-orbit coupling of lead and bismuth, their inexpensive nature, ready accessibility, photo-physically active complexes of their ions have been scarcely explored and still are challenging tasks.

Chapter-2

Motivation

Efficient light emitting compounds are important components in light emitting devices, which have potential applications in displays and area light sources. In particular the latter are considered as efficient, economic and thus environmentally friendly alternatives to presently used illumination systems. There are various technologies to realize such systems. A system investigated in detail is the triplet emitter Ir(ppy)$_3$ (Ir(C_6H_4-C_5H_4N)$_3$, tris(phenylenepyridyl)iridium(III), because this compound has a very short-lived excited triplet state, which is mainly populated in the course of the excitation process. In the group of Prof. Mitzel, the structural chemistry of this compound was investigated in detail and further quantum chemical calculations demonstrated the importance of spin-orbit coupling, which are still difficult to describe by standard theoretical methods. Such effects are also known from other organometallic compounds of the platinum metals. The obvious disadvantage of such compounds is the limited availability and the high costs of the platinum metals. The search for alternatives was directed to other transition metal and also lanthanide elements, but so far the heavy main group metals have only been very scarcely investigated in this direction. This is surprising in the light of the well documented strong spin-orbit coupling effects in the chemistry of elements like lead or bismuth. These elements have further advantages like low-price, ready accessibility and – in the case of bismuth – low toxicity.

Boron-centred soft ligands, as reviewed in the previous chapter were introduced in 1996 and later on several metal complexes of different applications (mainly of biological importance as models of enzyme, in catalysis etc.) have been prepared and characterized. However, amazingly only a few bismuth and lead complexes have been reported in the literature. Therefore keeping in view the softness of these systems, we have been motivated to establish preparative routes to their compounds of bismuth and lead. It was thought that the increased softness of these metals will lead to a stronger binding of the ligand and to an enhanced interaction between metal-centred and ligand-centred molecular orbitals thereby enhancing the desired spin-orbit coupling effects. The proposed chemistry in this project was aimed for the fundamental exploration of the preparative accessibility and properties of a broad range of such compounds, investigation of their structures in the solid and solution state followed by preliminary photo-physical measurement and optimization of the emitter quality after a feed-back from such measurements.

Chapter-3

Experimental/Results and discussion

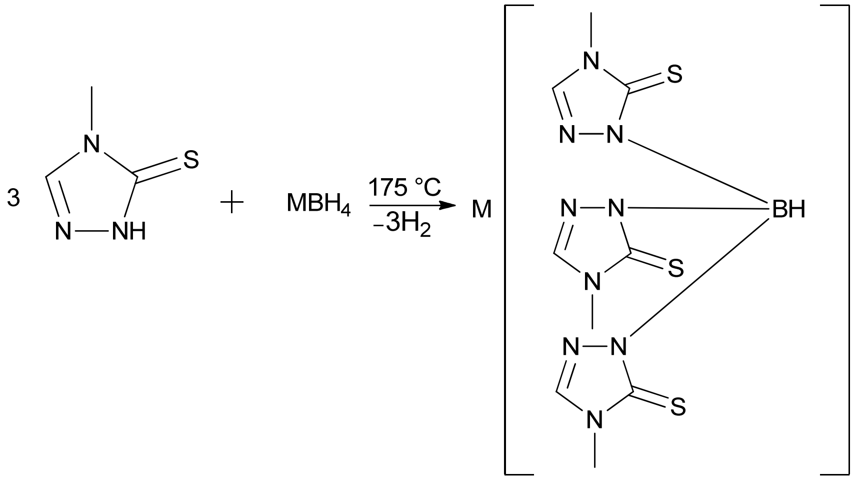
The experimental work carried out has either been published or is in the process of review, therefore in this chapter, the work will be briefly summarized. Photo-physical studies of few compounds are still under investigation in co-operation with Dr. Uwe Monkowius, Linz, Austria. Where appropriate, comparison of different synthesized compounds will be focused. The publications or manuscripts, describing more detail, will follow this chapter. For convenience, the description of this chapter will be done in different headings. These headings are as follow and will be discussed one by one.

3.1 Synthesis of Janus scorpionate ligands and their alkali metal complexes [Pub 1 & 5]
3.2 Synthesis of di-substituted boron-centred ligands and their alkali metal complexes[Pub 2 & Manuscript 5]
3.3 Synthesis of bismuth complexes[Pub 1,2 & Manuscripts 4,5]
3.4 Synthesis of lead complexes with soft ligands[Manuscript 3]
3.5 Photo-physical studies of synthesized complexes[Pub 1,2]

3.1 Synthesis of Janus scorpionate ligands and their alkali metal complexes 1 – 6[Pub 1 & manuscript 5]

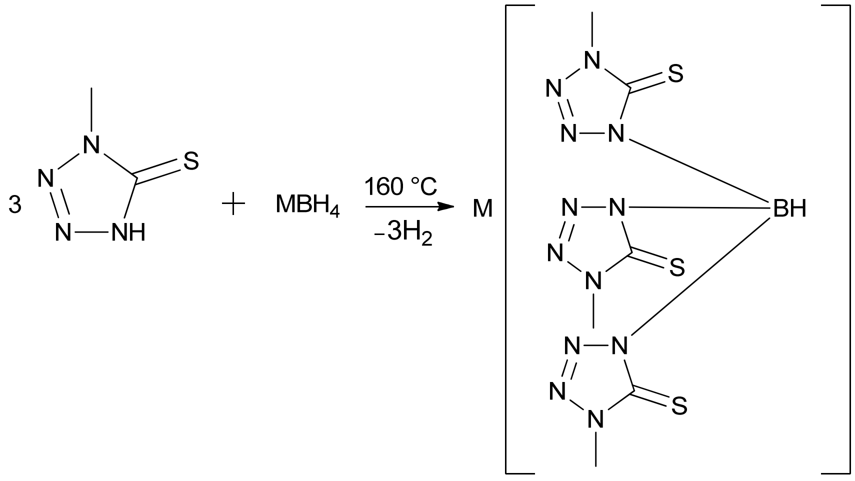
As discussed in general introduction, first and second generation Janus scorpionates were introduced by Silva et al. in 2006 and 2008 respectively.[64,65] Keeping in view the versatile Janus behaviour of these boron-centred soft ligands, we have synthesized two novel boron-centred soft ligands which behaved as typical Janus scorpionate ligands (Scheme 3.1). Both the $[Tr^{Me}]^-$ and $[Ttt^{Me}]^-$ ligands were produced *in-situ* via Trofimenko's protocol by the reaction of MBH_4 and respective heterocycle and were isolated in the form of alkali metal complexes $[MTr^{Me}]$ (**1** & **2**) and $[MTtt^{Me}]$ (**3** & **4**) (M = K, Na), respectively. Synthesis of $[MTr^{Me}]$ (**1** & **2**) was more straightforward compared to $[MTtt^{Me}]$ (**3** & **4**). The latter was obtained in lower yield and the isolation process was more laborious. $[MTtt^{Me}]$ (**3** & **4**) are freely soluble in common organic solvents, whereas $Bu_4N[Tr^{Me}]$ was synthesized for further synthetic utility of $[MTr^{Me}]$ (**1** & **2**) due to their limited solubility. Mixed complexes such as $[NaKTr^{Me}]_2$ (**5**) and

$[NaKTtt^{Me}]_2$ (**6**) were also synthesized with the intention to observe Janus type coordination behaviour and orientation of Na and K towards hard and soft side of the ligands (Scheme 3.2).



M[Tr^{Me}]

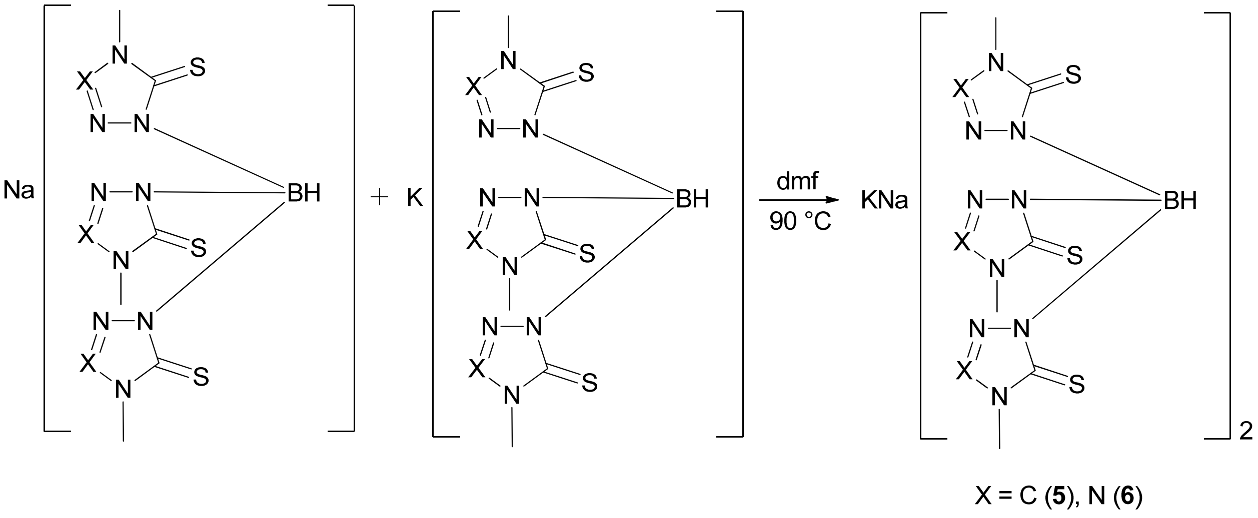
M = Na (**1**), K (**2**)



M[Ttt^{Me}]

M = Na (**3**), K (**4**)

Scheme 3.1. Synthesis of the Na, K complexes of $[Tr^{Me}]^-$ and $[Ttt^{Me}]^-$ **1** – **4**.



Scheme 3.2. Synthesis of mixed-metal complexes $[NaKTr^{Me}]_2$ (**5**) and $[NaKTtt^{Me}]_2$ (**6**).

3.1.1. *Structural elucidation of alkali metal complexes **1** – **6***

Solid state characterization was carried out by X-ray diffraction studies which revealed that $[MTr^{Me}]$ (**1**) exhibits non-polar polymeric chains whereas $[MTtt^{Me}]$ (**3** & **4**) crystallize as sheet-like structures. For illustration, the molecular structures of $[NaTr^{Me}]$ (**1**) and $[NaTtt^{Me}]$ (**3**) are shown in Figures 3.1 and 3.2, respectively.

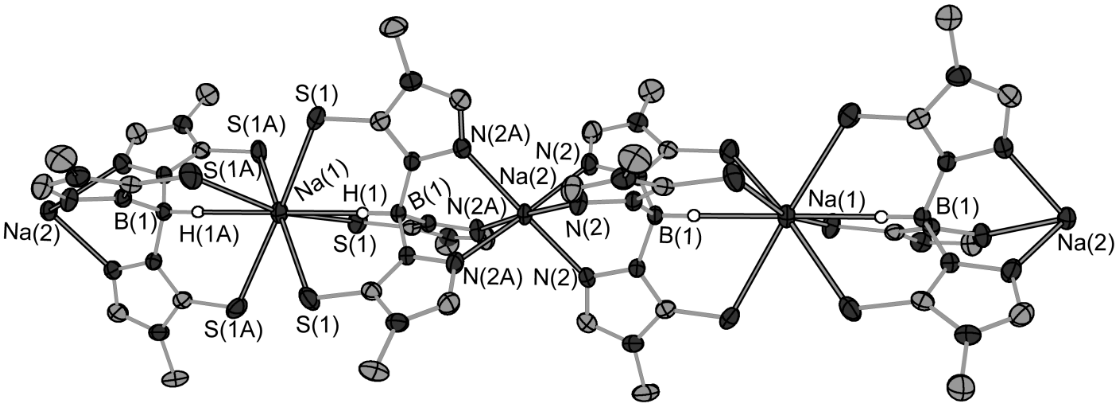


Figure 3.1. Part of the polymeric chain aggregate structure of $[Na(Tr^{Me})]$ (**1**) consisting of NaN_6 and NaH_2S_6 kernels with alternative orientation of the B–H bonds.[Pub 1]

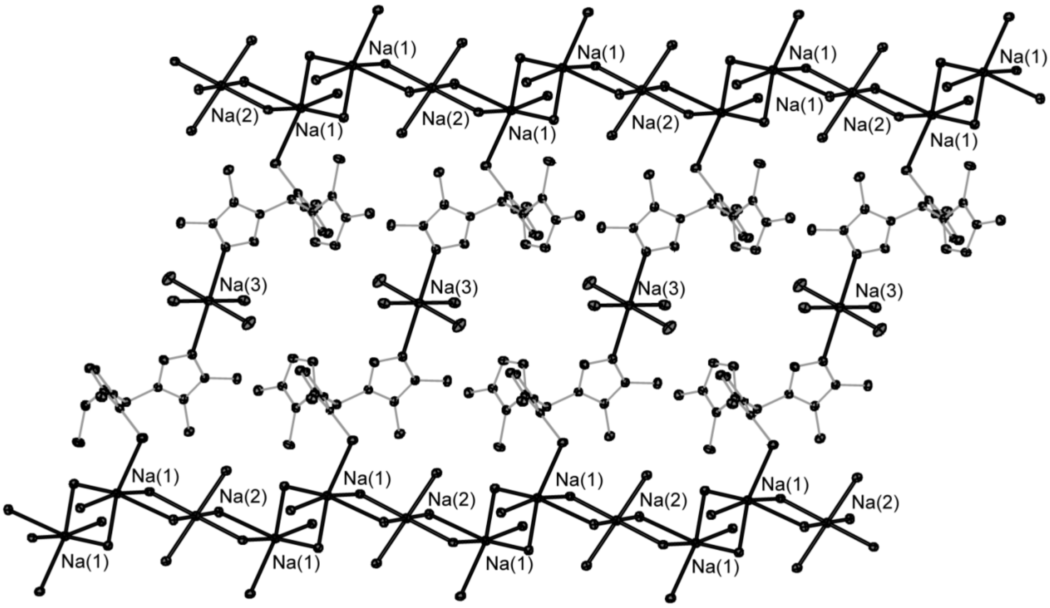


Figure 3.2. Part of the sheet-like structure of [Na(Ttt^{Me})] (**3**).[Manuscript 5]

Typical Janus behaviour of [Tr^{Me}]$^{-}$ can be shown in solid state structure of [NaK(Tr^{Me})$_2$] (**5**) (Figure 3.3), where one can see potassium on the soft side and sodium on hard side of the ligand. B–H bonds are alternatively arranged resulting non-polar polymeric chain. Unfortunately, the solid state structure of [KNa(Ttt^{Me})$_2$] (**6**) could not be determined by X-ray crystallography.

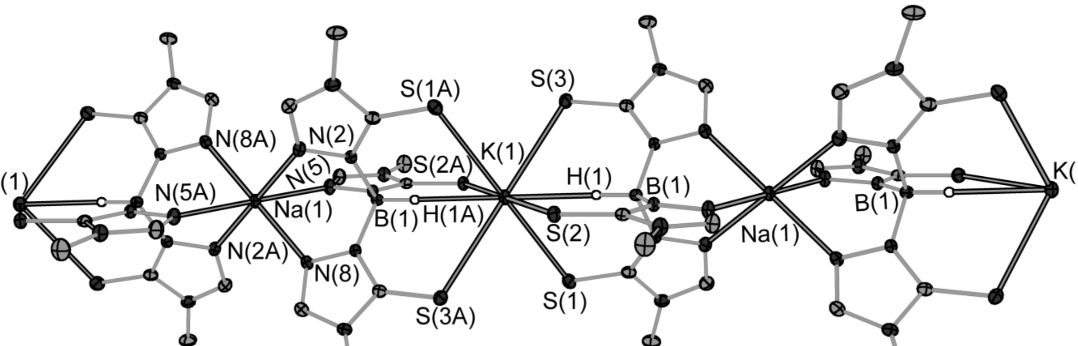


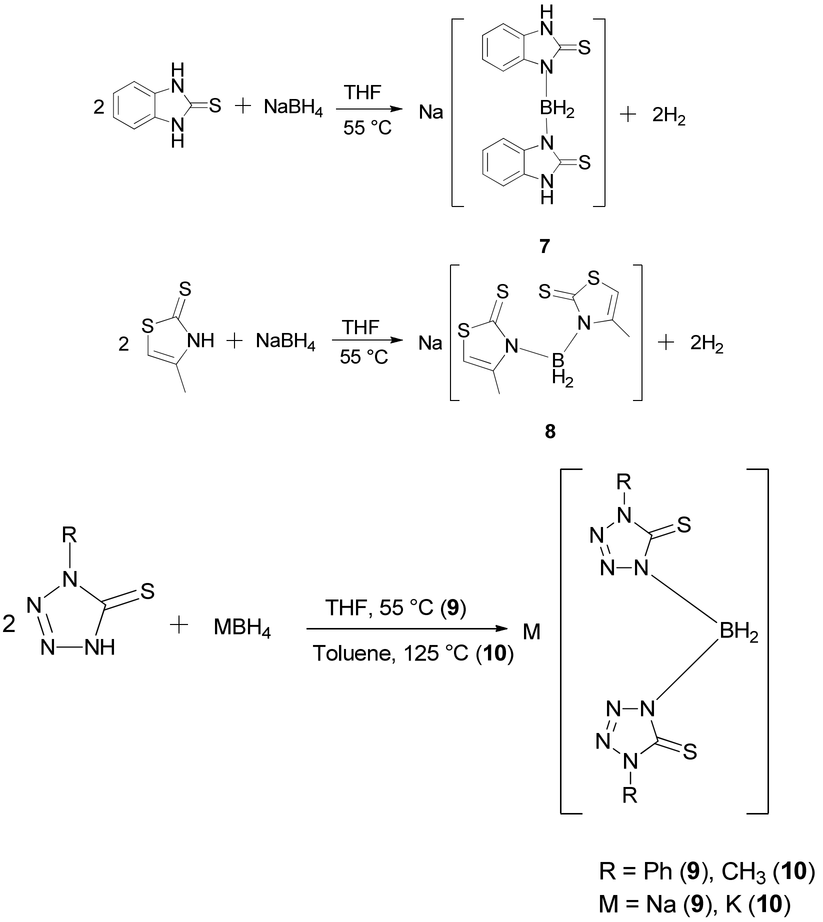
Figure 3.3. Part of the polymeric chain aggregate structure of [KNa(Tr^{Me})$_2$] (**5**) with alternative orientation of the B–H bonds.[Pub 1]

The M–S, M–N and B–H···M (M = K, Na) bond lengths in all the above described alkali metal complexes are comparable with each other as well as with related distances described by Silva et al. for M[HB(mtda^{R})$_3$] (where M = K, Na, [HB(mtda^{Me})$_3$]$^{-}$ = a Janus scorpionate ligand based on thiadiazole units).[64] Typical ranges described by Silva et al. are Na–N 2.30 – 3.15 Å, Na–S 3.01 – 3.65 Å, K–S 3.05 – 3.73 Å, K–N 2.31 – 3.58 Å, B–H···Na 2.03 – 2.87 and B–H···K 2.43 – 3.34 Å. The M–S, M–N and B–H···M bond lengths in [MTr^{Me}] (**1**, **2**, **5**) and [MTtt^{Me}] (**3**, **4**) lie not only within the above mentioned ranges but the majority of them lie close to the lower end of these ranges.

^{1}H, ^{13}C NMR and ^{1}H diffusion NMR experiments reveal that both [MTr^{Me}] (**1**, **2**, **5**) and [MTtt^{Me}] (**3**, **4**, **6**) are dissociated in dmf and dmso solutions. The alkali metal ions are solvated by these solvents. This hypothesis was further confirmed by ESI-MS spectrometry operated in negative mode, which reveals that compounds **1** – **6** exist as monomers instead of chain or sheet-like structures.(for more details please see publication 1 and manuscript 5).

3.2. Synthesis of di-substituted boron-centred soft ligands and their alkali metal complexes 7 – 10[Pub 2, manuscript 5]

Di-substituted boron-centred ligands are characterized by the presence of a BH_2 moiety and have found considerable attention in the previous years.[68-75] We have used three heterocycles, 2-mercapto-benzimidazole, 2-mercapto-4-methylthiazole and 1-phenyl-5-thiotetrazole for the *in-situ* synthesis of di-substituted boron-centred soft ligands. These ligands similar to Janus scorpionate ligands (**1** & **3**) were isolated in the form of sodium complexes as [NaBb] (**7**), [NaBt^{Me}] (**8**), [NaBtt^{Ph}] (**9**) (Scheme 3.3). In contrast to the synthesis of alkali metal Janus scorpionates **1** – **6**, these were prepared using THF as solvent at 55 °C. Additionally, a potassium complex [KBtt^{Me}] (**10**) was prepared in toluene at 125 °C (Scheme 3.3). All of these alkali metal complexes are colourless solids and stable towards air.



Scheme 3.3. Synthesis of the di-substituted boron-centred ligands and their alkali metal complexes **7** – **10**.

3.2.1 *Structural elucidation of alkali metal complexes* ***7** – **10***

All the four alkali metal complexes **7** – **10** were characterized in the solid state by X-ray crystallography. It has been observed that [NaBb] (**7**) crystallizes as monomeric sodium complex with distorted octahedral geometry, constituted by a [Bb]$^{-}$ ligand and four THF molecules. There are four independent molecules of [NaBb] in the unit cell. In contrast to [NaBb] (**7**), [NaBt$^{\mathrm{Me}}$] (**8**) and [NaBtt$^{\mathrm{Ph}}$] (**9**) exhibit polymeric chains in their solid state structures. As examples, the molecular structures of a monomeric [NaBb] (**7**) and a polymeric [NaBtt$^{\mathrm{Ph}}$] (**9**) are shown in Figures 3.4 and 3.5, respectively. In contrast to the above three sodium complexes **7** – **9**, the complex [KBtt$^{\mathrm{Me}}$] (**10**) crystallizes as sheet-like structure in solid state. The four ligands surrounding each potassium atom in

[KBtt^{Me}] (**10**) adopt the ligand coordination modes: two times κ^3-*H,N,S* and two times κ^1-*S*. There also occurs a disorder of 7 % in [KBtt^{Me}] (**10**), which can be described as a change of coordination mode from κ^3-*H,N,S* to κ^1-*S* and vice versa (see, manuscript 5).

Common feature of these alkali metal complexes **7** – **10** is the presence of B–H···M interactions. The strongest interaction of this type was found at 2.24(2) Å in [NaBb] (**7**), compared to 2.43(2) Å [NaBt^{Me}] (**8**), 2.72 Å [NaBtt^{Ph}] (**9**) and 2.71 Å [KBtt^{Me}] (**10**). These interactions are within the normal ranges reported in the literature for related distances (B–H···Na 2.03 – 2.87, B–H···K 2.43 – 3.34 Å).[64] Complexes **7** – **10** were also characterized by ^{1}H and ^{13}C NMR spectroscopy as well mass spectrometry. The characteristic feature in the ^{13}C NMR spectra is the chemical shift in the range *δ* 167.0 – 189.9 ppm that represents thione units (C═S) in compounds **7** – **10**.

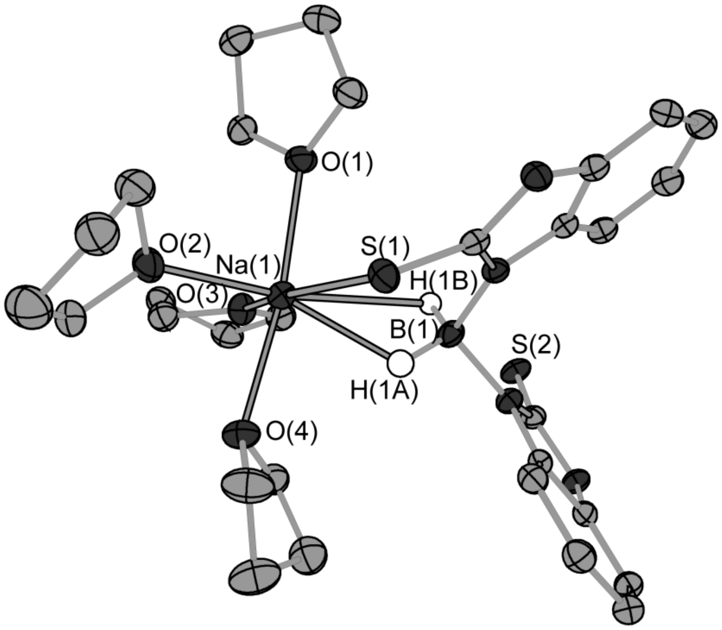


Figure 3.4. Solid state structure of molecule **a** in the unit cell of [NaBb] (**7**). Hydrogen atoms (except for H(1A) and H(1B)) have been omitted for clarity.[Pub 2]

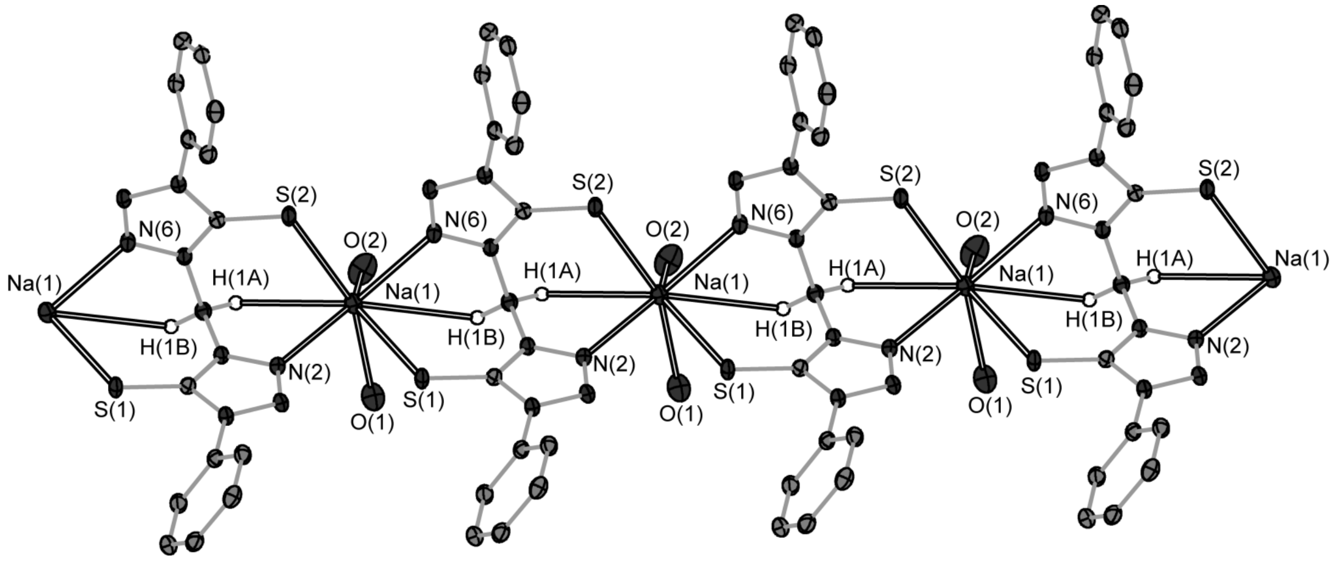


Figure 3.5. Part of the polymeric chain of [Na(Btt^{Ph})] (**9**).[Manuscript 5]

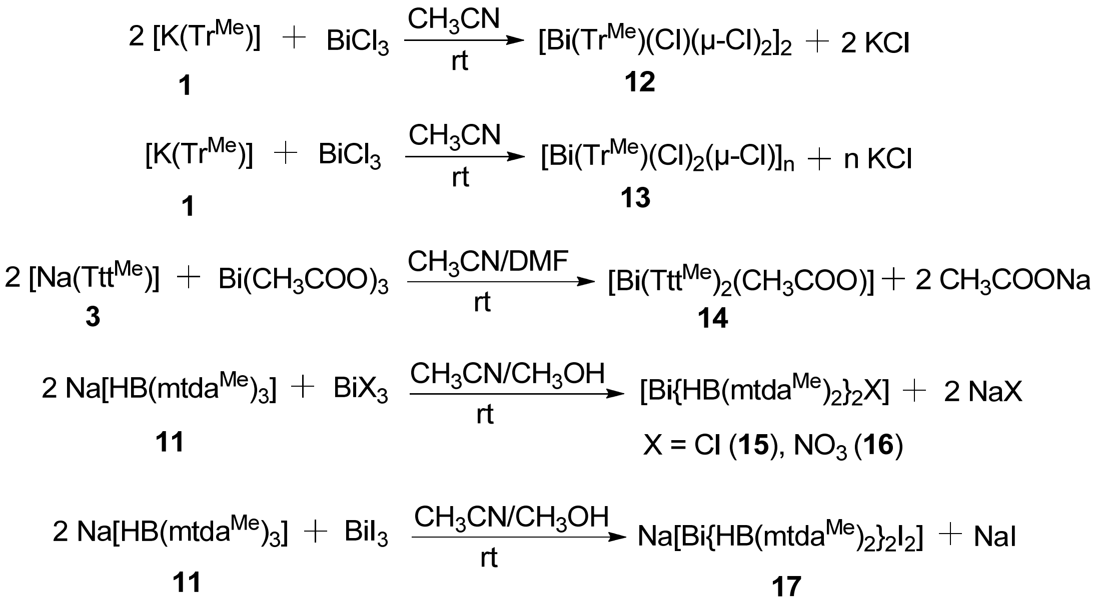
3.3. Synthesis and structural studies of bismuth complexes 12 – 31

After establishing successful syntheses of the above mentioned alkali metal complexes **1** – **6** with Janus scorpionates as well as with the di-substituted boron-centred soft ligands **7** – **10**, their reactivity was studied with BiX_3 (X = Cl^-, I^-, NO_3^- and CH_3COO^-) to prepare different bismuth complexes. For convenience, synthesis and structural elucidation of these complexes will be discussed under following headings.

3.3.1 Bismuth complexes **12** – **17** with Janus scorpionate ligands (i.e. tri-substituted boron-centred soft ligands)
3.3.2 Bismuth complexes **18** – **23** with di-substituted boron-centred soft ligands
3.3.3 Bismuth complexes **23** – **28** with the heterocyclic precursors as soft ligands
3.3.4 Mixed-ligand bismuth complexes **29** – **31** using boron-centred soft ligands as primary ligands

3.3.1. Synthesis of bismuth complexes 12 – 17 with Janus scorpionate ligands

K[Tr^{Me}] (**2**), Na[Ttt^{Me}] (**3**) and Na[HB($mtda^{Me}$)$_3$] (**11**)[65] were reacted with BiX_3 (X = Cl^-, I^-, NO_3^- and CH_3COO^-) to afford bismuth complexes **12** – **17**. K[Tr^{Me}] (**2**) and Na[Ttt^{Me}] (**3**) are novel compounds synthesized as described above, while Na[HB($mtda^{Me}$)$_3$] (**11**) was prepared according to a published protocol.[65] A general synthetic scheme for their syntheses is shown below (Scheme 3.4). All these bismuth complexes are coloured (**12**: orange yellow, **13**: yellow, **14**: orange, **15**: red, **16**: red, **17**: orange) and are stable solids.



$$\underset{\mathbf{1}}{2\,[\mathrm{K(Tr^{Me})}]} + \mathrm{BiCl_3} \xrightarrow[\mathrm{rt}]{\mathrm{CH_3CN}} \underset{\mathbf{12}}{[\mathrm{Bi(Tr^{Me})(Cl)(\mu\text{-}Cl)_2}]_2} + 2\,\mathrm{KCl}$$

$$\underset{\mathbf{1}}{[\mathrm{K(Tr^{Me})}]} + \mathrm{BiCl_3} \xrightarrow[\mathrm{rt}]{\mathrm{CH_3CN}} \underset{\mathbf{13}}{[\mathrm{Bi(Tr^{Me})(Cl)_2(\mu\text{-}Cl)}]_n} + n\,\mathrm{KCl}$$

$$\underset{\mathbf{3}}{2\,[\mathrm{Na(Ttt^{Me})}]} + \mathrm{Bi(CH_3COO)_3} \xrightarrow[\mathrm{rt}]{\mathrm{CH_3CN/DMF}} \underset{\mathbf{14}}{[\mathrm{Bi(Ttt^{Me})_2(CH_3COO)}]} + 2\,\mathrm{CH_3COONa}$$

$$\underset{\mathbf{11}}{2\,\mathrm{Na[HB(mtda^{Me})_3]}} + \mathrm{BiX_3} \xrightarrow[\mathrm{rt}]{\mathrm{CH_3CN/CH_3OH}} [\mathrm{Bi\{HB(mtda^{Me})_2\}_2X}] + 2\,\mathrm{NaX}$$

$\mathrm{X = Cl}$ (**15**), $\mathrm{NO_3}$ (**16**)

$$\underset{\mathbf{11}}{2\,\mathrm{Na[HB(mtda^{Me})_3]}} + \mathrm{BiI_3} \xrightarrow[\mathrm{rt}]{\mathrm{CH_3CN/CH_3OH}} \underset{\mathbf{17}}{\mathrm{Na[Bi\{HB(mtda^{Me})_2\}_2I_2]}} + \mathrm{NaI}$$

Scheme 3.4. Synthesis of bismuth complexes **12** – **17** with Janus scorpionate ligands.

3.3.1.1. *Structural elucidation of bismuth complexes **12** – **17***

In solid state bismuth complexes **12** – **17** were characterized by single crystal X-ray diffraction. Their structures have been discussed in details in publication 1 and manuscripts 4,5. Here a brief comparison is presented. The compositions of these complexes revealed from X-ray diffraction are as follow, $[\mathrm{Bi(Tr^{Me})(Cl)(\mu\text{-}Cl)_2}]_2$ (**12**) and $[\mathrm{Bi(Tr^{Me})(Cl)_2(\mu\text{-}Cl)}]_n$ (**13**), $[\mathrm{Bi(Ttt^{Me})_2(CH_3COO)}]$ (**14**), $[\mathrm{\{HB(mtda^{Me})_3\}_2BiCl}]$ (**15**), $[\mathrm{\{HB(mtda^{Me})_3\}_2Bi(NO_3)}]_n$ (**16**) and $\mathrm{Na[\{HB(mtda^{Me})_3\}_2BiI_2]}$ (**17**). Complexes **14**, **15** and **17** are monomeric, **12** is dimeric, while **13** and **16** are polymeric in nature. Among these complexes **14** and **16** have coordination number 7 at bismuth while the other possess coordination number 6. It has been observed that all the three ligands $[\mathrm{Tr^{Me}}]^-$, $[\mathrm{Ttt^{Me}}]^-$ and $[\mathrm{HB(mtda^{Me})_3}]^-$ coordinate with bismuth ions only through their sulphur donor functions in variable coordination modes such as κ^3-*S,S,S* (**12**, **13**), κ^3-*S,S,S* and κ^2-*S,S* (**14**, **15**), κ^3-*S,S,S* and κ^1-*S* (**16**), κ^2-*S,S* (**17**). Generally, all the complexes have distorted octahedral geometries except **17** as evidenced from their bond angles. To achieve a regular octahedral coordination sphere around bismuth(III) ions, we have also used bigger anions like nitrate and acetate with the mindset that possibly these bigger, hard-donor anions will remain outside the coordination sphere, enhancing the probability of the usual symmetrical tridentate κ^3-*S,S,S* coordination mode and finally resulting in a regular S_6 coordination environment. Spicer et al. also pointed out previously that a regular S_6 coordination sphere would be unattainable in bismuth complexes in the presence of halide ions; they reported that in the presence of halide ions, the balance of orbital energies is sufficiently changed to allow a directional lone pair to be observed.[83,99] Therefore, in contrast to **12** – **16**, complex **17** has two salient features (a) the almost octahedral geometry at bismuth and (b) the real Janus-type behaviour of the ligand $[HB(mtda^{Me})_3]^-$ towards Bi on the soft and Na on hard side (Figure 3.6) (for more details see publication 4). In general, Bi–S bond lengths in complexes **12** – **17** span over the range 2.666(2) – 2.996(2) Å. For comparison, a search of the Cambridge Structural Data Base for trivalent bismuth complexes with soft scorpionate ligands (version 5.33, updated May, 2012) yielded 9 hits (codes: FILZIK, HEBZOE, HEBZUK, HEBZUK01, HIXNAD, HIXNEH, IRARIC, QUOKOC, WUYHIH), with Bi–S bond lengths in the range 2.63 – 2.83 Å.

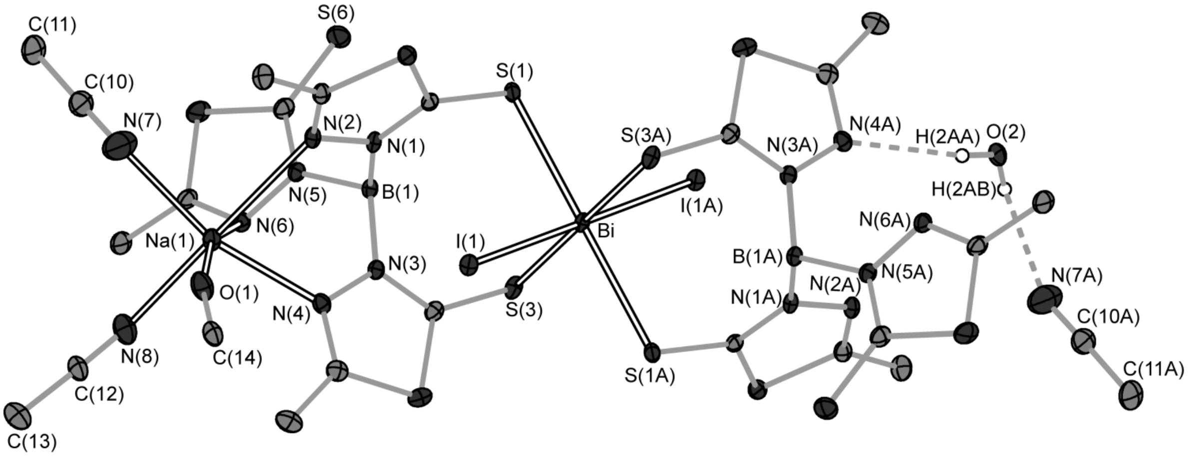
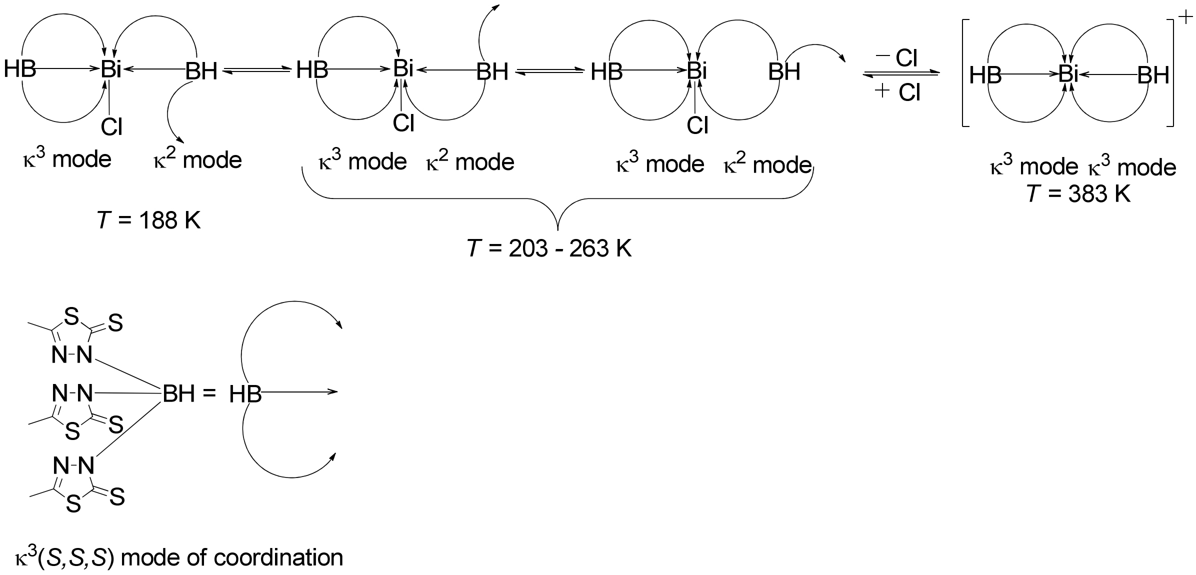


Figure 3.6. Molecular structure of $[\{[(CH_3CN)_2(CH_3OH)Na]\mu\text{-}[Na\ \kappa^3\text{-}N,N',N''\text{:}Bi\ \kappa^2\text{-}S,S'\{HB(mtda^{Me})_3]\}_2BiI_2]\cdot CH_3CN\cdot H_2O$ (**17**).[Manuscript 4]

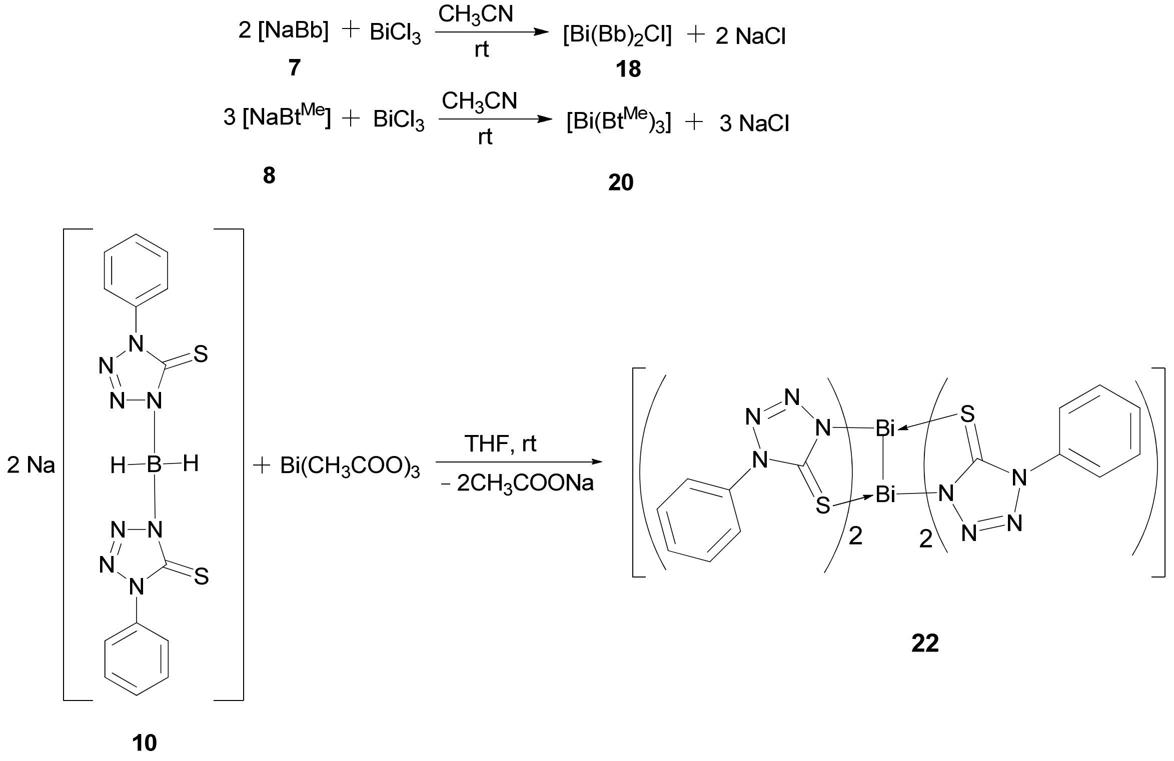
Bismuth complexes **12** – **17** were also characterized in solution by ^{1}H and ^{13}C NMR spectroscopy. The three complexes **15**, **16** and **17** exhibit a broad singlet for their methyl protons at 2.52, 2.57 and 2.52 ppm, respectively, compared to δ = 2.37 ppm for free ligand $[HB(mtda^{Me})_3]^-$ which indicates a fluxional coordination behaviour in these complexes. The dynamics have been studied exemplarily on compound **15** by variable temperature NMR spectroscopy in the range of 188 and 383 K using CD_2Cl_2 and $CD_2Cl_2CD_2Cl_2$ as solvents (for details, see manuscript 4). At 188 K one of these methyl resonances starts to split, so it possibly belongs to a ligand with coordination mode (κ^2-*S,S*) (Scheme 3.5). We assume that at low temperature one of the Janus scorpionate ligand coordinates in a κ^3 mode while the other one is coordinated dynamically to the bismuth atom in a κ^2 fashion according to Scheme 3.5.



Scheme 3.5. Proposed schematic illustration for the dynamics of complex **15**.

3.3.2. Synthesis of bismuth complexes with di-substituted boron-centred soft ligands 18 – 23

For this category of bismuth complexes, [NaBb] (**7**) (Bb = dihydrobis(2-mercapto-benzimidazolyl)borate) and $[NaBt^{Me}]$ (**8**) (Btt^{Me} = dihydrobis(2-mercapto-4-methyl-thiazolyl)borate) were reacted with $BiCl_3$ at room temperature to afford bismuth complexes [$BiBb_2Cl$] (**18**) and [$Bi(Bt^{Me})_3$] (**20**), respectively (Scheme 3.6). Another complex [$BiBbCl(\mu\text{-}Cl)_2]_2$ (**19**) was obtained as a trace crystalline product from the mother liquor of **18**. Similarly another complex [$Bi(Bt^{Me})_3]\cdot CHCl_3$ (**21**) was obtained by the cooling of saturated chloroform solution of **20**. The reaction of [$NaBtt^{Ph}$] (**10**) with $Bi(CH_3COO)_3$ in THF and acetonitrile solvents resulted the unusual synthesis of the low-valent Bi(II) complexes **22** and **23** with a short Bi–Bi bond. It is clear that the di-substituted ligand [$Na(Btt^{Ph})$] (**10**) with the B–H functions (acting as reducing agent) is decomposed and the resulting 1-phenyl-5-thiotetrazolyl ions act as ligands. Both **22** and **23** are red. Reglinski et al. were also disappointed when they observed ligand degradation of [$Tm^{Me}]^-$ (hydrotris(methimazolyl)borate) upon reaction with $CuCl_2$ and obtained [$Cu^ICl(mtH)(\mu\text{-}mtH)]_2$ (mtH = free heterocyclic methimazole ligand, a decomposition product of [$Tm^{Me}]^-$).[48] All these complexes, **18** – **23**, are coloured (**18**: yellow, **19**: yellow, **20**: red, **21**: red, **22**: red, **23**: red) and stable solids.



Scheme 3.6. Synthesis of bismuth complexes **18**, **20**, **22** with di-substituted boron centred soft ligands.

*3.3.2.1. Structural elucidation of bismuth complexes **18** – **23***

Single crystal X-ray diffraction studies were performed for complexes **18** – **23**. These studied revealed their compositions as follow [BiBb$_2$Cl] (**18**), [BiBbCl(μ-Cl)$_2$]$_2$ (**19**), [BiBt^{Me}$_3$]·CH$_2$Cl$_2$ (**20**), [BiBt^{Me}$_3$]·CHCl$_3$ (**21**), [Bi(L^2)$_2$]$_2$·THF (**22**) and [Bi(L^2)$_2$]$_2$·2CH$_3$CN (**23**). The resulting geometries around bismuth atoms in these complexes are distorted and the lone pairs are stereochemically active as evidenced from their bond angles. Bi–S bond lengths in complexes **18** – **23** cover the range 2.604(2) – 2.796(2) Å and are relatively shorter than those in **12** – **17** (Bi–S, 2.666(2) – 2.996(2) Å). Bismuth complex **18** displays a unique and quite short B–H···Bi interaction at a distance of 2.58(10) Å (Bi···B 3.50(1) Å, which is unprecedented in bismuth chemistry with related ligands (Figure 3.7). However, this can be compared with the related structure of [Tl(Bm^{Me})]$_x$, which has a (B)H···Tl distance of 2.69 Å (Tl–B 3.50 Å).[49] Furthermore, in complex **18**, the ligand coordination mode is κ^3-*H,S,S* (Figure 3.7) compared to κ^2-*S,S* in **20**. During solution studies of **18** and **20**, the signals of the BH$_2$ moieties in their respective ^{1}H NMR and ^{11}B NMR spectra were not observed. A similar observation has also been reported in the literature of related complexes.[59] Therefore, in the solution state, especially for **18**, it is difficult to comment on the stability of B–H···Bi interactions. However, the presence of B–H···Bi interactions in complex **3** has been further verified in the solid state by the observation of two B–H stretching bands (2449 and 2423 cm^{-1}) in its IR spectrum compared to one band (2407 cm^{-1}) in [NaBb] (**7**). This is in agreement with literature on poly(mercaptoimidazolyl)borate chemistry.[68b] Crystals of both, **22** and **23**, contain solvent molecules and the Bi$_2$L$_4$ units are located about a crystallographic centre of symmetry, but the structures are not iso-structural. The Bi–Bi distances are 3.037(1) Å (**22**) and 3.045(1) Å (**22**). The molecular structure of **22** is shown in Figure 3.8.

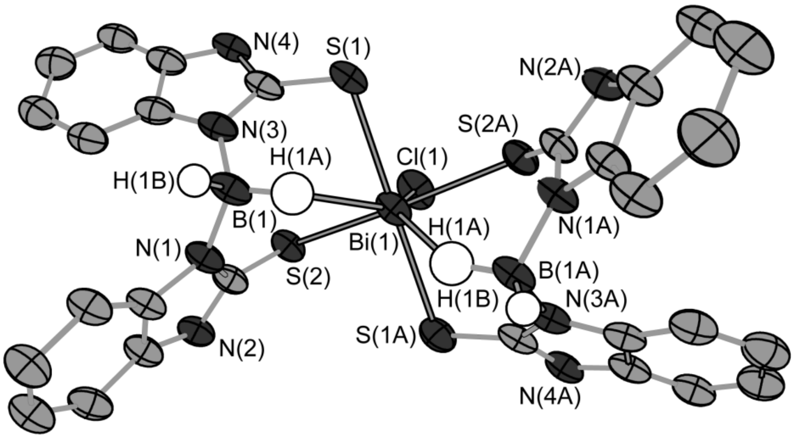


Figure 3.7. Molecular structure of [$BiBb_2Cl$] (**18**) displaying B–H···Bi interactions.[Pub 2]

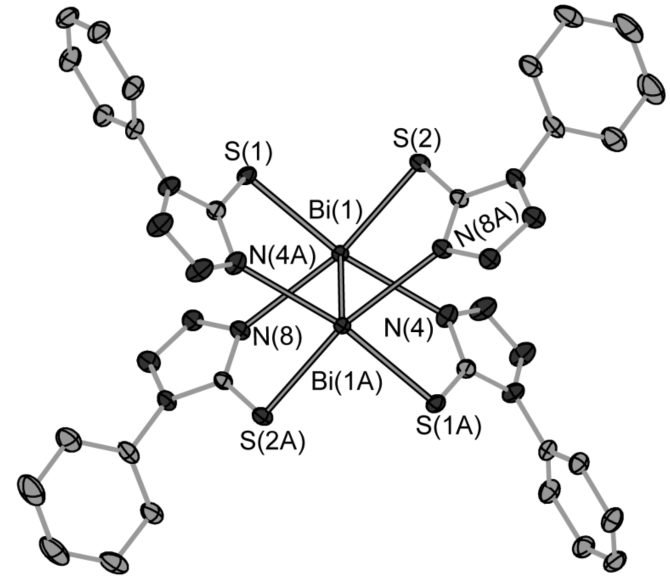
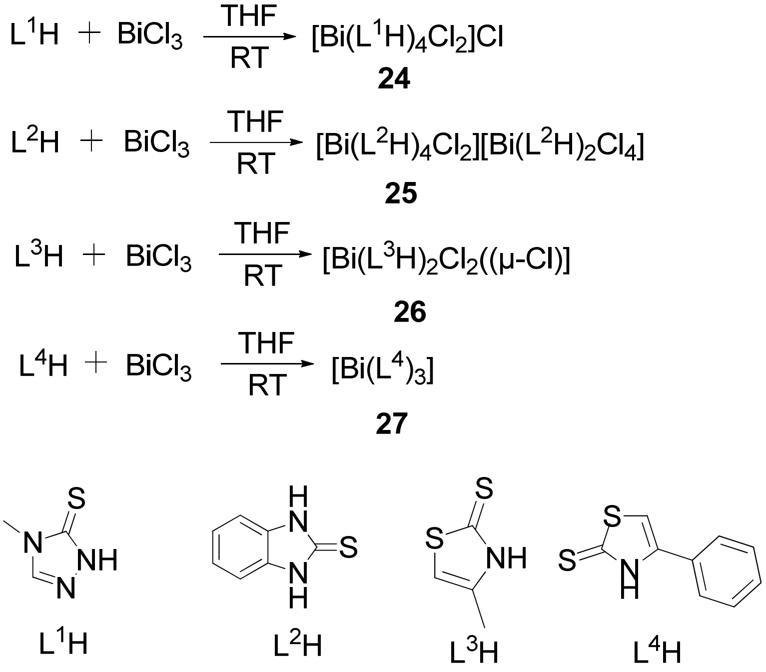


Figure 3.8. Molecular structure of bismuth complex **22** with short Bi–Bi interaction.[Manuscript 5]

3.3.3. **Synthesis of bismuth complexes 24 – 27 with the heterocyclic precursors as soft ligands**

During the synthesis of above mentioned bismuth complexes **12** – **20**, significant distortion in the geometries and the presence of stereochemically active lone pair was observed except Na[{HB(mtda^{Me})$_3$}$_2$BiI$_2$] (**17**). In order to see the effect of the smaller soft ligand on geometries, Bi–S bond strengths and stereochemical activity of lone pair, syntheses of bismuth complexes with four heterocyclic precursors (3-mercapto-4-methyl-1,2,4-triazole (L^1H), 2-mercapto-benzimidazole (L^2H), 2-mercapto-4-methylthiazole (L^3H) and 2-mercapto-4-phenylthiazole (L^4H) were performed (Scheme 3.7). The resulting bismuth complexes **24** – **27** are also coloured (**24**: yellow, **25**: orange, **26**: orange, **27**: yellow) and stable towards air. Compared to bismuth complexes **12** – **20**, these were produced in higher yield and are better soluble in common solvents.



$$L^1H + BiCl_3 \xrightarrow[RT]{THF} \underset{\mathbf{24}}{[Bi(L^1H)_4Cl_2]Cl}$$

$$L^2H + BiCl_3 \xrightarrow[RT]{THF} \underset{\mathbf{25}}{[Bi(L^2H)_4Cl_2][Bi(L^2H)_2Cl_4]}$$

$$L^3H + BiCl_3 \xrightarrow[RT]{THF} \underset{\mathbf{26}}{[Bi(L^3H)_2Cl_2((\mu\text{-}Cl)]}$$

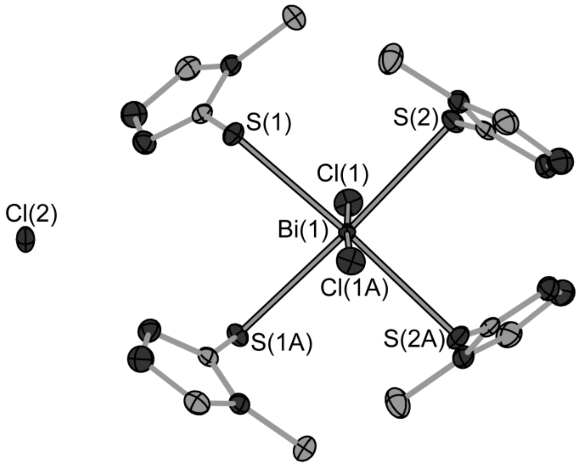
$$L^4H + BiCl_3 \xrightarrow[RT]{THF} \underset{\mathbf{27}}{[Bi(L^4)_3]}$$

Scheme 3.7. Synthesis of bismuth complexes **24** – **27** with heterocyclic precursors as soft ligands.

*3.3.3.1. Structure elucidation of bismuth complexes **24** – **27***

Single crystal X-ray diffraction studies revealed their structural compositions as $[Bi(L^1H)_4(Cl)_2]Cl$ (**24**), $[Bi(L^1H)_4Cl_2][Bi(L^1H)_2Cl_4]$ (**25**), $[Bi(L^2H)_2Cl_2(\mu\text{-}Cl)]_2$ (**26**) and $[Bi(L^4)_3]$ (**27**). The molecular structures of these complexes are shown in Figure 3.9. In contrast to **12** – **20**, complexes **24** – **27** possess relatively regular octahedral environments as evidenced from their bond angles. **24**, **25** and **27** are monomeric while

26 is dimeric in nature and bridged via chloro ligands. The heterocyclic ligands (L^1H – L^3H) in complexes **24**, **25** and **26** behave monodentate and coordinate through their sulphur donor atoms and the triple positive charge on bismuth is balanced by chloro ligands. However, in complex **27**, the heterocyclic ligand (L^4H) coordinates the central bismuth ion in a monoanionic bidentate manner (via N and S donor sites) after deprotonation. Similar to **27**, another neutral bismuth complex $[Bi(L)_3]$ (**28**) (L = 1-phenyl-5-thiotetrazolyl) was isolated by exposing the solution of complex **22** to air for several days (for details, see manuscript 5). The heterocyclic ligand, 1-phenyl-5-thiotetrazole (LH) also acts as monoanionic bidentate via sulphur and nitrogen sites after deprotonation.



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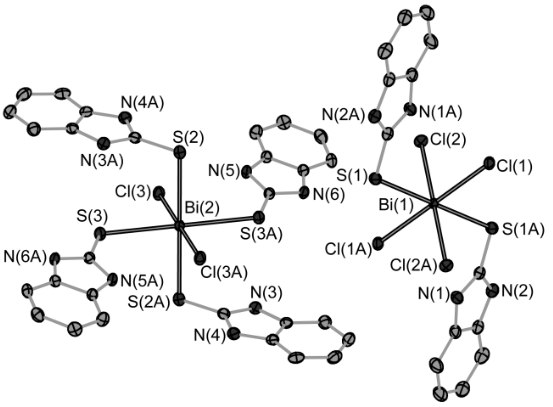

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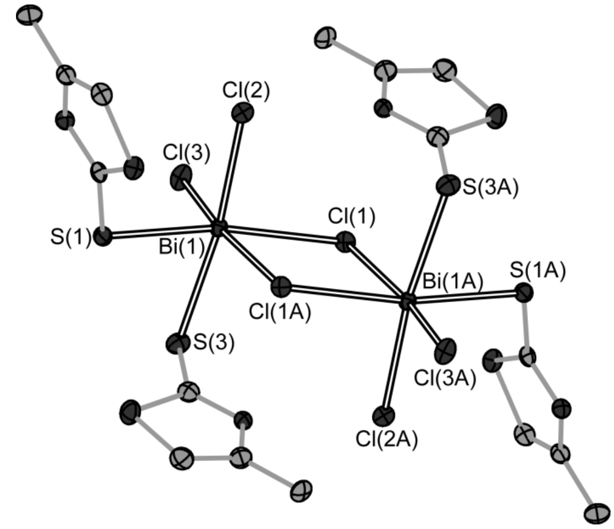

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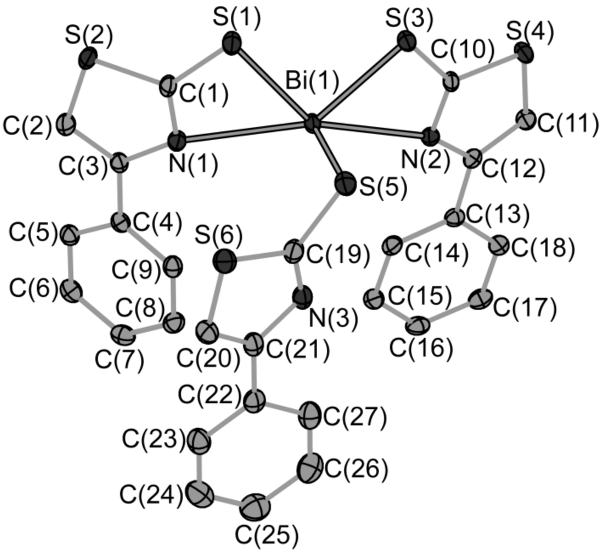
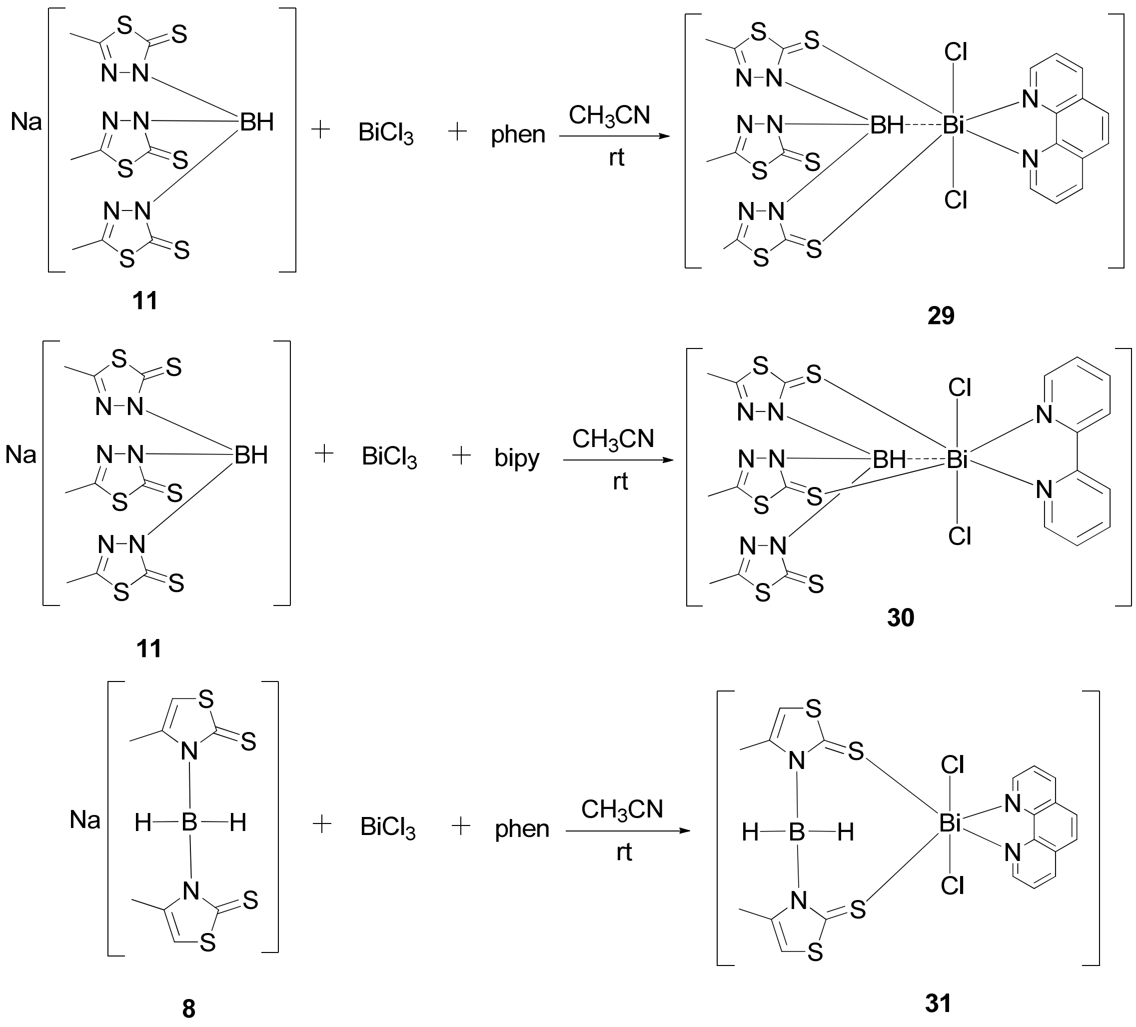


27

Figure 3.9. Molecular structures of bismuth complexes **24** – **27** with heterocyclic precursors as soft ligands.

3.3.4. **Mixed-ligand bismuth complexes 29 – 31 using boron-centred soft as primary ligands**

The synthetic chemistry of bismuth was further extended with co-ligands such as 1,10-phenanthroline and 2,2’-bipyridyl while keeping boron-centred soft ligands as primary ligands. The purpose was to see the effect on (a) structural aspects of bismuth geometries upon introduction of these neutral bidentate ligands (b) luminescence properties of these complexes due to their inherently conjugated nature. In this category, three novel mixed-ligand bismuth complexes were synthesized as outlined in Scheme 3.8.



Scheme 3.8. Synthesis of mixed bismuth complexes **29** – **31**.

The mixed-ligand complexes **29** – **31** are also coloured solids (**29**: yellow, **30**: orange red, **31**: yellow). **29** and **30** have poor solubilities in common organic solvents compared to **31**.

*3.3.4.1. Structural elucidation of mixed-ligand bismuth complexes **29** – **31***

Single crystal X-ray diffraction showed the composition of three mixed bismuth complexes as, $[\{HB(mtda^{Me})_3\}Bi(phen)Cl_2]$ (**29**), $[\{HB(mtda^{Me})_3\}Bi(Bipy)Cl_2]$ (**30**) and $[Bt^{Me}Bi(phen)Cl_2]$ (**31**). Molecular structures of **29** and **31** are shown in Figure 3.10. To best of our knowledge, mixed-ligand complexes **29** – **31** are unprecedented in bismuth chemistry based on boron-centred soft ligands. The mixed-ligand complexes **29**, **30** and **31** have coordination number 7 and 6 respectively. The constitutions of these complexes are similar and are accomplished by a boron-centred soft ligand ($[HB(mtda^{Me})_3]^-$ (**29**, **30**), $[Bt^{Me}]^-$ (**31**)), two terminally bound chloro ligands and a bidentate co-ligand (phenanthroline/bipyridyl). The three complexes adopt distorted geometries as revealed from their bond angles. Therefore the presence of stereochemically active lone pairs at the bismuth ions cannot be neglected in these three cases. Bi–S and Bi–N in complexes **29** and **30** are in the range 2.943(2) – 2.966(2) Å and 2.435(2) – 2.513(2) Å respectively. The similar bond lengths in complex **31** are Bi–S 2.740(2) – 2.992(2) and Bi–N 2.480(3) – 2.483(3) Å. Generally Bi–S bond lengths in $[\{HB(mtda^{Me})_3\}Bi(phen)Cl_2]$ (**29**), $[\{HB(mtda^{Me})_3\}Bi(bipy)Cl_2]$ (**30**) and $[Btt^{Me}Bi(phen)Cl_2]$ (**31**) are comparatively longer than those in analoguous complexes $[\{HB(mtda^{Me})_3\}_2BiCl]$ (**15**) and $[(Bt^{Me})_3Bi]$ (**20**) without co-ligands. In contrast to **31**, complexes **29** and **30** feature interestingly (B)H···Bi interactions at 2.76(3) Å for **29** and 2.71(2) Å in length for **30**. This B–H···Bi interaction is also contrasting with bismuth complexes $[\{HB(mtda^{Me})_3\}_2BiCl]$ (**15**), $[\{HB(mtda^{Me})_3\}_2Bi(NO_3)]_n$ (**16**) and $Na[\{HB(mtda^{Me})_3\}_2BiI_2]$ (**17**).

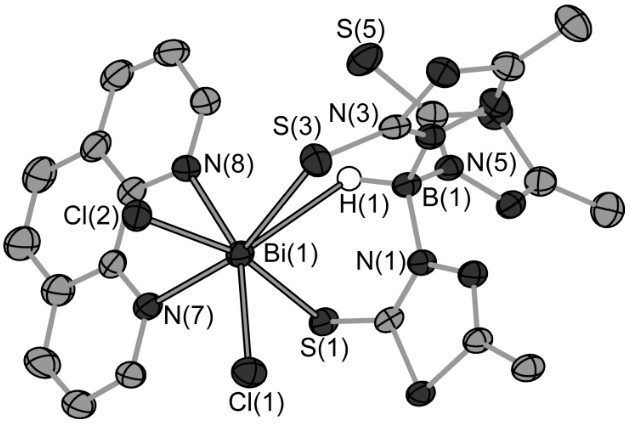
The mixed-ligand complexes **29** and **30** were found to be dissociated in high polar solvents like dmf or dmso. This was confirmed by determining the diffusion co-efficients using the proton NMR resonance of the methyl group of $[HB(mtda^{Me})_3]^-$ and that of the aromatic amine i.e. the co-ligands. The diffusion coefficients of the complexes **29** ($5.04\cdot10^{-10}$ m^2 s^{-1} (phen), $4.93\cdot10^{-10}$ m^2 s^{-1} $[HB(mtda^{Me})_3]^-$) and **30** ($8.60\cdot10^{-10}$ m^2 s^{-1} (bipy), $4.54\cdot10^{-10}$ m^2 s^{-1} $[HB(mtda^{Me})_3]^-$) differ from the diffusion coefficients of their free co-ligands (phen $8.73\cdot10^{-10}$ m^2 s^{-1} and bipy $1.01\cdot10^{-10}$ m^2 s^{-1}), but are the same as that of free $[HB(mtda^{Me})_3]^-$ ($4.57\cdot10^{-10}$ m^2 s^{-1}). This observation supports the dissociation of **29** and **30** in dmf as follows.

$$[\{HB(mtda^{Me})_3\}Bi(phen)Cl_2] \xrightleftharpoons[-\,dmf]{+\,dmf} [(phen)BiCl_2]^+ + [HB(mtda^{Me})_3]^-$$

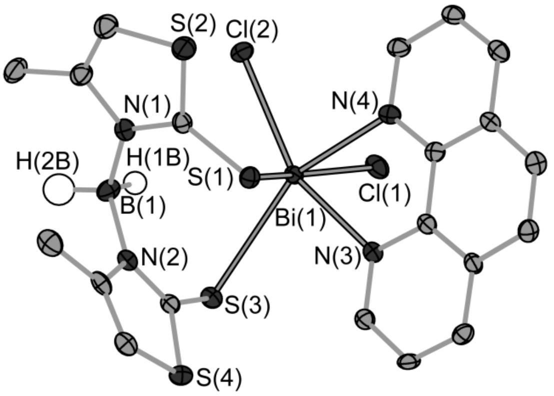
29

$$[\{HB(mtda^{Me})_3\}Bi(bipy)Cl_2] \xrightleftharpoons[-\,dmf]{+\,dmf} [(bipy)BiCl_2]^+ + [HB(mtda^{Me})_3]^-$$

30



29

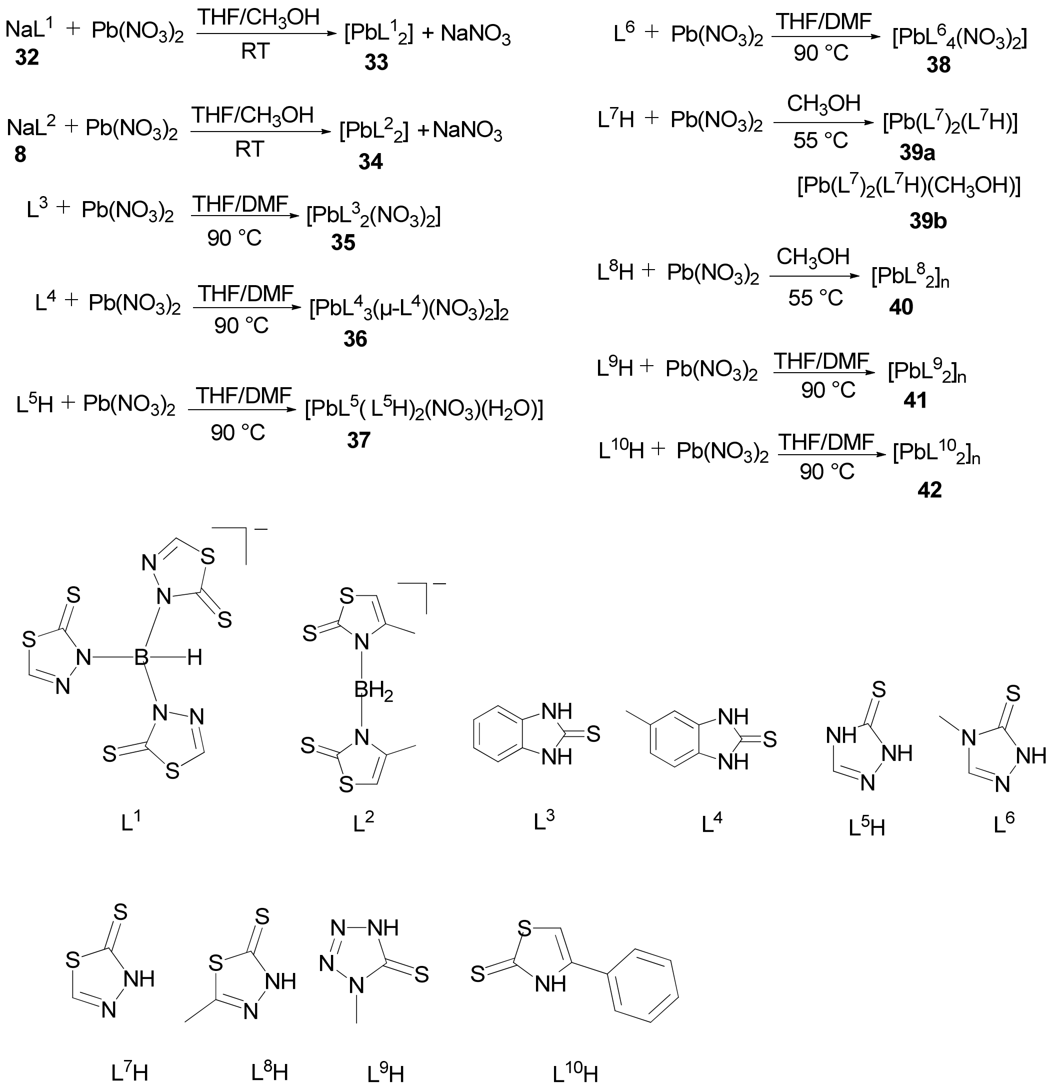


31

Figure 3.10. Molecular structures of mixed complexes [{HB(mtda^{Me})$_3$}Bi(phen)Cl$_2$] (**29**) and [Btt^{Me}Bi(phen)Cl$_2$] (**31**). Hydrogen atoms except B–H and solvent molecules have been omitted for clarity.[Manuscript 5]

3.4. Synthesis of lead complexes with soft ligands 33 – 42

In continuation of the efforts for bismuth complexes, some lead complexes using soft ligands were also prepared and structurally characterized. For this purpose, a tri- and a di-substituted boron-centred soft ligand along with eight small heterocyclic soft ligands were chosen to study the structural and bonding aspects of lead(II) ions. An important aspect of this study was to observe the influence of the lone pair on the coordination geometries of lead (II) ions. Manuscript 3 contains all the studies carried out on these complexes. Where appropriate a comparison has been drawn with the corresponding bismuth analogues. Compared to intensely coloured bismuth complexes **12** – **31**, the lead complexes are either colourless or yellow solids. The yields of the lead complexes **33** – **42** are higher than those of the bismuth complexes **12** – **31**. However the solubility of lead(II) complexes in common organic solvents is very low. This is perhaps because of the formation of aggregate (polymers/sheet-like) structures in the majority of the lead complexes. A general scheme for the synthesis of lead(II) complexes **33** – **42** is shown below. NaL^1 (**32**) was synthesized according to a published protocol.[64]

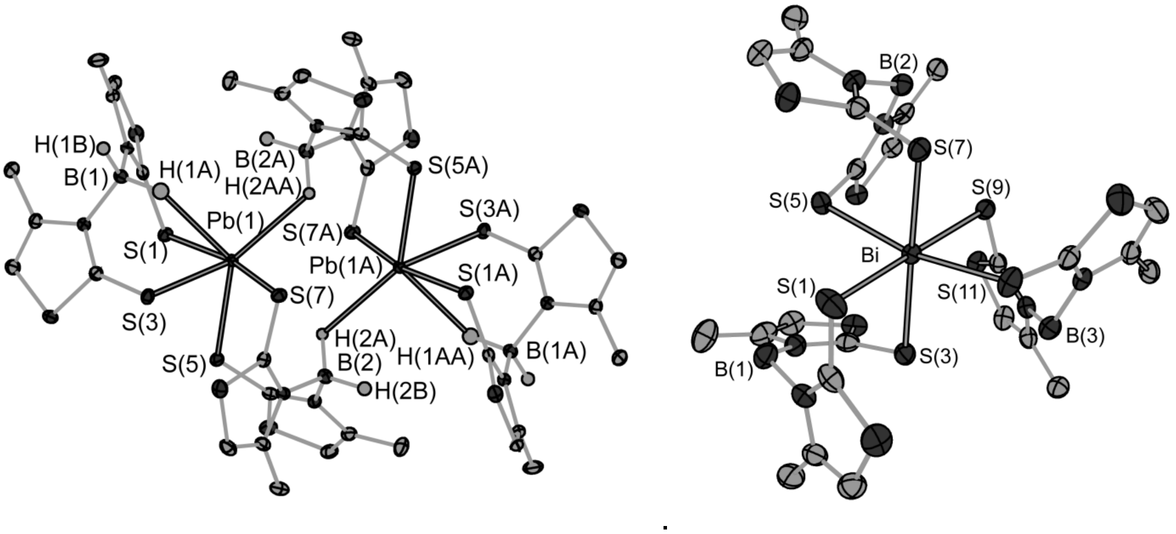


Scheme 3.9. Synthesis of lead(II) complexes **33** – **42** with soft ligands.

*3.4.1. Structural elucidation of lead(II) complexes **33** – **42***

Single crystal X-ray crystallography revealed molecular structures of complexes **33** – **42** with compositions of $[Pb(L^1)_2(L^7H)_2L']$ **33** (where L' is 1-methyl-2-pyrrolidinone), $[PbL^2_2]$ **34** (where L^2 = dihydrobis(thiazolyl)borate(Bt^{Me})), $[PbL^3_2(NO_3)_2]$ **35**, $[PbL^4_3(\mu\text{-}L^4)(NO_3)_2]_2$ **36**, $[Pb(L^5)(L^5H)_2(NO_3)(H_2O)]_n$ **37**, $[PbL^6_4(NO_3)_2]$ **38**, $[Pb(L^7)_2(L^7H)]_n$ **39a**,

$[Pb(L^7)_2(L^7H)(CH_3OH)]_n$ **39b**, $[PbL^8{}_2]_n$ **40**, $[PbL^9{}_2]_n$ **41**, $[PbL^{10}{}_2]_n$ **42**. Complex **38** is monomeric, **34** and **36** are dimeric, while all others exhibit either polymeric or sheet-like structures in the solid state. A dimeric complex $[PbL^2{}_2]$ **34** is shown in Figure 3.11a. For comparison its bismuth analogue **20** is also shown in Figure 3.11b.



a **b**

Figure 3.11. Molecular structures of (a) $[Pb(L^2)_2]$ (**34**) and (b) $[Bi(Bt^{Me})_3]$ (**20**) (where = L^2 = Bt^{Me}).[Pub 2, Manuscript 5]

In lead complex **34** (Figure 3.11a), the central lead ion is coordinated by four sulphur atoms and a hydrogen atom of an $–BH_2$ unit. The interesting feature of the complex is the Pb···H interaction at a distance of B(1)–H(1A)···Pb 2.66(2) Å by one $–BH_2$ unit. The second $–BH_2$ unit has a distance of B(2)–H(2A)···Pb 3.02 Å which is too large to be of bonding significance. However, it makes a weaker contact of 2.84 Å with a lead atom of a neighbouring molecule forming a dimer about a centre of inversion. In contrast to **34**, its bismuth analogue $[Bi(Bt^{Me})_3]$ (**20**) (Figure 3.11b) exhibits no B–H···Bi interaction. Furthermore the geometry around bismuth is distorted octahedral compared to distorted square pyramidal in **34**. The ligand coordination mode in **20** from the three surrounding ligands is κ^2-*S,S* in contrast to κ^3-*H,S,S* in **34**.

As pointed out above, the lead complexes have poor solubility in common solvents except dmf or dmso. However, in these solvents, most of the complexes show dissociation. Some of them dissociate significantly, some partially while some do not dissociate. This was confirmed from ^{1}H DOSY experiments on complexes **34**, **35** and **38** using dmf-*d7* as solvent. The diffusion coefficients were compared with those of their respective free ligand compounds. On the basis of diffusion coefficient data it can be argued that complexes **35** and **38** are highly dissociated as the diffusion coefficients are almost the same within experimental error as those of the free ligand compounds (see manuscript 3). However, the CH proton signal of complex **34** allows to extract a significantly different diffusion coefficient $2.34 \cdot 10^{-10}$ m^2 s^{-1} compared to that of the free ligand compound [NaL^2] (**8**) ($2.62 \cdot 10^{-10}$ m^2 s^{-1}) which reveals that the complex **34** is not dissociated in dmf solution.

3.5. Photo-physical studies of synthesized complexes

Some of the synthesized bismuth complexes were preliminary investigated for their photo-physical behaviour and have been discussed in respective publications/manuscripts (1, 2, 4, 5). Generally it has been observed that upon complexation of the Bi(III) ions by the heterocyclic thione units, the π-π* absorption bands are bathochromically shifted (e.g 286 and 279 nm for **12** and **24**, respectively). Weak bands, which might be due to sp absorptions and/or S→Bi ligand to metal charge transfer states (LMCT), also appear in these spectra; for instance it evolves above 300 nm for **12** and at 290 nm for **24**. Similarly **12** exhibits a broad emission band centred around 485 nm (Figure 3.12) and **24** exhibit similar band at 504 nm (see publication 1). The wavelength of these luminescences can be compared with other emissive Bi(III) complexes reported previously.[100-103] Some of the complexes were only emissive in the solid state (for instance **20**: $\lambda_{\max}$ = 586 nm, publication 2). At 77 K in ethanol glass, **25** features emission bands at 537 nm. Upon measuring the emission spectra of solid **25** at r.t. and 77 K, thermochromic behaviour was noticed. At room temperature, a crystalline sample of **25** is orange and changes its colour to yellow when cooled with liquid nitrogen (Figure 3.13). Thermochromism of bismuth compounds is a well-known phenomenon and ascribed to structural changes like phase transitions or alterations of interatomic distances.[104]

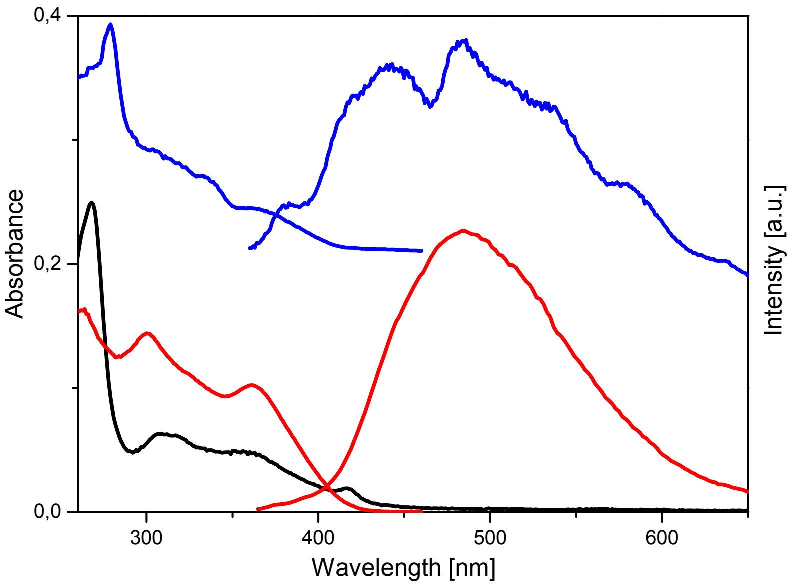


Figure 3.12. Electronic absorption spectrum (black), excitation and emission spectra of **12** in dcm at r.t. (blue) and 77 K (red, $c = 1.7 \cdot 10^{-5}$ mol/L; $\lambda_{\mathrm{exc}} = 350$ nm, $\lambda_{\mathrm{dec}} = 480$ nm).[Pub 1]

Figure 3.13. Digital pictures of crystals of **25** at room temperature (left) and after immersion in liquid nitrogen (right).[Pub 2]

Chapter-4

Summary

The proposed chemistry in this project was aimed for the fundamental exploration of the preparative accessibility and properties of a broad range of boron centred soft ligands and their metal complexes particularly with bismuth(III) ions, investigation of their structures in the solid and solution state followed by preliminary photo-physical measurements and optimization of the emitter quality after a feed-back from such measurements. Consequently three main types of soft ligands were synthesized. (1) Tri-substituted boron-centred soft ligands (Janus scorpionate ligands), (2) di-substituted boron-centred soft ligands (3) heterocyclic precursors as soft ligands. Two novel Janus scorpionate ligands $[Tr^{Me}]^-$ and $[Ttt^{Me}]^-$ were produced *in-situ* by the reaction of MBH_4 and respective heterocycle (3-mercapto-4-methyl-1,2,4-triazole and 5-mercapto-1-methyltetrazole) and were isolated in the form of alkali metal complexes $[MTr^{Me}]$ (**1** & **2**) and $[MTtt^{Me}]$ (**3** & **4**) (M = K, Na), respectively. Later on, two mixed complexes such as $[NaK(Tr^{Me})_2]$ (**5**) and $[NaK(Ttt^{Me})_2]$ (**6**) were also synthesized with the intention to observe Janus type coordination behaviour and orientation of Na and K towards hard and soft sites of these ligands. These alkali metal complexes exhibit polymeric and sheet-like structures in solid state. $K[Tr^{Me}]$ (**2**), $Na[Ttt^{Me}]$ (**3**) and $Na[HB(mtda^{Me})_3]$ (**11**)[65] (**11** is a reported Janus scorpionate ligand) were reacted with BiX_3 (X = Cl^-, I^-, NO_3^- and CH_3COO^-) to afford bismuth complexes $[Bi(Tr^{Me})(Cl)(\mu\text{-}Cl)_2]_2$ (**12**) and $[Bi(Tr^{Me})(Cl)_2(\mu\text{-}Cl)]_n$ (**13**), $[Bi(Ttt^{Me})_2(CH_3COO)]$ (**14**), $[\{HB(mtda^{Me})_3\}_2BiCl]$ (**15**), $[\{HB(mtda^{Me})_3\}_2Bi(NO_3)]_n$ (**16**) and $Na[\{HB(mtda^{Me})_3\}_2BiI_2]$ (**17**). The resulting bismuth complexes are monomeric (**14**, **15** and **17**), dimeric (**12**) and polymeric (**13**, **16**) in nature. Except **17**, all of them have distorted geometries with stereochemically active lone pairs on the bismuth atoms. In contrast to Trofimenko's protocol for **1** – **6**, alkali metal complexes [NaBb] (**7**), $[NaBt^{Me}]$ (**8**), $[NaBtt^{Ph}]$ (**9**) and $[KBtt^{Me}]$ (**10**) of di-substituted boron-centred soft ligands were prepared using THF/toluene solutions. [NaBb] (**7**), $[NaBt^{Me}]$ (**8**), $[NaBtt^{Ph}]$ (**9**) were reacted with BiX_3 (X = Cl^-, CH_3COO^-) to yield bismuth complexes $[BiBb_2Cl]$ (**18**), $[BiBbCl(\mu\text{-}Cl)_2]_2$ (**19**), $[BiBt^{Me}{}_3]\cdot CH_2Cl_2$ (**20**), $[BiBt^{Me}{}_3]\cdot CHCl_3$ (**21**), $[Bi(L^2)_2]_2\cdot THF$ (**22**) and $[Bi(L^2)_2]_2\cdot 2CH_3CN$ (**23**). Complex **18** exhibits a (B)H···Bi interaction at 2.58 Å which is unprecedented in bismuth chemistry. Complexes **22** and **23** have Bi^{2+} instead of Bi^{3+} as central ions which is because of a reduction reaction which occurred during their synthesis. The third category of heterocyclic precursors as soft ligands (3-mercapto-4-methyl-1,2,4-triazole (L^1H), 2-mercapto-benzimidazole (L^2H), 2-mercapto-4-methylthiazole (L^3H) and 2-mercapto-4-phenylthiazole (L^4H)) upon reaction with $BiCl_3$ resulted in bismuth complexes $[Bi(L^1H)_4(Cl)_2]Cl$ (**24**), $[Bi(L^1H)_4Cl_2][Bi(L^1H)_2Cl_4]$ (**25**), $[Bi(L^2H)_2Cl_2(\mu\text{-}Cl)]_2$ (**26**) and $[Bi(L^4)_3]$ (**27**). These complexes possess relatively regular coordination geometries when compared with above two types of bismuth complexes **12** – **17** and **18** – **23**. Generally the Bi–S bond lengths in **24** – **27** are shorter revealing strong coordination compared to **12** – **23**. Finally three mixed-ligand bismuth complexes $[\{HB(mtda^{Me})_3\}Bi(phen)Cl_2]$ (**29**), $[\{HB(mtda^{Me})_3\}Bi(bipy)Cl_2]$ (**30**) and $[Btt^{Me}Bi(phen)Cl_2]$ (**31**) were prepared by using boron-centred soft ligands as primary ligands. **29** and **30** feature interestingly (B)H···Bi interactions at 2.76(3) Å for **29** and 2.71(2) Å for **30**; these are weaker compared to 2.58 Å found in **18**.

Lead(II) complexes were also synthesized by the reaction of a tri-, a di-substituted boron-centred soft ligand and eight small heterocyclic soft ligands with $Pb(NO_3)_2$. The resulting complexes are $[Pb(L^1)_2(L^7H)_2L']$ **33** (where L' is 1-methyl-2-pyrrolidinone), $[PbL^2{}_2]$ **34** (where L^2 = dihydrobis(thiazolyl)borate(Bt^{Me})), $[PbL^3{}_2(NO_3)_2]$ **35**, $[PbL^4{}_3(\mu\text{-}L^4)(NO_3)_2]_2$ **36**, $[Pb(L^5)(L^5H)_2(NO_3)(H_2O)]_n$ **37**, $[PbL^6{}_4(NO_3)_2]$ **38**, $[Pb(L^7)_2(L^7H)]_n$ **39a**, $[Pb(L^7)_2(L^7H)(CH_3OH)]_n$ **39b**, $[PbL^8{}_2]_n$ **40**, $[PbL^9{}_2]_n$ **41**, $[PbL^{10}{}_2]_n$ **42.** The coordination numbers of these complexes vary from 4 to 8 and the majority of them are polymeric in nature with hemidirected environments around the lead ions.

Preliminary photo-physical studies were carried out on a few selected bismuth complexes such as **12**, **20**, **24**, **25** etc. Generally, it has been observed that upon complexation of the Bi(III) ion by heterocyclic thione units, the π-π* absorption band are bathochromically shifted. MC sp transitions were also observable. Some of the complexes are not emissive in solution, however, at 77 K in ethanol glasss show emission bands (e.g **25** exhibit this band at 537 nm). **25** also exhibits thermochromic behaviour, its crystalline sample is orange at room temperature and changes its colour to yellow when cooled with liquid nitrogen.

Conclusively this work provided a successful approach to study the versatile coordination behavior (such as κ^3-*S,S,S*, κ^2-*S,S,* κ^1-*S,* κ^3-*H,S,S,* κ^4-*H,S,S,S;* κ^2-*H,S,* κ^3-*H,H,S,* κ^3-*H,N,S,* κ^3-*N,N,N,* κ^2-*N,N* and κ^1-*N*) of tri- and di-substituted boron-centred soft ligands towards Na, K, Bi(III) and Pb(II) ions. Additionally for bismuth complexes, the use of different anions or conjugated neutral systems as co-ligands influenced the stereochemically activity of lone pair resulting interesting bonding situations e.g unprecedented B–H···Bi interactions. These unprecedented interactions in bismuth chemistry can be further explored to investigate bismuth-hydride activation or Bi→B dative bond formation (metalloboranes). Bismuth complexes based on smaller soft heterocyclic ligands were found to be better luminescent compared to those based on tri- and di-substituted boron-centred soft ligands, as the former lead to a stronger binding of the ligand (as revealed from M–S bond lengths) and to an enhanced interaction between metal-centred and ligand-centred molecular orbitals thus enhancing the desired spin-orbit coupling effects. From these preliminary luminescence studies, it can be suggested that if such soft systems are used and the lewis-acidity of the bismuth atom is further increased by some electron withdrawing groups like perfluoro alky/aryl substituents etc., the desire of strong spin-orbit coupling effects as well as the stability of the complexes will be enhanced and this approach will decisively contribute to further improvement of luminescence activity for their potential applications in displays and area light sources.

Chapter-5

Acknowledgment

I feel great pleasure in expressing gratitude to my research supervisor, Prof. Dr. Norbert W. Mitzel, Professor of Inorganic and Structural Chemistry, Faculty of Chemistry, Bielefeld University, Germany for all his contributions especially time, provoking guidance and inspirational coaching. He really encouraged my different attempts to complete this research work. It is great honor for me to be a part of his research group.

I also express my special thanks to Prof. Dr. Berthold Hoge, Faculty of Chemistry, Bielefeld University, Germany for being my second examiner and for his valuable suggestions. From time to time co-operation of Dr. Andreas Mix regarding solution NMR studies of my compounds is highly acknowledged. I also gratefully acknowledge the valuable discussions with Dr. Hans Georg Stammler and Frau Beate Neuman during the many crystallographic studies they did for this work. I am very much thankful to Dr. Uwe Monkowius, Linz, Austria for photo-physical measurements of the synthesized compounds. Nice inputs and ideas from Dr. Raphael Berger while writing the application for DAAD fellowship are also gratefully acknowledged. I am thankful to co-workers of Prof. Mitzel group especially Jan-Hendrik Lamm, Benedikt Werder, Eugen Weisheim, Christian Reuter, Alexander Widner, Janek Tomaschautzky, Jan Hortsman, Lisa Kuhlman, Martin Pieper, Jan Schwabedissen, Leif Arne Körte, Johanna Glatthor, Sebastian Blomeyer, Dr. Yuri Vishnevskiy and Dr. Stefan Hopp, Britta Rummel and Verena Orth. Dr. Anja Nieland and other past co-workers of the group are also acknowledged. Thanks to Eugen, Jan and Martin for proof reading of the work. My sincere thanks are also to Roswitha Becker (secretary to Prof. Mitzel), Gerd Lipinski, Klaus-Peter Mester (NMR section), Brigitte Michel (elemental analyses) and Mian Qi (for internship).

I am grateful to my parents, brothers, Thatho and Prof. Dr. Javed Iqbal (late) who always supported me, from the beginning of my educational carrier. I extend my love to Aroma and Afresham whom I have missed a lot. Last but not least, I find it very important to say special thanks for the financial support of DAAD.

Muhammad Imran

Chapter-6

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Chapter-7

Publications/Manuscripts

Publications

1. **The versatile behaviour of a novel Janus scorpionate ligand towards sodium, potassium and bismuth(III) ions**

   Muhammad Imran, Beate Neumann, Hans-Georg Stammler, Uwe Monkowius, Martin Ertl and Norbert W. Mitzel, *Dalton Trans.*, 2013, **42**, 15785 – 15795

2. **Borate-based ligands with two soft heterocycle/thione groups and their sodium and bismuth complexes**

   Muhammad Imran, Beate Neumann, Hans-Georg Stammler, Uwe Monkowius, Martin Ertl and Norbert W. Mitzel, *Dalton Trans.*, 2014, **43**, 1267 – 1278

Manuscripts

Manuscripts **3**, **4** and **5** contains the synthetic and structural studies carried out by us. However these will be submitted after getting input regarding their photo-physical behaviour which is under investigation in-co-operation with Dr. Uwe Monkowius, Linz, Austria. Manuscripts **6** and **7** are crystallographic reports that will be submitted soon.

3. **Structural chemistry of hemi and holo directed lead(II) complexes in soft environment**

   Muhammad Imran, Andreas Mix, Beate Neumann, Hans-Georg Stammler, Uwe Monkowius and Norbert W. Mitzel, *Cryst. Eng. Comm.,* "in preparation"

4. **Synthesis, structural and photo-physical studies of bismuth(III) complexes with a Janus scorpionate and co-ligands**

   Muhammad Imran, Andreas Mix, Beate Neumann, Hans-Georg Stammler, Uwe Monkowius and Norbert W. Mitzel, *Dalton Trans.*, "in preparation"

5. **Boron-centred soft ligands based on tetrazole units and their complexes with sodium, potassium and bismuth(III) ions**

   Muhammad Imran, Andreas Mix, Beate Neumann, Hans-Georg Stammler, Uwe Monkowius and Norbert W. Mitzel, *Dalton Trans.*, "in preparation"

6. **Crystallographic report on dihydrobis(2-mercapto-4-methylthiazolyl)borate) mixed-ligand bismuth complex [Bi(bt^{Me})(phen)Cl$_2$]**

   Muhammad Imran, Beate Neumann, Hans-Georg Stammler and Norbert W. Mitzel, *Appl. Organometal. Chem.,* ‘‘ready for submission’’

7. **Crystallographic report on Monomeric bismuth complex with 2-mercapto-4-phenylthiazole ligand [Bi(C$_9$H$_6$NS$_2$)$_3$]**

   Muhammad Imran, Beate Neumann, Hans-Georg Stammler and Norbert W. Mitzel, *Acta Crystallogr*. Sect. E ‘‘ready for submission’

Publication-1

Dalton Transactions

RSCPublishing

PAPER

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View Journal | View Issue

Cite this: *Dalton Trans.*, 2013, **42**, 15785

The versatile behaviour of a novel Janus scorpionate ligand towards sodium, potassium and bismuth(III) ions†

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Received 26th July 2013,
Accepted 10th September 2013

DOI: 10.1039/c3dt52030g

www.rsc.org/dalton

Alkali metal salts of a novel Janus scorpionate ligand $[(\mathrm{Tr^{Me}})]^-$ with hard and soft donor sites (N, S) were synthesized by the reaction of 3-mercapto-4-methyl-1,2,4-triazole (L) with $NaBH_4$ and KBH_4, respectively, *via* Trofimenko's protocol. The resulting compounds were the sodium and potassium complexes $[\mathrm{Na(Tr^{Me})}]$ (**1**), $[\mathrm{K(Tr^{Me})}]$ (**2**) and the mixed ion compound $[\mathrm{KNa(Tr^{Me})}]$ (**3**). $[\mathrm{K(Tr^{Me})}]$ (**2**) was reacted with bismuth(III) chloride to afford the complexes $[\mathrm{Bi(Tr^{Me})(Cl)(\mu\text{-}Cl)_2}]_2$ (**5**) and $[\mathrm{Bi(Tr^{Me})(Cl)_2(\mu\text{-}Cl)}]_n$ (**6**). Compound **5** was formed when **2** was applied to $BiCl_3$ in a molar ratio 2 : 1, while **6** was achieved when a ratio of 1 : 1 was used. The reaction of 3-mercapto-4-methyl-1,2,4-triazole (L) with $BiCl_3$ led to the formation of the complex $[\mathrm{Bi(L)_4(Cl)_2}]\mathrm{Cl}$ (**7**). The products were characterized by NMR and IR spectroscopy, elemental analyses and mass spectrometry. Solid state structures were determined by X-ray diffraction of single crystals of **1**, **3**, **3a**, **5**, **6** and **7**. The alkali metal scorpionates **1–3** are coordination polymers with alternating orientation of the ligands. They dissociate in solution as observed in NMR measurements. Negative mode ESI-MS data also indicate the presence of monomers. The bismuth complex **5** is dimeric and **6** is polymeric, and both are bridged *via* chloro ligands. The three bismuth complexes **5**, **6** and **7** have highly distorted octahedral coordination geometries. The influence of the stereochemically active lone pair was found to be most pronounced in the dimeric complex **5**. The ligand $\mathrm{Tr^{Me}}$ and all bismuth complexes were also screened for their photo-luminescence activity. Whereas solutions of $\mathrm{Tr^{Me}}$ exhibit no luminescence, **7** is only emissive at 77 K, and **5** is emissive both at r.t. and 77 K.

Introduction

Borate based tripodal ligands (also called scorpionate or Trofimenko ligands) such as hydridotris(pyrazolyl)borate (Tp) are well established ligands for coordination and organometallic chemistry and have been widely explored in structure and reactivity studies,[1] catalysis[2] and even bio-inorganic chemistry.[3,4] The well-known Tp-based ligand systems possess relatively hard donor sites. However, interest in the chemistry of ligands with softer donor atoms such as phosphorus or sulphur has increased tremendously in the last few years, and correspondingly, soft scorpionates have been introduced.[5–11] Such soft systems are not only considered to be advantageous for the stabilization of low-valent, electron-rich metals,[12,13] but also demonstrate a susceptibility to oxidation, thus giving rise to metal complexes with unusual oxidation states. The soft ligands exert weaker field strengths compared to hard ligands, as has been established in the examples of $[\mathrm{Fe(Tm^{Me})_2}]$,[14] and $[\mathrm{Fe(Tp^{Me})_2}]$ (Tm = hydrotris(methimazolyl)borate).[15] Moreover, these ligands have twisting and flexibility capabilities to accommodate metal ions of larger ionic radii and show variable coordination behaviour such as monodentate (κ^1-*S*), bidentate (κ^2-*S*,*S* or κ^2-*S*,*H*), and tridentate (κ^3-*S*,*S*,*S* or κ^3-*S*,*S*,*H*).[16,17] Since the first report of the soft ligand hydrotris(methimazolyl)borate (Tm) *via* Trofimenko's protocol,[18] some other hybrid tripodal ligands with both pyrazol and methimazole moieties have also been synthesized.[19,20]

Janus scorpionates are another category of flexible soft ligands in coordination chemistry. Their name "Janus" was derived from Roman mythology: the god of gates and doors, Janus, has a two-faced figure.[21–23] These are also closely related to Bailey's and Marchiò's ambidentate thioxotriazolylborate[20,24] and are also known as hybrid of Trofimenko's

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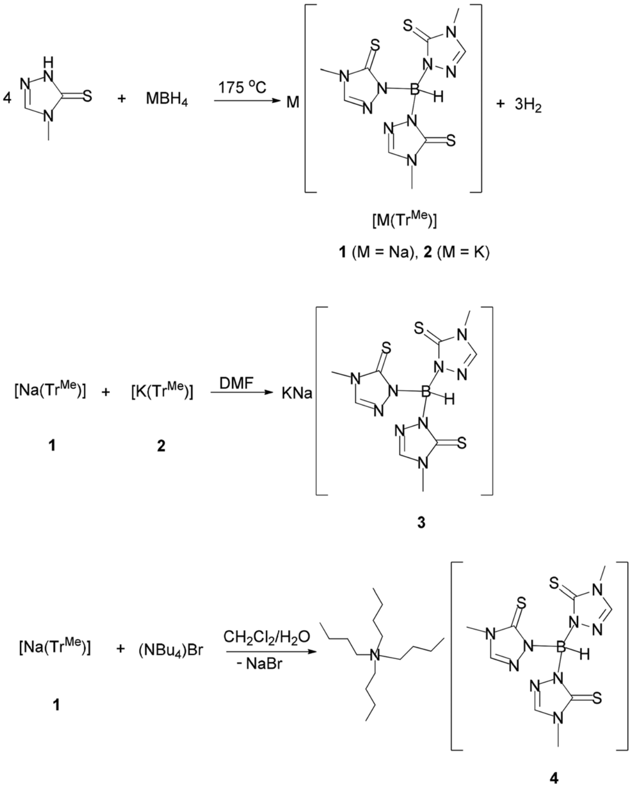
† CCDC 952327–952332. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52030g

tris(pyrazolyl)borate[1] and Reglinski's tris(mercaptoimidazolyl)-borate.[18] The characteristic feature of these ligands is the placement of boron-hydride moiety (B–H) towards the soft side defined by the three sulphur atoms. This restricts the repulsions between the lone pairs of electrons at the thione donor sites and the π-electrons of the attached ring.[21]

In this contribution, we report on a novel soft scorpionate ligand using Trofimenko's protocol and the precursor 3-mercapto-4-methyl-1,2,4-triazole, which can be described as a typical Janus scorpionate. We demonstrate its versatile coordination behaviour towards alkali metal and bismuth(III) ions. The chemistry of bismuth complexes synthesized from the precursor of this scorpionate ligand, *i.e.* 3-mercapto-4-methyl-1,2,4-triazole (L), will also be reported.

The aim of this contribution is to extend the concept of the soft Janus scorpionate, particularly with reference to their alkali metal polymeric assemblies, and bismuth chemistry. We also investigate the luminescent behaviour of the bismuth complexes as there is currently an active search for heavy metal-metal based "triplet-harvesting agents" in OLEDs. Due to the high degree of spin-orbit coupling, charge-neutral complexes of heavy metal ions promote emission from the normally non-emissive triplet excited states, which promises huge gains in emission efficiency. Bismuth as the heaviest non-radioactive metal ion is comparatively cheap and is therefore an attractive candidate to investigate the fundamental photophysical properties of its complexes.



Scheme 1 Synthesis of Janus scorpionate ligand alkali metal scorpionates **1–3**.

Results and discussion

Synthesis and structures of alkali metal scorpionates

As outlined in Scheme 1, the synthesis of the new alkali metal scorpionates $[Na(Tr^{Me})]$ (**1**) and $[K(Tr^{Me})]$ (**2**) was achieved by heating an excess of 3-mercapto-4-methyl-1,2,4-triazole (L) with the appropriate alkali metal borohydride *via* Trofimenko's protocol. The mixed metal compound $[KNa(Tr^{Me})]$ (**3**) was synthesized by combining **1** and **2** and using dmf as a solvent (Scheme 1) to observe the preferred binding of sodium and potassium ions to the soft and hard donor sites of the ligand $(Tr^{Me})^-$. The same mixed metal product $[KNa(Tr^{Me})]$ (**3a**) was also isolated in the form of a few crystals during the reaction of KBH_4 with 3-mercapto-4-methyl-1,2,4-triazole due to the sodium content in commercially available KBH_4.

The formation of the tetra-substituted borate species by applying an even larger excess of 3-mercapto-4-methyl-1,2,4-triazole (L) according to an analogous protocol[11,12] remained unattainable. Compounds **1–3** are highly soluble in polar solvents like dmso, dmf and even water, but less soluble in thf, toluene, methanol, acetonitrile and insoluble in non-polar organic solvents.[21]

A further derivative of $(Tr^{Me})^-$ with tetrabutylammonium as counter ion, compound **4**, was synthesized (Scheme 1) to overcome the solubility problems in certain solvents and to broaden the synthetic utility of the ligand. Compound **4** is freely soluble in common organic solvents; the same was earlier observed for $[NBu_4][HB(mtda^R)_3]$.[21,23]

Compounds **1–3** are stable in air for short periods of time; typically, storage in air for 24 h leaves the compounds unchanged. However, **4** should be stored under nitrogen as it is hygroscopic and increases weight upon exposure to air. For long time storage of all compounds, **1–4**, an inert atmosphere is necessary.

There is a lot of debate regarding the nomenclature of these borates in the literature. Originally, Trofimenko used the terms Tp and Bp for his tris- and bis(pyrazolyl) borates.[25] Referring to tripodal ligands based on 1,3,4-triazole-2-thione units, a different nomenclature has been used. For example, Bailey *et al.* and Riordan *et al.* used the term Tt for tris-(methylthioalkyl)borates.[20,26] Marchiò *et al.*[27] have also used the same terminology Tt^R (R = alkyl, aryl substituent) for 1,3,4-triazole-2-thione based borate ligands; however, later they modified Tt^R to Tr^R to reduce confusion.[24] The Janus scorpionate ligand $(Tr^{Me})^-$, described in this contribution, is also based on 1,3,4-triazole-2-thione, but with only one methyl substituent. Therefore we use the term Tr^{Me} to maintain consistency with the literature.[24,27] We replace the term Tt by $Tr^{Me,Me}$ for better clarity in the forthcoming part of our paper, as our novel ligand Tr^{Me} is closely related to it.

The solid state structures of the alkali metal scorpionates **1–3** were determined by single crystal X-ray diffraction. Crystals of **4** suitable for structure determination could not yet be grown. The structures are shown in Fig. 1–3. Selected bond

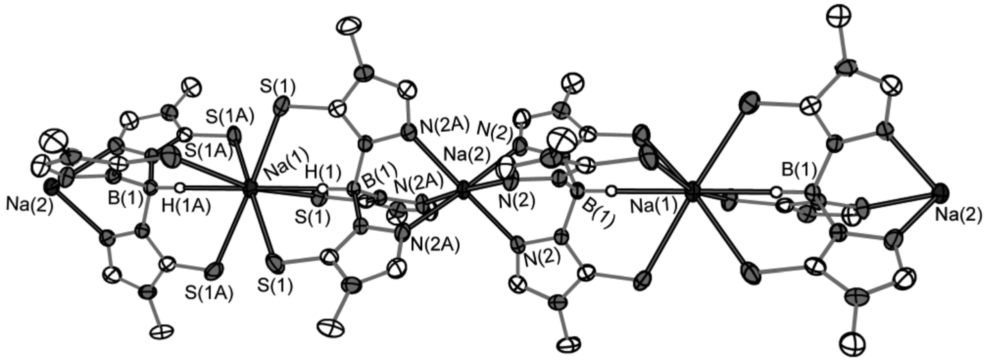


Fig. 1 Part of the polymeric chain aggregate of [Na(Tr^{Me})] (**1**) consisting of NaN_6 and NaH_2S_6 kernels with alternative orientation of the B–H bonds.

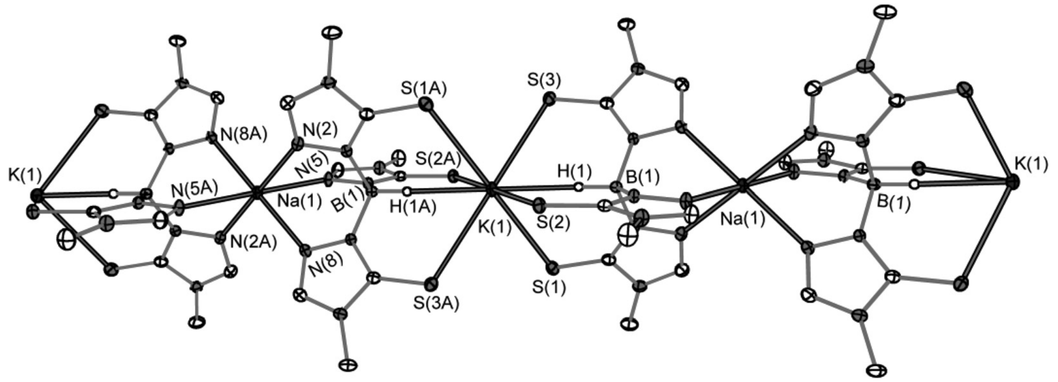


Fig. 2 Part of the polymeric chain aggregate structure of [KNa(Tr^{Me})] (**3**) consisting of NaN_6 and KH_2S_6 kernels with alternative orientation of the B–H bonds. Solvent molecule (dmf) is omitted.

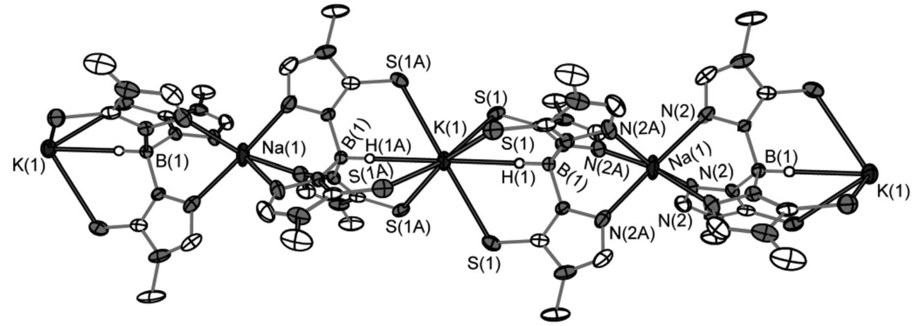


Fig. 3 Part of the polymeric chain aggregate structure of [KNa(Tr^{Me})] (**3a**) consisting of NaN_6 and KH_2S_6 kernels with alternative orientation of the B–H bonds.

Table 1 Selected bond lengths [Å] and angles [°] of compound **1**

Na(2)–N	2.412(2)
Na(1)–S	3.070(1)
B(1)–H(1)···Na(1)	2.35[a]
B(1)–Na(1)	3.352(3)
S–Na(1)–S (same ligand)	100.7(1)
S–Na(1)–S (two different ligands)	70.2(1)–167.5(1)
N–Na(2)–N (same ligand)	80.1(1)
N–Na(2)–N (two different ligands)	97.4(1)–175.9(1)
N–B(1)–N	110.6(2)
H–Na(1)–S (same ligand)	62.7[a]
H–Na(1)–S (two different ligands)	117.3[a]

[a] Hydrogen in calculated position.

lengths and bond angles are summarized in Tables 1 and 2. All three alkali metal scorpionates **1–3** crystallize as polymeric chain aggregates. This structural feature is contrasting the situation of analogous triazole based scorpionates such as hydrotris(thioxotriazolyl)borate (Tr^{Me,Me})$^-$,[20] hydrotris[(1,4-dihydro-4-methyl-3-(2-pyridyl)-5-thioxo-1,2,4-triazolyl]borate (Tr$^{Me,o\text{-}Py}$)$^-$,[24,28] hydrotris[(1,4-dihydro-4-mesityl-3-methyl-5-thioxo-1,2,4-triazolyl]borate (Tr^{Mes,Me})$^-$,[24] and hydrotris(4-ethyl-3-methyl-5-thioxo-1,2,4-triazolyl)borate (Tr^{Et,Me})$^-$,[27] where discrete monomeric complexes have been isolated. This might be attributed to the use of coordinating solvents like H_2O and dmf during crystallization, which is likely to prevent

Table 2 Selected bond lengths [Å] and angles [°] of compound **3** and **3a** (lgd = ligand)

3		**3a**	
K(1)–S(1)	3.187(1)	K(1)–S	3.286(1)
K(1)–S(2)	3.283(1)		
K(1)–S(3)	3.232(1)		
Na(1)–N(2)	2.426(1)	Na(1)–N	2.432(3)
Na(1)–N(5)	2.419(1)		
Na(1)–N(8)	2.409(1)		
BH(1)···K(1)	2.49(2)	BH(1)···K(1)	2.57[a]
B(1)–K(1)	3.545(2)	B(1)–K(1)	3.57(1)
S–K(1)–S	91.6(1)–103.2(1)	S–K(1)–S^{sl}	95.7(1)
S–K(1)–S^{dl}	76.8(1)–180.0	S–K(1)–S^{dl}	72.7(1)–162.5(1)
N–Na(1)–N^{sl}	77.5(1)–80.7(1)	N–Na(1)–N^{sl}	79.2(2)
N–Na(1)–N^{dl}	99.3(1)–180.0	N–Na(1)–N^{dl}	92.7(1)–165.8(1)
N–B(1)–N	109.2(1)–111.6(1)	N–B(1)–N	110.0(2)
H–K(1)–S^{sl}	59.4(3)–60.8(3)	H–K(1)–S^{sl}	58.9[a]
H–K(1)–S^{dl}	119.2(3)–120.6(3)	H–K(1)–S^{dl}	121.1[a]

[a] H atom in calculated position, sl = same ligands, dl = 2 different ligands.

polymerisation. However, aggregation processes as in the cases of **1–3** are not unprecedented, but scarcely reported in the literature. Closely related examples include the alkali metal scorpionates of Na[HB($mtda^R$)$_3$], K[HB($mtda^R$)$_3$] and KNa[HB($mtda^R$)$_3$] (where R = H, Me, mtda = mercaptothiadiazolyl).[21,23] The steric bulk and crystallization strategies of these reported alkali metal scorpionates are similar to our Tr^{Me} based alkali metal scorpionates **1–3** except the different heterocycle used.[21,23]

The molecular structure of coordination polymer **1** is shown in Fig. 1 and demonstrates a non-polar chain with alternative orientation of the ligand units, as is best seen by the alternating orientation of the B–H bonds. These B–H bonds are oriented towards the soft side of the scorpionate ligand. The structure is highly symmetric, as the crystal belongs to the trigonal space group $P\bar{3}1c$ and the whole coordination polymer has a threefold axis of symmetry plus inversion centres at the two different sodium sites.

These have two different coordination surroundings. One sodium atom is bound to two ligand units *via* their hard sites and represents an hexa-coordinate NaN_6 unit (ligand coordination mode κ^3-*N*,*N*,*N*), while the second is bound to the soft sides of two ligand units *via* three sulphur atoms and the hydrogen atom of the B–H function (ligand coordination mode κ^4-*H*,*S*,*S*,*S*), thus representing an octa-coordinate NaS_6H_2 surrounding. The NaN_6 unit is a distorted octahedron with an average value for the Na(2)–N distance of 2.412(2) Å, with N–Na(2)–N angles of 80.1(1)° for N atoms of the same ligand and N–Na(2)–N angles of 97.4(1)–175.9(1)° for N atoms of two different ligands. The NaS_6H_2 unit is characterized by a mean Na(1)–S distance of 3.070(1) Å and an (B)H–Na(1) distance of 2.352 Å (Na–B: 3.352(2) Å). The angles surrounding that unit are: S–Na(1)–S 100.7(1)° (same ligand) and 70.2(1)–167.5(1)° (two different ligands) and H–Na(1)–S 62.7° (same ligand), H–Na(1)–S 117.3° (two different ligands).

For comparison: typical ranges for such types of six- (NaN_6) and eight-coordinate sodium ions (NaS_6H_2) are 2.30–3.15 Å and 3.01–3.65 Å, respectively, as earlier described by Silva *et al.* for Na[HB(mtda)$_3$].[21] In the case of **1**, the bond lengths are not only within these ranges but also close to their lower ends. The same applies for the BH–Na distance, which is also shorter than the average value of 2.51 Å reported for such interactions.[21] Furthermore, Na[HB(mtda)$_3$][21] exhibits two types of polymeric chains in a crystal with polar and non-polar nature depending upon the orientation of the B–H bonds, while in our case **1**, only non-polar chain has been observed.

Compound **3** deviates in its composition from compound **1** in so far as it contains potassium and sodium atoms instead of two sodium atoms. Dimethylformamide (dmf) was used as solvent for its synthesis because of its strong coordinating ability. Consequently, we were expecting the chains of the aggregation polymers to be interrupted by dmf, which would result in monomeric or dimeric units as precedent in related cases in the literature.[20,26] However, this compound too retains its polymeric nature with alternate B–H bonds. The molecular structure of compound **3** is depicted in Fig. 2.

We got hold of a second form of compound **3** during the synthesis of compound **2**: from the raw product we obtained some crystals that turned out to contain sodium (an impurity) besides potassium, which obviously gets enriched during the crystallization process to give crystals with a Na : K ratio of 1 : 1. This form was obtained from thf/toluene and contained heavily disordered solvent molecules, the position of which could not be satisfactorily determined using X-ray diffraction (we name it **3a** for distinction; its molecular structure is depicted in Fig. 3). However, it is isostructural, with the same type of symmetry and the same space group (trigonal, $P\bar{3}1c$) as compound **1**, whereas compound **3** crystallizes in a lower-symmetric form in the triclinic space group $P\bar{1}$. This makes for some subtle deviations, but en gross, both structures are closely related. Similar to **3a**, the NaN_6 and KS_6H_2 units in crystals of **3** are arranged in the shown aggregation chain; however, dmf molecules are present within channels of the polymer.

Due to the presence of two metal ions with deviating Lewis acidity and hardness in both forms, **3** and **3a**, the distribution of sodium and potassium ions is not random. The hard sodium prefers the hard ligand donor sites and is present as hexa-coordinate NaN_6 units, while the softer potassium is found to be bound to the softer ligand sides and is present in KS_6H_2 units. The alternation and symmetry leads again to a non-polar aggregation polymer similar to KNa[HB(mtda)$_3$].[21] The (B)H···K distance of **3a** is 2.57 Å (B···K 3.570(6) Å), which is shorter compared to the average value of 2.85 Å found for related compounds as well as from KNa[HB(mtda)$_3$].[21] The Na(1)–N distance in this compound is 2.432(3) Å which is slightly longer than compound **1** (2.412(2) Å). The average K–S bond length is 3.286(1) Å and is also within the reported range for such eight-coordinate potassium ions.[21]

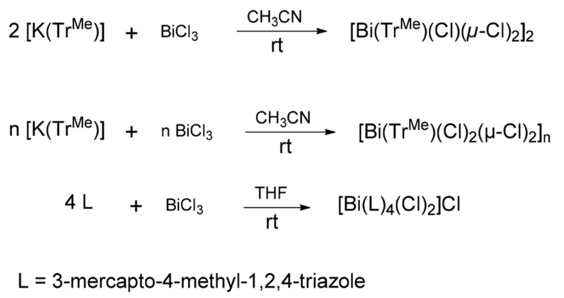
The K(1)–S bond lengths in **3** range from 3.187(1) to 3.283(2) Å with an average value of 3.232 Å, which is shorter than average K–S distance of 3.286 Å in compound **3a** and closely related KNa[HB(mtda)$_3$].[21] Similarly, the length of the (B)H⋯K interaction at 2.49(2) Å (K⋯B, 3.545(2) Å) is also shorter than observed for **3a** (Table 2).

Compounds **1–4** were further characterized by NMR studies using dimethylsulfoxide-d_6 (dmso-d_6) and dimethylformamide-d_7 (dmf-d_7) as solvents. The resonances observed were compared with each other. The ^{1}H NMR spectrum of **1** in dmso-d_6 exhibits two singlets at 3.36 and 8.04 ppm that can be assigned to the hydrogen atoms of the methyl group and the triazolyl ring, respectively. In the ^{13}C NMR spectrum, three resonances at 31.75, 140.52 and 168.99 ppm can be attributed to the methyl, triazolyl-CH and thione units, respectively. The other alkali metal scorpionates **2–3** as well as **4** show very similar chemical shifts in their respective ^{1}H and ^{13}C NMR spectra. In particular, the ^{13}C resonances of the C═S units would be expected to be different if coordinated to different cations. As this is not the case, one can conclude that the complexes are dissociated and the ions are solvated in dmf and dmso solutions. For details, see the data in the Experimental section. ^{11}B NMR spectra of **1–4** in dmso-d_6 show almost identical broad signals at −4.4 ppm, which is the characteristic region for borate compounds.[19,29] The operation of ESI-MS under negative mode also facilitated the dissociation nature of **1–4** with the same base peak at $m/z = 353$.

Synthesis and structures of bismuth complexes 5–7

Bismuth complexes of the ligand (Tr$^{\text{Me}}$)$^-$ have been synthesized by stirring the potassium salt of the scorpionate ligand, [K(Tr$^{\text{Me}}$)] (**2**), with BiCl$_3$ in a ratio of 2 : 1 and 1 : 1. In this way, two complexes were yielded, which contained chloride besides the (Tr$^{\text{Me}}$)$^-$ ligand. The experiment with the stoichiometric 2 : 1 ratio gave a complex of the composition [Bi(Tr$^{\text{Me}}$)(Cl)(μ-Cl)$_2$]$_2$ (**5**) while the 1 : 1 stoichiometry gave the coordination polymer [Bi(Tr$^{\text{Me}}$)(Cl)$_2$(μ-Cl)]$_n$ (**6**) (Scheme 2). Yields of **5** and **6** were 68% in both cases. The reaction of BiCl$_3$ with [NBu$_4$][(Tr$^{\text{Me}}$)] was also attempted. However, the separation of the side product NBu$_4$Cl is difficult, reducing the yield of the isolated bismuth complex.

For comparison of the binding of bismuth with the (Tr$^{\text{Me}}$)$^-$ ligand, we also carried out a reaction of BiCl$_3$ with the precursor of scorpionate ligand, 3-mercapto-4-methyl-1,2,4-triazole (L); this afforded the complex [Bi(L)$_4$(Cl)$_2$]Cl (**7**) in 81% yield.



$$2\,[\text{K(Tr}^{\text{Me}})] + \text{BiCl}_3 \xrightarrow[\text{rt}]{\text{CH}_3\text{CN}} [\text{Bi(Tr}^{\text{Me}})(\text{Cl})(\mu\text{-Cl})_2]_2$$

$$n\,[\text{K(Tr}^{\text{Me}})] + n\,\text{BiCl}_3 \xrightarrow[\text{rt}]{\text{CH}_3\text{CN}} [\text{Bi(Tr}^{\text{Me}})(\text{Cl})_2(\mu\text{-Cl})_2]_n$$

$$4\,\text{L} + \text{BiCl}_3 \xrightarrow[\text{rt}]{\text{THF}} [\text{Bi(L)}_4(\text{Cl})_2]\text{Cl}$$

L = 3-mercapto-4-methyl-1,2,4-triazole

Scheme 2 Syntheses of bismuth complexes **5–7**.

All three bismuth complexes **5–7** are coloured (**5** orange yellow, **6** yellow, **7** yellow). They are remarkably stable towards air and moisture and hence can be safely handled without inert atmosphere.

Complexes **5** and **6** are insoluble in non-polar solvents (ether, pentane, hexane, benzene) and slightly soluble in acetone, acetonitrile, dmf while **7** has good solubility in chloroform, acetone, thf, *etc*.

The molecular and crystal structures of the bismuth complexes **5–7** were determined by X-ray diffraction. They can be compared to the previously known molecular structures of bismuth complexes with tripodal ligands based on 1,2,4-triazole-thione such as (Tr$^{\text{Me,Me}}$)$^-$,[20] (Tr$^{\text{Et,Me}}$)$^-$,[27] and (Tr$^{\text{Ph,Me}}$)$^-$.[30] The configuration of these ligands around bismuth as well as the bulkiness around thione donor atoms prompted us to study the bismuth chemistry of our Janus scorpionate ligand (Tr$^{\text{Me}}$)$^-$ which has less steric bulk close to C═S group than the reported systems,[20,27,30] as it possesses only one methyl substituent attached to nitrogen.

The molecular structure of the bismuth complex **5** is shown in Fig. 4. To the best of our knowledge, it is the first dimeric bismuth complex with a Janus scorpionate ligand. Two heavily disordered acetone molecules from the solvent required for crystallization are present in the crystal lattice. The complex is dimeric and has a centre of inversion. The two bismuth atoms are asymmetrically bridged by two chloride ligands with bond lengths of 2.993(2) Å (Bi(1)–Cl(2)) and 2.961(2) Å (Bi(1)–Cl(2A)).

A second type of chloride ligand is terminally bound to the bismuth atoms with a distance of 2.678(2) Å and is in agreement with the literature.[31] Both scorpionate ligands coordinate in a tridentate fashion *via* their sulphur donor atoms (κ^3-*S*,*S*,*S*). The Bi(1)–S bond lengths have different values of 2.675(2), 2.688(2) and 2.825(2) Å to the atoms S(1), S(2) and S(3). These values are comparable with other scorpionate based monomeric complexes.[23,27,30,32,33] The structure of **5** resembles more closely those of [Tm$^{\text{Me}}$BiCl(μ-Cl)$_2$]$_2$ [34] and [Tm$^{t\text{-Bu}}$BiCl(μ-Cl)$_2$]$_2$.[10] The Bi–S bond lengths of **5** are slightly longer than [Tm$^{\text{Me}}$BiCl(μ-Cl)$_2$]$_2$ [34] but shorter than in [Tm$^{t\text{-Bu}}$BiCl(μ-Cl)$_2$]$_2$.[10] The latter contains more bulky groups; however, interestingly, they possesses regular octahedral geometry in contrast to **5**. It can be attributed to a stereochemically inactive lone pair that seems to be less exposed in [Tm$^{\text{Me}}$BiCl(μ-Cl)$_2$]$_2$.[34] Furthermore, these Bi–S bond lengths are within the range from 2.63 to 2.83 Å

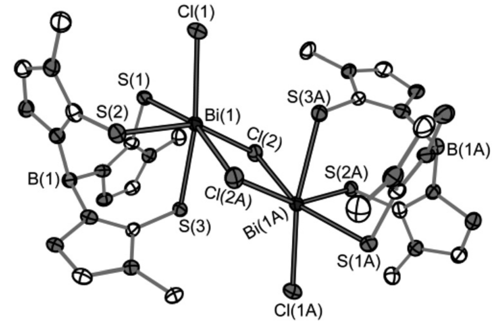


Fig. 4 Structure of the dimeric bismuth complex [Bi(Tr$^{\text{Me}}$)(Cl)(μ-Cl)$_2$]$_2$ (**5**).

Table 3 Selected bond lengths [Å] and angles [°] of compounds **5** and **6**

5	
Bi(1)–S(1)	2.675(2)
Bi(1)–S(2)	2.688(2)
Bi(1)–S(3)	2.825(2)
Bi(1)–Cl(1) (terminal)	2.678(2)
Bi(1)–Cl(2) (bridged)	2.993(2)
Bi(1)–Cl(2A) (bridged)	2.961(2)
S–Bi(1)–S (intra ligand)	88.1(1)–90.8(1)
S(1)–Bi(1)–Cl(1)	66.9(1)–161.2(1)
Cl–Bi(1)–Cl	100.3(1)–112.8(1)
N–B(1)–N	108.9(4)–111.5(4)
6	
Bi(1)–S(1)	2.666(2)
Bi(1)–S(2)	2.770(2)
Bi(1)–S(3)	2.701(2)
Bi(1)–Cl(2) (terminal)	2.695(2)
Bi(1)–Cl(1) (bridged)	2.846(2)
Bi(1)–Cl(1A) (bridged)	2.814(2)
S–Bi(1)–S (intra ligand)	89.9(1)–91.1(1)
S–Bi(1)–Cl	76.6(1)–168.9(1)
Cl–Bi(1)–Cl	93.0(1)–97.7(1)
N–B(1)–N	109.2(4)–111.1(5)

found in the CCDC crystal structure database for soft scorpionate based bismuth complexes.[35]

The intra-ligand S–Bi(1)–S angles in **5** are between 88.1(1) and 90.8(1)°. They are thus close to those expected for an octahedral geometry. In contrast, the Cl–Bi–Cl bond angles are much wider and range from 100.3(1) to 112.8(1)° (Table 3), which documents the distortion by a stereochemically active lone pair of electrons at bismuth and makes the complex distorted octahedral. Hence, it can be classified as hemidirecting.[36,37] The N–B(1)–N bond angles deviate only slightly from those expected for an ideal tetrahedral surrounding of boron atom; they range from 108.9(4) to 111.5(4)°.

In contrast to the above-described sodium and potassium complexes, there is no evidence for (B)H⋯Bi interaction, as the B–H bonds are oriented away from the bismuth site.

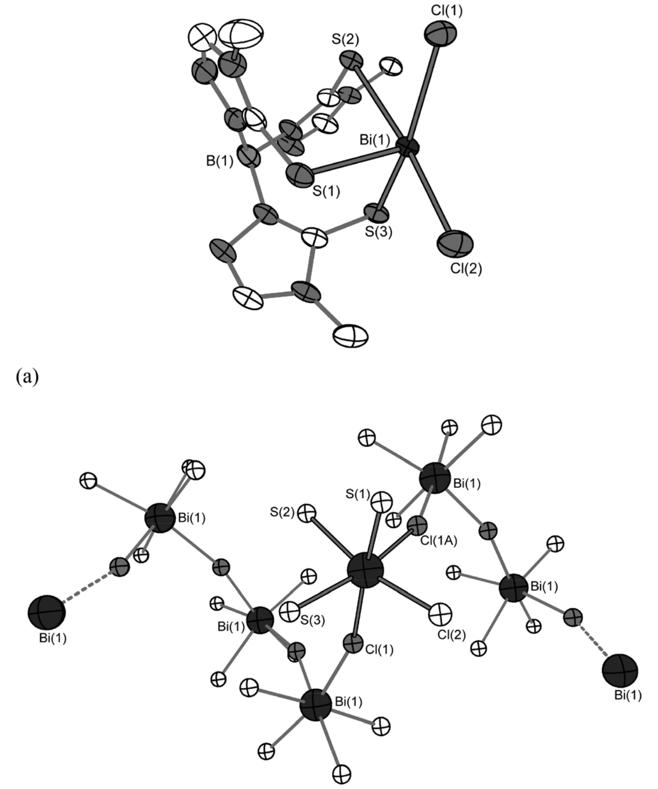


Fig. 5 (a) Unit of the molecular structure of the bismuth complex **6**, (b) infinite zigzag chain of **6** created by the symmetry of 4-fold screw axes.

The molecular structure of compound **6** is shown in Fig. 5. In this complex, the Janus scorpionate ligand also behaves as a tridentate ligand coordinating through its sulphur atoms while the remaining part of the coordination sphere of the bismuth ion is covered by three chloride ligands. One of them bridges two bismuth atoms leading to an infinite zigzag chain aggregate. The Bi–S bond lengths 2.666(2), 2.770(2), 2.700(2) Å to S(1), S(2) and S(3) are comparable with those in the above described structure of **5** and are also in the range covered by literature values.[10,23,27,30,32–34] The Bi–Cl bonds fall over a range of 2.695(2) to 2.846(2) Å, which is in agreement with bismuth polymeric structures based on thiosemicarbazide ligands.[38–40] All S–Bi(1)–S angles are in a narrow range between 89.9(1) and 91.1(1)°, the Cl–Bi(1)–Cl angles cover a range between 93.0(1) and 97.7(1)° and the S–Bi–Cl angles are in the range between 76.6(1) to 168.9(1)°. All this reflects distorted octahedral coordination geometry. The largest angles at the bismuth atom are those enclosed by the atoms S(1), Bi(1) and Cl(1). Although this distortion of the structure is less pronounced than in **5**, one could expect a stereochemically active lone pair of electrons to be oriented towards the area between these atoms. The N–B(1)–N angles are close to the ideal tetrahedral angle (values 109.2(4)–111.1(5)°).

^{1}H NMR and ^{13}C NMR data of complexes **5** and **6** were recorded in dmf-d_7 solutions and compared with that of the free ligand. Thus in the ^{1}H NMR spectrum of complex **5**, two signals at 3.81 and 8.89 ppm correspond to CH_3 and the triazolyl ring proton, respectively, and are downfield shifted compared to the free ligand (3.48 CH_3, 8.12 HC-triazolyl ring). This downfield shifting is comparable to reported values.[17] The analogous signals of complex **6** were observed at 3.77 and 8.75 ppm and are also downfield shifted compared to a free ligand. The important feature in the ^{13}C NMR spectrum of **6** is an upfield shift for the C=S resonance at 162.54 ppm compared to free ligands (168.56) and can be attributed to the coordination of the thione moiety to bismuth. Unfortunately, the chemical shift for the C=S function in the case of **5** could not be observed.

It should be noted that in the MALDI-MS and ESI-MS spectra of **5**, one peak was found at m/z = 917.2 which can be attributed to the $[(\mathrm{Tr}^{\mathrm{Me}})_2\mathrm{Bi}]^+$ fragment similar to that observed for related compounds $[\mathrm{Bi}(\mathrm{Tr}^{\mathrm{Et,Me}})_2]^+$ and $[\mathrm{Bi}(\mathrm{Tr}^{\mathrm{Me,Me}})_2]^+$.[23,27] Therefore the mass spectral data do not support the solid state composition $[\mathrm{Bi}(\mathrm{Tr}^{\mathrm{Me}})(\mathrm{Cl})(\mu\text{-Cl})_2]_2$ for complex **5**. However, elemental analysis data prove the solid state composition of dimeric bismuth complex **5** as obtained by means of X-ray crystallography.

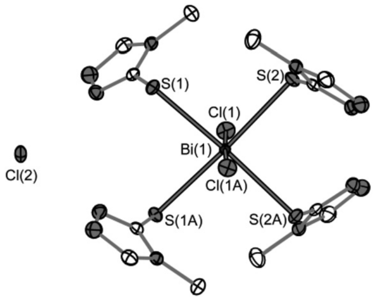


Fig. 6 Molecular structure of the bismuth complex **7**.

The molecular structure of compound **7**, $[Bi(L)_4(Cl)_2]Cl$, is shown in Fig. 6. The cationic complex has a relatively regular octahedral environment formed by four Bi–S and two Bi–Cl bonds. There are only slight deviations in the S–Bi(1)–S angles and Cl–Bi(1)–S angles from 90° (Table 4). The Bi–S bond lengths are 2.800(1) and 2.858(1) Å and are comparable to **5** and **6** as well as other bismuth complexes based on small soft heterocyclic ligands.[41–43]

^1H NMR and ^{13}C NMR spectroscopic data of this complex **7** in thf-d_8 were compared with 3-mercapto-4-methyl-1,2,4-triazole (L).[44] The data exhibit a similar pattern of chemical shift as discussed in above cases **5** and **6**.

Photophysical characterization

The ligand Tr^{Me} features an intense absorption at 250 nm assignable to a π–π* transition, but no luminescence at r.t. and 77 K (Table 5). Only two of all complexes, namely **5** and **7**, are emissive in solution and were further investigated by electronic spectroscopy. Upon complexation of the Bi(III) ion by the thioxotriazolyl heterocycle, the π–π* absorption band is bathochromic shifted to 286 and 279 nm for **5** and **7**, respectively. Weak bands which might be due to sp absorptions and/or S → Bi ligand to metal charge transfer states (LMCT) are evolving above 300 nm for **5**, and at 290 nm for **7**. Compound **5** exhibits a broad emission band centred around 485 nm, which became structured at 77 K. Both the excitation spectra at r.t. and 77 K resemble the absorption spectrum. Complex **7** is not emissive in solution at r.t. but at 77 K. At this temperature, it has a band at 504 nm. In general, s^2-metal cations can feature MC (metal-centred) sp transitions and – if ligands with low-lying HOMOs are bonded – also LMCTs.[45–47] An MC sp transition results in a considerable geometrical distortion of the molecule in the excited state, which leads either to an efficient quenching and non-emissive behaviour or to a large Stokes shift of the emission, as observed for **7** (Fig. 7). The wavelength of this luminescence is comparable to other emissive Bi^{3+} complexes reported previously.[48–54] Due to a similar position of the emission band in **5** (Fig. 8), we tentatively assign it to a similar excited state as in **7**. However, the emission band is much broader than in **5** and overlaps with the absorption, which means that a LMCT excited state might be involved as well. In a recent publication, we pointed out that according to td-dft calculations, the lowest energy excited states of Ph_3Bi lie close to each other and one has to expect a mixture of different transitions in this energy range.[55]

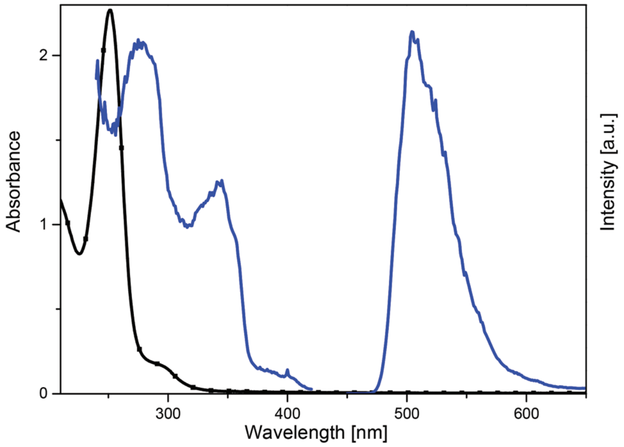


Fig. 7 Electronic absorption spectrum (black), excitation (blue, left) and emission (right) spectra of **7** in ethanol at 77 K ($c = 2.9 \times 10^{-5}$ mol L^{-1}; λ_{exc} = 350 nm, λ_{dec} = 500 nm).

Table 4 Selected bond lengths [Å] and angles [°] of compound **7**

Bi(1)–Cl(1)	2.658(1)
Bi(1)–S(1)	2.858(1)
Bi(1)–S(2)	2.800(1)
S(2)–Bi(1)–S(1)	92.8(1)
S(2)–Bi(1)–S(2A)	89.8(1)
S(2)–Bi(1)–S(1A)	164.5(1)
S(1)–Bi(1)–S(1A)	88.8(1)
S(1)–Bi(1)–S(2A)	164.5(1)
Cl–Bi–Cl (*trans*)	178.0(1)
Cl–Bi–S (*cis*)	81.9(1)–98.8(1)

Table 5 Electronic spectroscopic data of Tr^{Me}, **5** and **7**

	Absorption [nm] (log{ε/L mol^{-1} cm^{-1}})	T [K]	Excitation [nm]	Emission [nm]
$Tr^{Me\,a}$	250 (4.3)			
5^b	268 (4.2), 308 (3.6), 316 (3.6), 360 (3.5), 417 (3.1)	298	263, 300, 323 (sh), 361	485
		77	279, 305, 333, 363	381, 420, 441, 482, 534, 577, 634
7^a	251 (4.9), 290 (3.8)	77	276, 330 (sh), 343, 355 (sh), 387	504, 521 (sh)

[a] Ethanol. [b] dcm.

Conclusion

A new hard/soft Janus scorpionate was synthesized from 3-mercapto-4-methyl-1,2,4-triazole *via* Trofimenko's protocol. Relative to other scorpionate ligands bearing triazole moieties which form discrete monomeric alkali metal complexes as discussed,[23,24,27,28] we have successfully characterized polymeric structures with alkali metals that can be carefully used for

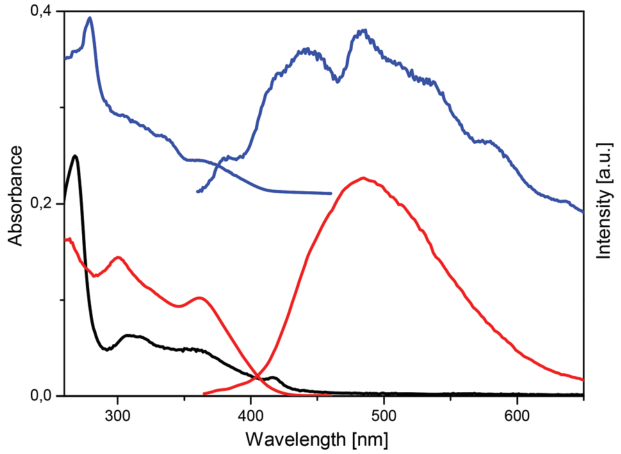


Fig. 8 Electronic absorption spectrum (black), excitation and emission spectra of **5** in dcm at r.t. (blue) and 77 K (red, $c = 1.7 \times 10^{-5}$ mol L^{-1}; $\lambda_{exc} = 350$ nm, $\lambda_{dec} = 480$ nm).

building soft hard assemblies.[21] In alkali metal scorpionates (**1–3**), both hard and soft sites of the ligand participate in binding alkali metal ions; however, only the soft side has been used by this ligand during coordination with larger bismuth ions as per preference according to the Pearson hard soft acid base concept. Depending upon the degree of distortion caused by the pronounced effect of a lone pair, bismuth complexes can be arranged in the following order (**5** > **6** > **7**). Solutions of Tr^{Me} exhibit no luminescence at r.t and 77 K. Only two complexes **5** and **7** are emissive in solution. In solution, complex **7** is not emissive at r.t., but at 77 K, it exhibits a band at 504 nm assignable to metal centred sp transition. **5** features a broad emission band centred around 485 nm, which became structured at 77 K. However, the emission band is much broader than in **7** and overlaps with the absorption, which indicates the possible involvement of an LMCT excited state.

Experimental

All the solvents used during this work were dried and distilled before use. KBH_4, $NaBH_4$, 3-mercapto-4-methyl-1,2,4-triazole and $BiCl_3$ were procured from Alfa Aesar, Acros Organic and used without further purification. NMR spectra were recorded using Bruker Avance 300, Bruker DRX 500 or Bruker Avance 500 spectrometers and the chemical shifts were referenced to the residual proton (^1H) or the carbon signals of the deuterated solvents and were reported in ppm. Elemental analyses were performed using a EuroEA Elemental Analyser. ESI-MS and MALDI-TOF spectra were measured using Esquire 3000 (Bruker Daltonik 2000) and Voyager DE PE Biosystem 2000 spectrometers. Melting points were determined using a Büchi B 545 melting point apparatus and are uncorrected. All operations were carried out under an inert atmosphere of nitrogen using Schlenk and glove box techniques. Described methods with certain modifications were followed for the synthesis of alkali metal scorpionates.[18,21,22]

$[Na(Tr^{Me})]$ (1)

$NaBH_4$ (0.213 g, 5.75 mmol) and 3-mercapto-4-methyl-1,2,4-triazole (2.69 g, 23.0 mmol) were ground separately and then mixed with stirrer in a Schlenk tube connected to a gas bubbler. The resulting homogeneous mixture was heated to 175 °C in an oil bath for 2.5 h. In the course of the reaction, at 125 °C, gas evolution was observed, which enhanced vigorously at 160 °C and finally ceased at 170 °C. This mixture was further heated to 175 °C for another 1.5 h and then cooled to room temperature. The solid obtained was washed with toluene (3 × 25 mL), thf (3 × 25 mL), diethyl ether (3 × 20 mL) and then dried under vacuum by heating to 60 °C for further 3 h. Yield: 84%; colourless powder; m.p. 306–309 °C (with decomposition); Anal. calcd for $C_{18}H_{26}B_2N_{18}Na_2S_6 \cdot H_2O$ (found): C 27.99 (27.45), H 3.65 (3.52), N 32.64 (31.78); IR (cm^{-1}, KBr pellet) 2440 (B–H), 1628 (C=N) 1211 (C=S); ^1H NMR (dmso-d_6) $\delta = 8.04$ (s, 3H, HC=N), 3.36 (s, 9H, H_3C); ^{13}C NMR (dmso-d_6) $\delta = 168.95$ (C=S), 140.52 (C=N), 31.75 (H_3C); ^{11}B NMR (dmso-d_6) $\delta = -4.31$ (br); ^1H NMR (dmf-d_7) $\delta = 8.13$ (s, 3H, HC=N), 3.48 (s, 9H, H_3C); ^{13}C NMR (dmf-d_7) $\delta = 168.52$ (C=S), 140.60 (C=N), 31.37 (H_3C); ^{11}B NMR (dmf-d_7) $\delta = -2.37$ (br); ESI-MS (negative mode) *m*/*z* [assignment] = 353.9 $[(Tr^{Me})]^-$.

$[K(Tr^{Me})]$ (2)

This compound was prepared by reacting KBH_4 (0.304 g, 5.75 mmol) and 3-mercapto-4-methyl-1,2,4-triazole (2.69 g, 23.0 mmol) according to the same procedure as described above for **1**. Gas evolution was observed when the oil bath reached 140 °C and ceased at 175 °C. The resulting mixture was further heated to 175 °C for 1 h and then cooled to room temperature. Yield 72%, colourless powder, m.p: 300–303 °C, Anal. calcd for $C_{18}H_{26}B_2N_{18}Na_2KS_6$ (found): C 27.24 (26.90), H 3.30 (3.40), N 31.77 (30.64); IR (cm^{-1}, KBr pellet) 2449 (B–H), 1620 (C=N), 1213 (C=S); ^1H NMR (dmso-d_6) $\delta = 8.04$ (s, 3H, HC=N), 3.36 (s, 9H, H_3C); ^{13}C NMR (dmso-d_6) $\delta = 168.73$ (C=S), 140.38 (C=N), 31.88 (H_3C); ^{11}B NMR (dmso-d_6) $\delta = -4.42$ (br) ^1H NMR (dmf-d_7) $\delta = 8.12$ (s, 3H, HC=N), 3.48 (s, 9H, H_3C); ^{13}C NMR (dmf-d_7) $\delta = 168.56$ (C=S), 140.75 (C=N), 31.47 (H_3C); ^{11}B NMR (dmf-d_7) $\delta = -2.29$ (br); ESI-MS (negative mode) *m*/*z* [assignment] = 353.8 $[(Tr^{Me})^-]$.

$[KNa(Tr^{Me})]$ (3)

$[Na(Tr^{Me})]$ (**1**) (0.188 g, 0.501 mmol) and $[K(Tr^{Me})]$ (**2**) (0.196 g, 0.501 mmol) were dissolved in a 80 mL of dmf and then stirred along with heating at 95 °C for 5 h. The resulting solution was filtered hot and slowly cooled to room temperature, leading to the precipitation of colourless crystals. The crystals were isolated by filtration and were dried to leave **3** as a colourless powder. The solid isolated was washed with thf (3 × 30 mL), diethyl ether (3 × 30 mL) and finally dried under vacuum for 6 h by heating up to 70 °C. Yield 96%; colourless powder; m.p. 320–324 °C; Anal. calcd for $C_{18}H_{26}B_2N_{18}Na_2KS_6 \cdot 2dmf$, (found): C, 30.67 (31.15), H, 4.29 (4.40), N, 29.81 (30.44); IR (cm^{-1}, KBr pellet) 2409 (B–H), 1618

(C═N), 1215 (C═S); ^{1}H NMR (dmso-d_6) δ = 8.03 (s, 3H, HC═N), 3.36 (s, 9H, H_3C); ^{13}C NMR (dmso-d_6) δ = 168.75 (C═S), 140.35 (C═N), 31.64 (H_3C); ^{11}B NMR (dmso-d_6) δ = −4.42 (br); ^{1}H NMR (dmf-d_7) δ = 8.32 (s, 3H, HC═N), 3.54 (s, 9H, H_3C); ^{13}C NMR (dmf-d_7) δ = 168.52 (C═S), 140.60 (C═N), 31.37 (H_3C); ^{11}B NMR (dmf-d_7) δ = −2.37 (br); ESI-MS (negative mode) *m*/*z* [assignment] = 353.8 [$(Tr^{Me})^-$].

[NBu$_4$][(Tr^{Me})] (4)

Solutions of [Na(Tr^{Me})] (**1**) (0.828 g, 2.21 mmol) in 20 mL of water and NBu_4Br (0.616 g, 2.20 mmol) in 20 mL of CH_2Cl_2 were mixed in a 100 mL flask and stirred for 3 h. Then the two phases were separated and the aqueous phase was washed with CH_2Cl_2 (2 × 25 mL). Again both the phases were separated. The process was repeated three times and finally the combined CH_2Cl_2 were washed with 25 mL of H_2O, and the phases were again separated. The solvent was removed from the organic phase by vacuum distillation and the resulting solid was dried under vacuum for 3 h at room temperature and stored under N_2 atmosphere. Yield 81%; colourless powder; m.p. 211–215 °C (with decomposition); Anal. calcd for $C_{25}H_{49}N_{10}S_3B\cdot0.25\ H_2O$, (found): C 50.32 (50.04), H 8.28 (8.25), N 23.47 (23.30); IR (cm^{-1}, KBr pellet) 2456 (B–H), 1618 (C═N), 1211 (C═S); ^{1}H NMR (dmso-d_6) δ = 8.03 (s, 3H, HC═N), 3.36 (s, 9H, H_3C-heterocycle), 3.17 (t, 8H, N–CH_2), 1.57 (m, 8H, CH_2), 1.30 (m, 8H, CH_2), 0.94 (t, 12H, CH_3); ^{13}C NMR (dmso-d_6) δ = 168.72 (C═S), 140.32 (C═N), 57.73 (N–CH_2), 31.64 (H_3C-heterocycle), 23.39 (CH_2), 19.17 (CH_2), 14.12 (CH_3); ^{13}C NMR (DEPT-135) (dmso-d_6) δ = 140.32 (C═N). 57.99 (N–CH_2), 31.65 (H_3C-heterocycle), 23.36 (CH_2), 19.47 (CH_2), 14.01 (CH_3); ^{1}H NMR (dmf-d_7) δ = 8.22 (s, 3H, HC═N), 3.70 (s, 9H, H_3C-heterocycle), 3.11 (t, 8H, N–CH_2), 1.95 (m, 8H, CH_2), 1.59 (m, 8H, CH_2), 1.14 (t, 12H, CH_3); ^{13}C NMR (dmf-d_7) δ = 169.52 (C═S), 139.62 (C═N), 58.31 (N–CH_2), 31.13 (H_3C-heterocycle), 23.66 (CH_2), 19.96 (CH_2), 13.03 (CH_3); ^{13}C NMR (DEPT-135) (dmf-d_7) δ = 139.84 (C═N), 58.44 (N–CH_2), 31.13 (H_3C-heterocycle), 23.69 (CH_2), 19.52 (CH_2), 13.35 (CH_3); ^{1}H NMR ($CDCl_3$) δ = 7.73 (s, 3H, HC═N), 3.50 (s, 9H, H_3C-heterocycle), 3.42 (t, 8H, N–CH_2), 1.69 (m, 8H, CH_2), 1.41 (m, 8H, CH_2), 0.94 (t, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 168.95 (C═S), 140.25 (C═N), 58.99 (N–CH_2), 31.95 (H_3C-heterocycle), 24.05 (CH_2), 19.76 (CH_2), 13.46 (CH_3); ^{13}C NMR (DEPT-135) ($CDCl_3$), 140.25 (C═N). 58.99 (N–CH_2), 31.95 (H_3C-heterocycle), 24.11 (CH_2), 19.76 (CH_2), 13.75 (CH_3); ^{11}B NMR ($CDCl_3$), δ = −4.52 (br); ESI-MS (negative mode) *m*/*z* [assignment] = 353.9 [$(Tr^{Me})]^-$.

[Bi(Tr^{Me})(Cl)(μ-Cl)$_2$]$_2$ (5)

[K(Tr^{Me})] (**2**) (0.282 g, 0.720 mmol) and $BiCl_3$ (0.113 g, 0.360 mmol) were dissolved and stirred separately in 20 mL of acetonitrile. Then the solution of **2** was slowly added to that of $BiCl_3$ solution under N_2 atmosphere. The resulting orange yellow solution was stirred at room temperature for 6 h and then filtered. The volume of the sample was reduced under vacuum. An orange yellow solid was obtained, which was washed with a small amount of acetonitrile and dichloromethane. The product was recrystallized from a mixture of acetone–pentane (3 : 1). Yield 68%; m.p. 250–254 °C (with decomposition); Anal. calcd for $C_{18}H_{26}Bi_2B_2N_{18}S_6Cl_4\cdot C_3H_6O$ (found): C 19.02 (20.49), H 2.43 (3.10), N 19.01 (18.99), S 14.50 (13.89); ^{1}H NMR (dmf-d_7), δ = 8.89 (s, 6H, HC═N), 3.81 (s, 18H, H_3C); ^{13}C NMR (dmf-d_7) δ = 144.80 (C═N), 32.34 (H_3C), the C═S carbon atom could not be detected; MALDI-MS and ESI-MS *m*/*z* [assignment] = 917.2 [$Bi(Tr^{Me})_2{}^+$].

[Bi(Tr^{Me})(Cl)$_2$(μ-Cl)]$_n$ (6)

This complex was prepared according to the same procedure as described above by reacting equimolar solutions of [K(Tr^{Me})] (0.141 g, 0.361 mmol) and $BiCl_3$ (0.113 g, 0.360 mmol). Yield, 68%; m.p. 278–280 °C (with decomposition); Anal. calcd for $C_9H_{13}BBiCl_2N_9S_3$ (found): C 16.14 (15.01), H 1.96 (1.85), N, 18.83 (16.88), S, 14.37 (12.97), ^{1}H NMR (dmf-d_7) δ = 8.75 (s, 3H, HC═N), 3.77 (s, 9H, H_3C), ^{13}C NMR (dmf-d_7) δ = 162.54 (C═S), 144.80 (C═N), 32.34 (H_3C); ESI-MS(+) *m*/*z* [assignment] = 562 [$Bi(Tr^{Me})^+$].

[Bi(L)$_4$(Cl)$_2$]Cl (7)

A solution of 3-mercapto-4-methyl-1,2,4-triazole (0.684 g, 6.00 mmol) in 10 mL of thf was added drop-wise into partially dissolved $BiCl_3$ (0.630 g, 2.00 mmol) in 10 mL of thf. Upon mixing, a clear yellow solution was obtained that was stirred at room temperature for 24 h and then concentrated under vacuum to 7 mL. The resulting solution was kept at room temperature for several weeks, which led to precipitation of yellow crystals. The crystals were filtered off, washed with small amounts of thf, then methanol and dried. The product was finally recrystallized from thf. Yield 81%; m.p. 220 °C (with decomposition); Anal. calcd for $C_{12}H_{20}BiCl_3N_{12}S_4$ (found): C 18.57 (19.10), H 2.59 (2.71), N 21.66 (21.24), S 16.53 (16.57); ^{1}H NMR (thf-d_8) δ = 8.03 (s, 4H, HC═N), 3.37 (s, 12H, H_3C); ^{13}C NMR (thf-d_8) δ = 165.66 (C═S), 139.77 (C═N), 29.08 (H_3C); ^{1}H NMR ($CDCl_3$), δ = 7.80 (s, 4H, HC═N), 3.63 (s, 12H, H_3C); ^{13}C NMR ($CDCl_3$) δ = 166.64 (C═S), 143.26 (C═N), 31.70 (H_3C); ESI-MS(+) *m*/*z* [assignment] = 669 [$Bi(L)_4{}^+$].

Electronic spectroscopy

For photophysical characterization, spectroscopic-grade solvents were used throughout all measurements. Absorption spectra were recorded with a Varian Cary 300 double beam spectrometer. Emission spectra at 300 and at 77 K were measured with a steady-state fluorescence spectrometer (Jobin Yvon Fluorolog 3).

X-ray crystallographic analysis

X-ray diffraction data were collected from **1**, **3**, **3a**, **5**, **6** and **7** (Table 6). The crystals were obtained by slow evaporation of the mixture of thf–toluene (**1**, **3a**), slow cooling of saturated solution in dmf (**3**), slow evaporation of acetone solution (**5**) and slow evaporation of the concentrated mother liquor solution (**6**) slow diffusion of *n*-pentane into thf solution (**7**). Single-crystals suitable for X-ray diffraction were picked under inert paratone oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer. The data for **1**, **3**, **5**

Table 6 X-ray crystallographic data for compounds **1**, **3**, **3a**, **5**, **6** and **7**

Compound	1	3	3a	5	6	7
Empirical formula	$C_{18}H_{26}B_2N_{18}Na_2S_6$	$C_{18}H_{26}B_2KN_{18}NaS_6\cdot 2(C_3H_7NO)$	$C_{18}H_{26}B_2KN_{18}NaS_6$	$C_{18}H_{26}B_2Bi_2Cl_4N_{18}S_6\cdot 2(C_3H_6O)$	$C_9H_{13}BBiCl_2N_9S_3$	$C_{12}H_{20}BiCl_3N_{12}S_4$
M_r	754.53	916.83	770.64	1384.46	634.15	775.97
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Trigonal	Triclinic	Trigonal	Triclinic	Tetragonal	Monoclinic
Space group	$P\bar{3}1c$	$P\bar{1}$	$P\bar{3}1c$	$P\bar{1}$	$I4_1/a$	$C2/c$
a (Å)	13.1216(3)	10.4389(1)	13.0298(7)	10.324(4)	30.8530(12)	17.7736(12)
b (Å)	13.1216(3)	10.5802(1)	13.0298(7)	11.303(6)	30.8530(12)	11.6737(12)
c (Å)	13.5926(2)	10.6206(1)	14.0697(916)	11.545(6)	9.6827(5)	14.194(26)
α (°)	90	93.3316(6)	90	94.49(4)	90	90
β (°)	90	96.2652(6)	90	102.35(5)	90	113.552(7)
γ (°)	120	116.4806(7)	120	114.39(3)	90	90
Z	2	1	2	1	16	4
V (Å^3)	2026.78(7)	1036.120(17)	2068.7(2)	1177.3(10)	9217.0(7)	2699.6(5)
F(000)	776	476	792	664	4800	1496
Cryst size (mm)	0.30 × 0.28 × 0.08	0.30 × 0.26 × 0.20	0.45 × 0.20 × 0.17	0.18 × 0.11 × 0.02	0.21 × 0.02 × 0.02	0.30 × 0.16 × 0.07
Refl measured	37 797	45 873	47 618	24 943	123 597	34 793
Unique refl (R_{int})	1991	6042	1560	5380	4109	3915
Parameters	72	336	72	233	229	156
R ($I > 2\sigma(I)$)	0.0417	0.0259	0.0658	0.0345	0.0251	0.0164
R_w (all reflections)	0.1445	0.0680	0.1562	0.0711	0.0591	0.0327
Goodness-of-fit	1.175	1.026	1.174	1.025	1.014	1.080
CCDC no.	952327	952328	952329	952330	952331	952332

and **7** were collected on a Bruker Nonius Kappa CCD diffractometer, while the data for compounds **3a** and **6** were collected using Bruker AXS Kappa with APEX II, all with Mo-K$_\alpha$ radiation. A summary of data collection and structure refinement is reported in Table 5. The structures were solved by direct methods and refined by full-matrix least squares cycles (programs SHELXS-97 or SHELXL-97).[56] All hydrogen atoms of **3**, B–H of **5**, N–H of **7** were refined isotropically, while the positions of all hydrogen atoms of **1**, **3a**, **6**; all C–H of **7** and all hydrogen atoms of **5** (except B–H) were calculated and included in the refinements using riding models. In compound, the contributions of **1** disordered solvent molecules were corrected using the SQUEEZE procedure of PLATON[57] while for **3a** and **6**, the SQUEEZE procedure of Olex2[58] was used.

CCDC 952327–962332 contain the supplementary crystallographic data for this paper.

Acknowledgements

We are thankful to Klaus-Peter Mester for recording the NMR spectra and to Brigitte Michel (both Bielefeld) for the elemental analyses. M. I. acknowledges with special thanks the Deutscher Akademischer Austausch Dienst (DAAD) for providing a PhD stipend.

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Publication-2

Dalton Transactions

PAPER

Cite this: *Dalton Trans.*, 2014, **43**, 1267

Borate-based ligands with two soft heterocycle/thione groups and their sodium and bismuth complexes†

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Received 20th September 2013,
Accepted 23rd October 2013

DOI: 10.1039/c3dt52607k

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Two novel sodium complexes [NaBb] (**1**) (Bb = dihydrobis(2-mercapto-benzimidazolyl)borate) and [NaBt^{Me}] (**2**) (Bt^{Me} = dihydrobis(2-mercapto-4-methylthiazolyl)borate) have been prepared and characterized by using two heterocycles, 2-mercapto-benzimidazole and 2-mercapto-4-methylthiazole, as well as $NaBH_4$ as precursors. The dipodal boron centred soft ligands Bb and Bt^{Me} were prepared *in situ*. The reactivity of [NaBb] (**1**) and [NaBt^{Me}] (**2**) towards Bi(III) ions has been studied. The resulting complex [BiBb$_2$Cl] (**3**) contains an MS_4 core with κ^3-*S,S,H* coordination mode, while the complex [BiBt$^{Me}{}_3$] (**4**) with an MS_6 core adopts a coordination mode κ^2-*S,S*. A reaction of $BiCl_3$ with the heterocyclic precursors 2-mercapto-benzimidazole (L^1) and 2-mercapto-4-methylthiazole (L^2) was also attempted; this afforded the monomeric [BiL$^1{}_4$Cl$_2$][BiL$^1{}_2$Cl$_4$] (**5**) and dimeric [BiL$^2{}_2$(μ-Cl)Cl]$_2$ (**6**) bismuth complexes. The bismuth complexes possess distorted octahedral geometries except **3** for which a face-capped octahedron is found. The presence of (B)H⋯Bi interactions has been identified by X-ray diffraction in **3** with a H⋯Bi distance of 2.58(1) Å which is uniquely short and unprecedented. Two of the synthesized complexes (**4** and **5**) have been investigated by luminescence spectroscopy. They feature emission bands in the solid state at room temperature at 674 (**4**) and 586 nm (**5**), which are hypsochromically shifted in (frozen) ethanolic solutions at 77 K to 618 and 537 nm, respectively.

Introduction

Boron centred ligands with tripodal and dipodal nature were introduced by Trofimenko in 1966 and have since then led to complexes with a wide range of structure and reactivity.[1–3] A large number of modifications[1c,d,4,5] in these hard donor ligands incorporating pyrazole units have been applied. Later on, the first synthesis of their soft analogue, namely (hydrotris(methimazolyl)borate (Tm), has been reported (methimazolyl = 1-methyl-1*H*-imidazole-2(3*H*)-thione-3-yl).[6] The discovery of this soft analogue attracted the attention of many researchers because of its scope for the stabilization of low-valent electron-rich metal ions,[5,7] flexibility and versatility regarding coordination behaviour.[8,9] After this first report of a tripodal soft ligand, hydrotris(methimazolyl)borate (Tm), a disubstituted version of hydrobis(methimazolyl)borate (Bm),[10] has been introduced which is considered to be the soft congener of dihydrobis(pyrazolyl)borate (Bp).[1] Similar to the tripodal hydrotris(methimazolyl)borate (Tm), Bm is capable of providing bidentate or tridentate coordination modes *via* thione donor functions and agostic hydrogen bonding.[11]

Other notable examples of di-substituted boron centred soft ligands include dihydrobis(2-thiopyridone)borate (Bmp)$^-$,[12] dihydrobis(thioxotriazolyl)borate (Bt)$^-$ [13,14] and dihydrobis(1-methyl-5-thiotetrazolyl)borate (Btt^{Me})$^-$.[15] These ligands have been studied to explore (B)H⋯M interactions, particularly with reference to metalaboranes.[15–18] A literature search reveals that the chemistry of bismuth in this context (using di-substituted ligands) has so far been widely ignored despite its soft nature. This prompted us to develop bismuth chemistry in this direction, because the π-systems within these ligands can function as a chromophoric unit, which can be combined with the heavy-atom effects of bismuth (spin–orbit coupling) to design photophysically interesting and relatively cheap systems (compare for instance the efficient triplet emitter and OLED material tris(pyridylphenyl)iridium(III)).[19] Therefore we present herein the synthesis and properties of novel sodium and

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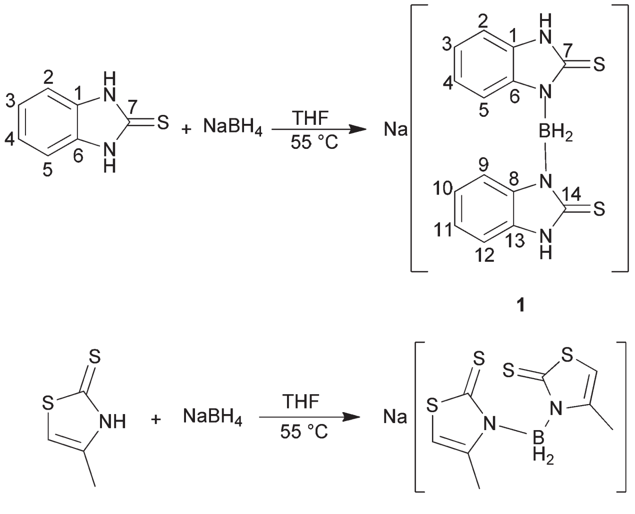
† CCDC 961729–961736. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52607k

bismuth complexes based on disubstituted boron centred soft ligands $[Bb]^-$ (dihydrobis(2-mercapto-benzimidazolyl)borate) and $[Bt^{Me}]^-$ (dihydrobis(2-mercapto-4-methylthiazolyl)borate). Synthetic chemistry of bismuth complexes resulting from heterocyclic precursors, 2-mercapto-benzimidazole (L^1) and 2-mercapto-4-methylthiazole (L^2), as well as luminescence studies are also part of this contribution.

Results and discussion

Sodium complexes [NaBb] (**1**) and $[NaBt^{Me}]$ (**2**) with the disubstituted ligands $[Bb]^-$ and $[Bt^{Me}]^-$ were synthesized by heating mixtures of $NaBH_4$ and the respective heterocycle in thf to 55 °C for 8 h (Scheme 1). After work-up, the desired products **1** and **2** were obtained in good yields. They are freely soluble in common solvents like thf, methanol, acetonitrile, chloroform, water, dmf and dmso. Both complexes, **1** and **2**, are colourless solids and pretty resistant towards aerobic oxidation and hydrolysis. These characteristics make them useful in further synthetic use. These complexes were characterized by NMR and IR spectroscopy, by mass spectrometry, by elemental analyses and finally by single crystal X-ray diffraction.

^1H and ^{13}C NMR spectra of **1** and **2** were recorded in dmso-d_6, thf-d_8 and $CDCl_3$. The ^1H NMR spectrum of **1** in dmso-d_6 shows two sets of signals. A doublet at 7.38 ppm is assigned to the protons at C5 and C9 (see Scheme 1 for labelling of **1**). A multiplet at 6.84–7.02 ppm can be attributed to the other ring protons at C2, C3, C4, C10, C11 and C12. The integration of each set of signals represents two and six protons, respectively. Two relatively broad signals at 11.75 and 3.73 ppm can be assigned to NH and BH protons, respectively – in agreement with the literature on $Li[(H_2B(tim^{Me})_2]$ (tim^{Me} 2-mercapto-1-methylimidazole).[11] The ^{13}C NMR spectrum of **1** exhibits a resonance at 171.66 ppm, attributable to (C7, C14) representing the C═S groups. A list of chemical shifts for the carbon atoms present in this case is given in the experimental data. The ^{11}B NMR spectrum displays a broad signal at −10.4 ppm which is in agreement with the literature reports.[12] Additional evidence for the identification of **1** comes from a negative-mode ESI-MS spectrum which exhibits a single peak at $m/z = 310$ assigned to the disubstituted species $[Bb]^-$.



Scheme 1 Synthesis of the sodium complexes of disubstituted boron centred ligands (**1** and **2**).

Two resonances at 6.22 and 2.36 ppm in the ^1H NMR spectrum of compound **2** are due to the ring and methyl protons, respectively. The ^{13}C NMR of this compound is also in agreement with the constitution of **2**. The C═S resonance is more down-field shifted at 189.85 ppm compared to **1** (C═S, 171.72 ppm). The ^{11}B NMR spectrum also displays a broad signal at −11.4 ppm similar to **1** and related compounds.[12] Likewise, the identification of **2** was authenticated by the ESI-MS (−) spectrum which shows a single peak at $m/z = 272$ assigned to the disubstituted species $[Bt^{Me}]^-$. However, under ESI (+) mode operation the other cationic fragments like $[Na_3L_2]^+$ and $[Na_4L_3]^+$ have also been observed.

Final authentication of the structures of **1** and **2** was achieved from X-ray single crystal diffraction studies. The solid state structures of **1** and **2** are presented in Fig. 1 and 2 with selected bond lengths and angles given in Tables 1 and 2, respectively.

The molecular structure of compound **1** in the solid state represents itself as a monomeric sodium complex. The asymmetric unit contains four independent molecules of **1**.

To simplify the discussion, we discuss the parameters of only one molecule **a** (Fig. 1, Table 1). The coordination environment around the sodium ion in this case comprises a sulphur atom, two B–H moieties and four thf ligands. Thus the ligand $[Bb]^-$ exerts a tridentate (κ^3-*H*,*H*,*S*) mode. The Na–S bond in this case has a length of 3.091(1) Å, which is within the expected range. The second sulphur atom of the ligand does not make any contact with sodium. A (B)H⋯Na interaction can be found at a distance of 2.24(2) Å and 2.88(2) Å for ((B)H(1A)⋯Na) and ((B)H(1B)⋯Na), respectively. The H⋯Na

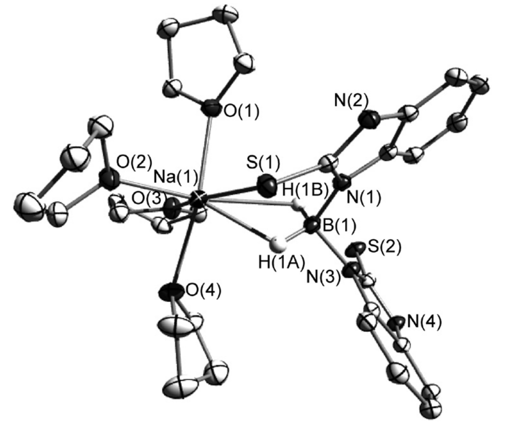


Fig. 1 Solid state structure of molecule **a** in the unit cell of [NaBb] (**1**). Hydrogen atoms (except for H(1A) and H(1B)) have been omitted for clarity; displacement ellipsoids are drawn at the 50% level.

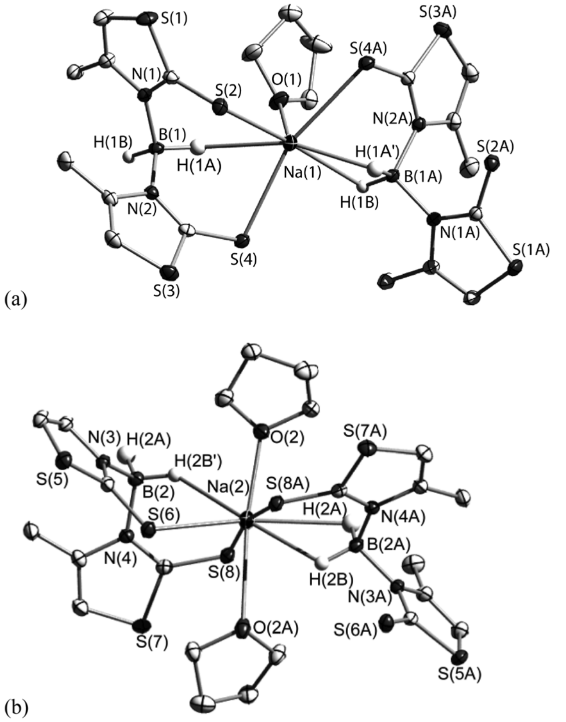


Fig. 2 Coordination environment around sodium in molecules **a** and **b** of the unit cell of [NaBt^{Me}] (**2**).

Table 1 Selected bond lengths [Å] and bond angles [°] of the four independent molecules **1a–1d**

Parameters	**a**	**b**	**c**	**d**
Na–S	3.091(1)	2.923(1)	3.067(1)	2.907(1)
(B)$H_{a,b}$···Na	2.24(2), 2.87(2)	2.36(2), 3.33(2)	2.30(2), 3.40(2)	2.34(2), 3.35(2)
Na–B	2.918(2)	3.150(2)	3.188(2)	3.161(2)
Na–O	2.300(2)– 2.360(2)	2.340(2)– 2.390(2)	2.280(2)– 2.365(1)	2.320(2)– 2.397(2)
S–Na–H_a	62.4(4)	65.5(3)	64.2(4)	66.4(4)
S–Na–B	68.7(1)	67.8(1)	65.9(1)	68.2(1)
O–Na–O(*cis*)	82.8(1)– 97.1(1)	83.6(1)– 103.4(1)	83.0(1)– 107.7(1)	85.1(1)– 104.1(1)
O–Na–O(*trans*)	168.3(1)	175.2(1)	171.0(1)	177.0(1)

For **a**, Na = Na(1), H_a = H(1A), H_b = H(1B), B = B(1), S = S(1), O = O(1–4). For **b**, Na = Na(2), H_a = H(2B), H_b = H(2A), B = B(2), S = S(3), O = O(5–8). For **c**, Na = Na(3), H_a = H(3A), H_b = H(3B), B = B(3), S = S(5), O = O(9–12). For **d**, Na = Na(4), H_a = H(4A), H_b = H(4B), B = B(4), S = S(7), O = O(13–16).

Table 2 Selected bond lengths [Å] and bond angles [°] of the two independent molecules **a** and **b** of compound **2**

Molecule **a**		Molecule **b**	
Na(1)–S(2)	2.835(1)	Na(2)–S(6)	2.844(1)
Na(1)–S(4)	2.865(1)	Na(2)–S(8)	2.836(1)
Na(1)–S(4A)	2.950(1)	Na(2)–S(8A)	2.889(1)
B(1)–H(1A)···Na(1)	2.57(2)	B(2)–H(2B)···Na(2)	2.43(2)
B(1)–H(1B)···Na(1)	2.60(2)	B(2)–H(2A)···Na(2)	2.80(2)
B(1)–H(1A′)···Na(1)	2.35(2)	B(2)–H(2B′)···Na(2)	2.73(2)
Na(1)–B(1)	2.871(2)	Na(2)–B(2A)	3.015(2)
Na(1)–O(1)	2.347(1)	Na(2)–O(2)	2.463(1)
S(2)–Na(1)–S(4)	94.9(1)	Na(2)–O(2A)	2.988(2)
S(2)–Na(1)–S(4A)	92.0(1)	S(6)–Na(2)–S(8)	99.1(1)
S(4)–Na(1)–S(4A)	160.4(1)	S(6)–Na(2)–S(8A)	84.0(1)
S(2)–Na(1)–H(1A)	71.2(3)	S(8)–Na(2)–S(8A)	168.5(1)
S(4)–Na(1)–H(1A)	61.4(3)	S(6)–Na(2)–B(2A)	143.0(1)
O(1)–Na(1)–H(1A)	65.6(3)	S(8)–Na(2)–B(2A)	105.0(1)
		O(2)–Na(2)–O(2A)	173.3(1)

distances of these interactions can be compared with related interactions reported by Silva *et al.* for Na[HB(mtda)$_3$], K[HB(mtda)$_3$] and KNa[HB(mtda)$_3$] (where mtda = 2-mercapto-1,3,4-thiadiazole).[20] It is interesting to note that the other three independent molecules show only one significant (B)H···Na interaction while the second H···Na distance is quite long (see Table 1). The four unsymmetrical thf molecules give rise to variable Na–O lengths ranging from 2.300(2) to 2.360(2) Å (Table 1). The bond angles in this octahedral environment are characterized as follows: S(1)–Na(1)–H(1A) 62.4(4)°, S(1)–Na(1)–B(1) 68.7(1)°, *cis*-O–Na(1)–O 82.8(1)° –97.1(1)°, *trans*-O–Na(1)–O 168.3(1)°.

The crystal structure of [NaBt^{Me}] (**2**, Table 2) is different from that of **1**. This compound crystallizes as a polymeric structure with two independent molecules in its unit cell, each forming a chain with 2_1 symmetry along the ***b*** axis. The coordination environment around the sodium ion in molecules **a** and **b** of the unit cell of [NaBt^{Me}] (**2**) is shown in Fig. 2, while the polymeric parts of these molecules are shown in Fig. 3. Both [Bt^{Me}]$^-$ ligands around sodium in molecules **a** and **b** are tridentate; however, one coordinates in a κ^3-*S*,*S*,*H* mode, while the second exerts a κ^3-*H*,*H*,*S* coordination mode. The Na–S bond lengths are in the range between 2.835(1) and 2.950(1) Å and are in agreement with the literature values of M[HB(mtda)$_3$] (where mtda is 2-mercapto-1,3,4-thiadiazole, M = Na, K).[20] Furthermore, in molecule **a** there are two coordinated thf molecules attached to the sodium ion; however, only one thf molecule is coordinated to sodium in the case of **b**. Another difference of the two independent molecules in the unit is the bite angles. These bite angles are 94.9(1)° (S(4)–Na(1)–S(2)) for molecule **a** and 99.1(1)° (S(6)–Na(2)–S(8)) for **b**.

Bismuth complexes

Moderate to good yields of bismuth complexes **3–6** have been obtained by the reaction of [NaBb] (**1**), [NaBt^{Me}] (**2**), 2-mercapto-benzimidazole (L^1) and 2-mercapto-4-methylthiazole (L^2) with $BiCl_3$ in an appropriate ratio (Scheme 2). Complexes **3–6** were characterized by NMR, IR spectroscopy, mass spectrometry, elemental analyses and finally by single crystal X-ray diffraction.

After work-up during the synthesis of **3**, a trace amount of crystalline material with a different composition, [BiBbCl(μ-Cl)$_2$]$_2$ (**3a**), was obtained by slow evaporation of the mother liquor; its composition was determined by X-ray crystallography. All the bismuth complexes are coloured (**3**: yellow, **3a**: yellow, **4a**: red, **4b**: red, **5**: orange, **6**: orange) and stable towards aerobic oxidation. Complexes **3** and **4** are soluble in most common solvents like thf, CH_3CN, CH_2Cl_2, CH_3OH,

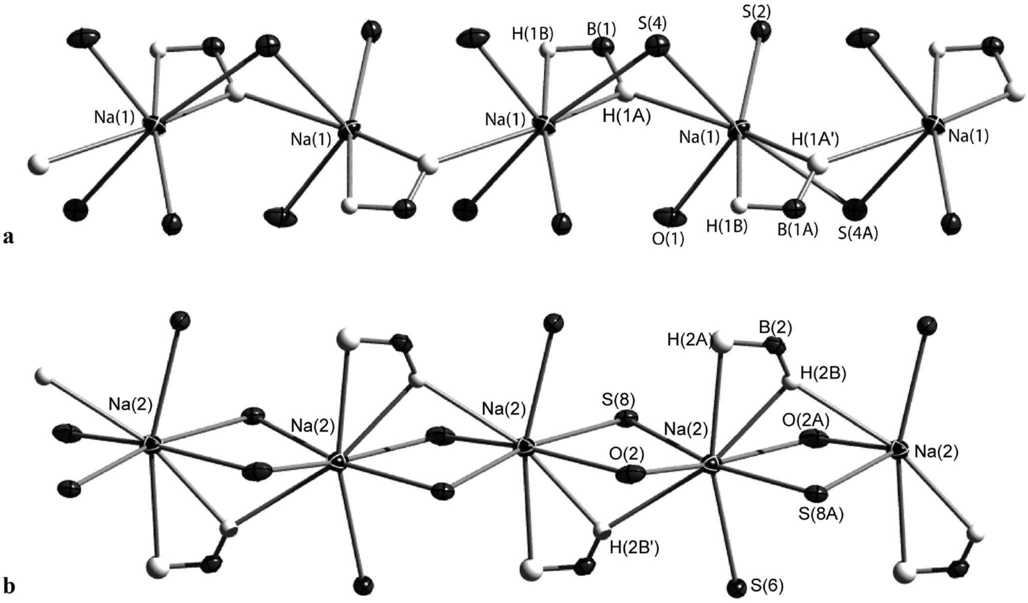
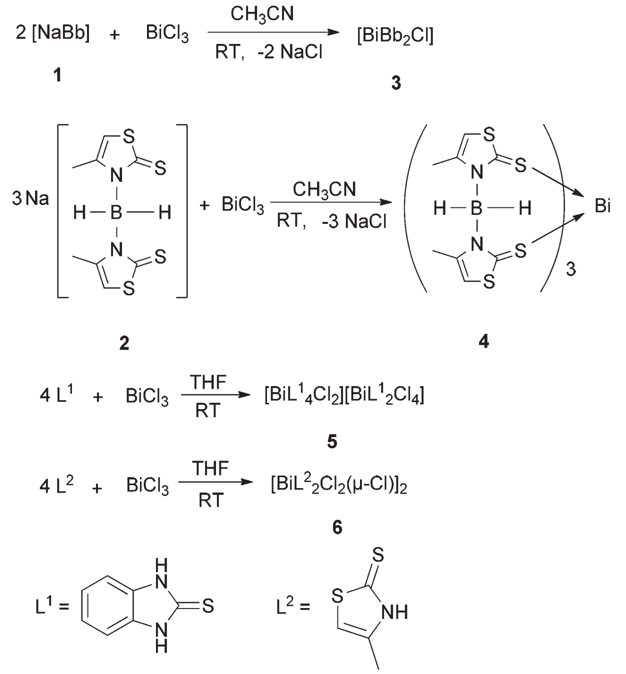


Fig. 3 Part of polymeric chain in molecules **a** and **b** of [NaBt^{Me}] **2**. Hydrogen atoms except H(1A), H(1B), and H(2B) have been omitted for clarity; displacement ellipsoids are drawn at the 50% level.



Scheme 2 Synthesis of bismuth complexes **3–6**.

$CHCl_3$, while **5** and **6** are only slightly soluble in thf, CH_3CN and acetone.

The ^1H NMR and ^{13}C NMR spectra of complexes **3–6** were compared with those of [NaBb] (**1**) and [NaBt^{Me}] (**2**) (see the Experimental section) as well as with 2-mercapto-benzimidazole (L^1) and 2-mercapto-4-methylthiazole (L^2).[21]

Compared to the [NaBb] (**1**), the ^1H NMR spectrum of complex **3** in thf-d_8 solution exhibits a downfield shifted singlet at 12.15 ppm and a multiplet at 7.04–7.33 ppm assigned to HN and ring protons, respectively. Similarly, the ^1H NMR spectrum of complex **4** shows a downfield shift for the CH-ring and methyl protons at 6.46 and 2.27 ppm, respectively. In the ^1H NMR and ^{11}B NMR spectra of both complexes (**3** and **4**), the signals of the BH_2 moieties were not observed. A similar observation has also been reported in the literature.[7] Therefore, in the solution state, especially for **3**, it is difficult to comment on the stability of (B)H⋯Bi interactions.

However, the presence of (B)H⋯Bi interactions in complex **3** has been verified in the solid state by the observation of two B–H stretching bands (2449 and 2423 cm^{-1}) in its IR spectrum compared to one band (2407 cm^{-1}) in [NaBb] (**1**) and is in agreement with the literature on poly(mercaptomethimazolyl)-borate chemistry.[10b] This observation was subsequently further confirmed by X-ray diffraction study (see below).

The common salient feature of the ^{13}C NMR spectra of **3–6** is an upfield shift of the C═S signals (except for **3** where it was not observed), when compared with the spectra of [NaBb] (**1**), [NaBt^{Me}] (**2**), L^1 and L^2. This upfield shift of the C═S group indicates the coordination of a thione group to the metal atom (see the Experimental section).

Single crystal X-ray crystallography revealed molecular structures of bismuth complexes **3–6** with a composition of [$BiBb_2Cl$] (**3**), [$BiBbCl(\mu\text{-}Cl)_2$]$_2$ (**3a**), [$BiBt^{Me}_3$]·CH_2Cl_2 (**4a**), [$BiBt^{Me}_3$]·$CHCl_3$ (**4b**), [$BiL^1_4Cl_2$][$BiL^1_2Cl_4$] (**5**), and [$BiL^2_2Cl_2(\mu\text{-}Cl)$]$_2$ (**6**). Selected bond lengths and angles are presented in Tables 3–6 and their molecular structures are shown in Fig. 4–7.

In the molecular structure of **3** (Fig. 4a), the bismuth atom is coordinated by four sulphur atoms, one chlorine atom, and one hydrogen atom, which forms a (B)H⋯Bi interaction, defining one eight-membered and two six-membered rings. Overall, the geometry can be best described as face-capped octahedron

Table 3 Selected bond lengths [Å] and bond angles [°] of compounds **3** and **3a**

3		3a	
Bi(1)–S(1)	2.766(2)	Bi(1)–S(1)	2.604(2)
Bi(1)–S(2)	2.794(2)	Bi(1)–S(2)	2.773(2)
B(1)–H(1A)···Bi	2.58(10)	B(1)–H···Bi	2.69^a
Bi(1)–B(1)	3.50(1)	Bi(1)–B(1)	3.49(2)
C(1)–S(1)	1.71(1)	C(1)–S(1)	1.74(1)
C(8)–S(2)	1.71(1)	C(8)–S(2)	1.73(1)
Bi(1)–Cl(1)	2.551(3)	Bi–Cl(1)	2.566(2)
		Bi–Cl(2)	2.715(2)
		Bi–Cl(2A)	3.045(2)
S(1)–Bi(1)–S(2)	92.8(1)	S(1)–Bi(1)–S(2)	94.8(1)
Cl(1)–Bi(1)–S(1)	77.3(1)	Cl(1)–Bi(1)–S(1)	93.8(1)
Cl(1)–Bi(1)–S(2)	89.4(1)	Cl(1)–Bi(1)–Cl(2)	84.4(1)
S(1)–Bi(1)–S(2A)	87.0(1)	Cl(1)–Bi(1)–S(2)	71.7(1)
S(1)–Bi(1)–S(1A)	154.6(1)	Cl(2)–Bi(1)–S(2)	154.4(1)
S(2)–Bi(1)–S(2A)	178.8(1)	Cl(2)–Bi(1)–Cl(2A)	80.0(1)
N(3)–B(1)–N(1)	108.8(6)	N(3)–B(1)–N(1)	109.3(6)

[a] H atom in calcd position.

Table 4 Selected bond lengths [Å] and angles [°] of compounds **4a** and **4b**

	4a	4b
Bi(1)–S(7)	2.746(2)	2.745(2)
Bi(1)–S(9)	2.796(2)	2.763(2)
Bi(1)–S(5)	2.816(2)	2.790(2)
Bi(1)–S(1)	2.831(2)	2.948(2)
Bi(1)–S(11)	2.837(2)	2.869(2)
Bi(1)–S(3)	2.870(2)	2.856(2)
S···S (interligand distances)	3.860–4.085	3.810–4.280
S–Bi–S(*cis*)	75.1(1)–101.6(1)	69.4(1)–128.2(1)
S–Bi–S(*trans*)	162.7(1)–175.4(1)	156.0(1)–166.3(1)
N–B–N	111.2(4)–112.0(4)	110.6(3)–110.8(3)

Table 5 Selected bond lengths [Å] and bond angles [°] of compound **5**

Cationic fragment		Anionic fragment	
Bi(2)–S(2)	2.839(1)	Bi(1)–S(1)	2.839(1)
Bi(2)–S(3)	2.819(1)	Bi(1)–Cl(1)	2.677(1)
Bi(2)–Cl(3)	2.694(1)	Bi(1)–Cl(2)	2.709(1)
S(3)–Bi(2)–S(2)	85.5(1)	S(1)–Bi(1)–S(1A)	180
S(3)–Bi(2)–S(3A)	180	Cl(1)–Bi(1)–S(1)	96.1(1)
Cl(3)–Bi(2)–S(3)	100.6(1)	Cl(2)–Bi(1)–S(1)	91.4(1)
Cl(3)–Bi(2)–S(2)	87.9(1)	Cl(2A)–Bi(1)–S(1)	88.6(1)
Cl(3A)–Bi(2)–S(2)	92.1(1)	Cl(1)–Bi(1)–Cl(2)	94.1(1)
Cl(3)–Bi(2)–Cl(3A)	180	Cl(1)–Bi(1)–Cl(1A)	180
		Cl(2)–Bi(1)–Cl(2A)	180

Table 6 Selected bond lengths [Å] and bond angles [°] of compound **6**

Bi(1)–Cl(2)	2.772(1)	S(1)–Bi(1)–S(3)	78.9(1)
Bi(1)–Cl(3)	2.589(1)	Cl(3)–Bi(1)–S(3)	88.0(1)
Bi(1)–Cl(1)	2.840(1)	Cl(3)–Bi(1)–S(1)	96.2(1)
Bi(1)–Cl(1A)	2.939(1)	Cl(2)–Bi(1)–S(3)	170.5(1)
		Cl(2)–Bi(1)–S(1)	91.9(1)
		Cl(1)–Bi(1)–S(3)	91.3(1)
		Cl(1)–Bi(1)–S(1)	93.8(1)
		Cl(2)–Bi(1)–Cl(3)	95.1(2)
		Cl(1)–Bi(1)–Cl(1A)	81.8(1)

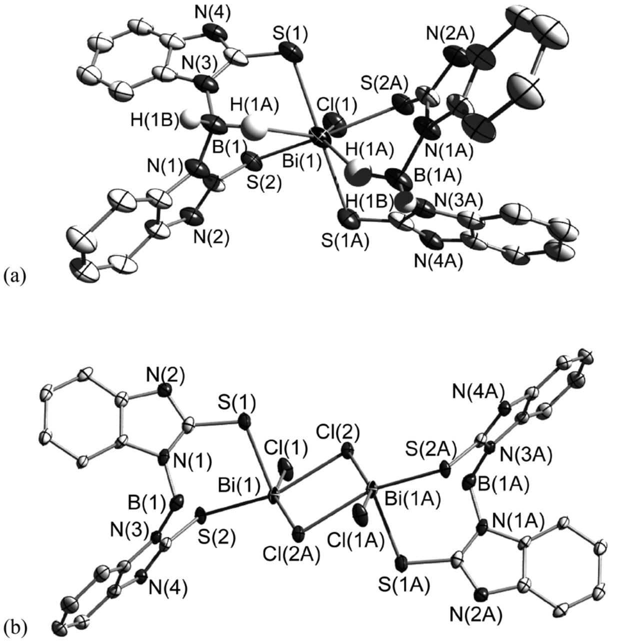


Fig. 4 (a) Solid state structure of [BiBb$_2$Cl] **3**. (b) Solid state structure of [BiBbCl-(μ-Cl)$_2$]$_2$ **3a**. Hydrogen atoms except H(1A) and H(1B) have been omitted for clarity; displacement ellipsoids are drawn at the 50% level.

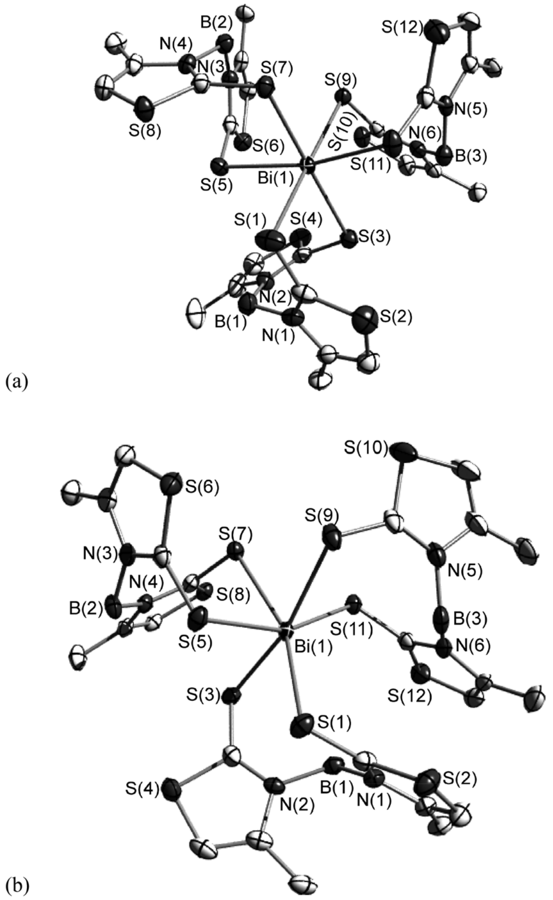


Fig. 5 Solid state structure of (a) [BiBt$^{Me}{}_3$]·CH$_2$Cl$_2$ (**4a**) and (b) [BiBt$^{Me}{}_3$]·CHCl$_3$ (**4b**). Hydrogen atoms and solvent molecules have been omitted for clarity; displacement ellipsoids are drawn at the 50% level.

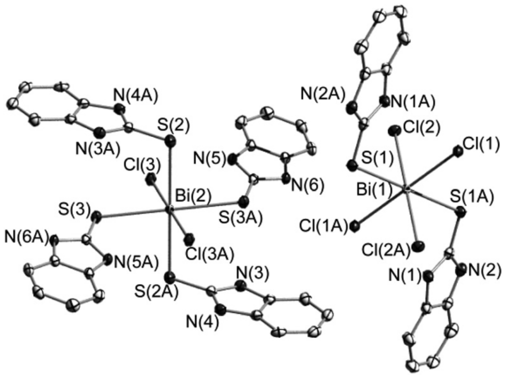


Fig. 6 Solid state structure of $[BiL^1{}_4Cl_2][BiL^1{}_2Cl_4]$ **5**. Hydrogen atoms have been omitted for clarity; displacement ellipsoids are drawn at the 50% level.

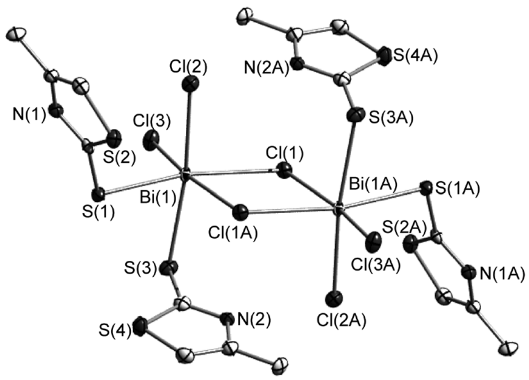


Fig. 7 Solid state structure of $[BiL^2{}_2Cl_2(\mu\text{-}Cl)]_2$ (**6**). Hydrogen atoms have been omitted for clarity; displacement ellipsoids are drawn at the 50% level.

with coordination number 7. The (B)H⋯Bi interaction has a distance of 2.58(10) Å (Bi⋯B 3.50(1) Å). This interaction makes complex **3** a unique and unprecedented example according to the Cambridge Structural Database.[22] However, this can be compared with a related structure of $[Tl(Bm^{Me})]_x$ which has a (B)H⋯Tl distance of 2.69 Å (Tl–B 3.50 Å).[23] Such interaction results in the formation of two six-membered rings rather than one eight-membered ring. The formation of two six-membered rings insert stabilizing effects as reported earlier.[12,24] The bond lengths for Bi(1)–S(1) and Bi(1)–S(2) are 2.766(2) and 2.794(2) Å, respectively. These values are in agreement with related distances of $BiCl_3(L^2)$ (where L^2 = *N*,*N*′-diethyl-dithiooxamide) and $[Bi(Tm)_2]^+$ (Tm = hydrotris(methimazolyl)-borate).[25] Similarly, the Bi–Cl bond length at 2.551(3) Å is also in agreement with the expected values of terminal Bi–Cl bonds.[26]

The molecular structure of the bismuth complex **3a** is shown in Fig. 4b. It is a dimeric complex with chloro ligands lying at the centre of inversion and bridging the two bismuth atoms in an asymmetric mode with bond lengths of 2.715(2) Å (Bi(1)–Cl(2)) and 3.045(2) Å (Bi(1)–Cl(2A) Å). A second type of chloride ligand is terminally bound to the bismuth atoms with a distance of 2.566(2) Å. The Bi–S bond lengths have values of 2.604(2) and 2.773(2) Å for Bi(1)–S(1) and Bi(1)–S(2), respectively, and are comparable with monomeric[27] and dimeric[25b,26] bismuth complexes already reported in the literature. Bismuth complexes based on thiosemicarbazone have also been reported to show Bi–S bond lengths in a similar range.[28] The geometry of the complex is distorted octahedral as evidenced by the angles Cl(1)–Bi(1)–Cl(2) 84.4(1)°, Cl(1)–Bi(1)–S(2) 71.7(1)°, Cl(2)–Bi(1)–Cl(2A) 80.0(1)° and Cl(2)–Bi(1)–S(2) 154.4(1)°. The N–B–N angle with a value of 109.3(6)° is ideally tetrahedral.

Crystals of complex **4** have been obtained from two different solvents resulting in two distinct structures with dichloromethane **4a** and chloroform **4b** as crystal solvates. Both are monoclinic, but with different space groups: **4a** $P2_1/n$, **4b** $C2/c$. The molecular structure of **4a** is shown in Fig. 5a. In this complex, six sulphur atoms of three asymmetric ligands coordinate the bismuth atom resulting in a neutral but distorted octahedral complex. The six Bi–S bond lengths span a range of 2.746(2) to 2.870(2) Å which is in agreement with other related structures reported in the literature.[29–35] The inter-ligand S⋯S distances range between 3.860 and 4.085 Å and thus exceed the sum of the van der Waals radii at 3.60 Å.[29] Two topological triangles formed by S(1), S(7), S(11) and S(3), S(5), S(9) have also different values of S⋯S distances with a value larger in the triangular face opposite to S(1), S(7) and S(11) face. Such longer S⋯S distances might be due to bismuth lone-pair repulsion as discussed by Lawton *et al.*[30]

Selected bond lengths and angles for this complex are summarized in Table 4. The *cis* angles formed by the S–Bi–S units vary between 75.1(1) and 101.6(1)°. It can be safely argued that in the present case a stereo-chemically active lone pair affects the geometry. This observation is similar to those previously noted for $[BiTm_2]^+$ [25b] and other complexes in the literature.[36,37]

The molecular structure of the $CHCl_3$ solvate **4b** is shown in Fig. 5b. Selected bond lengths and angles for this structure are summarized in Table 4. A comparison with its dichloromethane solvate **4a** reveals at first sight no substantial difference; however, the distortion of the bismuth coordination sphere in the two compounds varies. The MS_6 core of **4b** has unequal Bi–S bond lengths ranging from 2.745(2) to 2.948(2) Å, *i.e.* they are slightly greater than in **4a**. The inter-ligand S⋯S distances are in the range between 3.810 and 4.280 Å and are also larger than those in **4a**. Similarly, all the *cis* as well as *trans* angles deviate more from an ideal octahedral geometry compared to **4a** (Table 4). Additionally in **4b**, weak hydrogen bonding has been found between a chlorine atom of the solvent ($CHCl_3$) and one hydrogen atom of each, BH_2, CH_3 and heterocyclic ring CH moieties. However, no close contact between the bismuth atom and $CHCl_3$ molecules was observed.

The pronounced distortion observed in **4b** is probably due to crystal packing, influenced by the bigger size of chloroform and its hydrogen bonding contacts. The larger values of the S⋯S distances (3.810–4.280 Å) as compared to **4a** also seem to be the result of increased lone pair influence in this case.

The molecular structure of **5** is depicted in Fig. 6. It is a combination of $[BiL^1{}_4Cl_2]^+$ cation and $[BiL^1{}_2Cl_4]^-$ anion, both have central bismuth atoms with coordination number six. In the cationic part, the bismuth atom is bonded to four L^1 and two chloro ligands, while in the anionic part, the situation is reversed. Due to the centres of inversion at both bismuth positions, all *trans* distances are equal. In the cation, there are thus two groups of Bi–S bond lengths with values of 2.819(1) and 2.839(1) Å (Table 5). Both *trans* positioned Bi–Cl bonds lengths are 2.694(1) Å. The Bi–S and Bi–Cl bond lengths are comparable with previously determined structures of bismuth complexes with similar heterocyclic ligands.[38,39] The *cis* angles in the cation and the anion are close to ideal octahedral values (Table 5).

The molecular structure of **6** is again dimeric with a centre of inversion in the middle of the $Bi_2(\mu\text{-}Cl)_2$ rhomb (Fig. 7). The bismuth atoms adopt a slightly distorted octahedral geometry as is manifest from *cis* bond angles with values between 78.9(1) and 96.2(1)° (Table 6). Each bismuth atom is coordinated by thione sulphur atoms of two L^2 and four chloro ligands. Two of the chloro ligands are bridging while the other two are bound terminally to bismuth atoms. The Bi(1)–S(1) and Bi(1)–S(3) bond lengths are 2.686(1) and 2.762(1) Å, respectively, and are within the expected range as described in the literature.[40,41] The two terminal Bi–Cl bonds (Bi(1)–Cl(2) 2.772(1), Bi(1)–Cl(3) 2.589(1) Å) are shorter than the bridging Bi–Cl bonds (Bi(1)–Cl(1) 2.840(2), (Bi(1)–Cl(1A) 2.939(2) Å).

Photophysical characterisation

Two of the complexes were chosen (**4** and **5**) for a basic photophysical characterisation. Compound **4** features an intense π–π* absorption band of the heterocycle at 316 nm and weak absorptions at lower energy. In general, s^2-metal cations can feature (metal-centred) s–p transitions, which is a transition between the filled s-orbital and an empty p-orbital. In cases where electron rich ligands are bonded, also ligand to metal charge transfer states (LMCTs) are possible.[42–45] Therefore, this long wavelength absorption of **4** might be due to s–p transitions and/or a S→Bi LMCT with the highest occupied molecular orbital (HOMO) located on the electron-rich sulphur atom. Interestingly, no comparable low energy bands could be detected for **5**. Both complexes are emissive in the solid state (**4**: λ_{max} = 674 nm, **5**: λ_{max} = 586 nm, see Table 7, Fig. 8 and 9). In solution, no authentic emission could be detected under ambient conditions. At 77 K in ethanol glass, **4** and **5** feature emission bands at 618 and 537 nm, respectively. Under this condition, the excitation spectrum of **5** resembles very closely the absorption spectrum at r.t., whereas for **4**, the intensities of the signals at 77 K and r.t. differ considerably. An s–p transition results in a considerable geometrical distortion of the molecule in the excited state, which leads either to an efficient quenching and non-emissive behaviour or to a large Stokes shift of the emission, as it is observed for both complexes (Fig. 8 and 9). The wavelength of this luminescence is comparable to other emissive Bi^{3+} complexes reported previously.[45–51] Therefore, we tentatively assign the emissions in both complexes to an excited state resulting from an s–p transition. However, for **5** the emission band at 77 K is broad and overlaps with the

Table 7 Electronic spectroscopic data for compounds **4** and **5**

	Absorption[a] [nm] (log{ε/L mol^{-1} cm^{-1}})	Temp [*K*]	Excitation [nm]	Emission [nm]
4	235 (sh, 3.96), 318 (4.53), 416 (3.57)	298[b]		674
		77[a]	274, 327, 353, 418	618
5	219 (3.75), 246 (3.75), 297 (3.86), 305 (3.94)	298[b]		586
		77[a]	252 (sh), 300, 307, 400	537

[a] In ethanol. [b] Solid state.

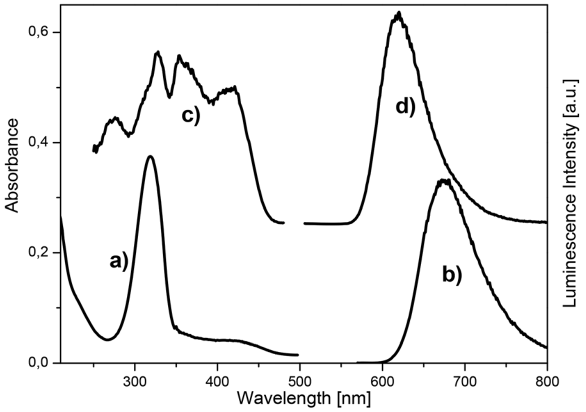


Fig. 8 (a) Absorption spectrum of **4** in ethanol ($c = 1.1 \times 10^{-5}$ mol L^{-1}); (b) emission of a crystalline sample of **4** at 77 K (λ_{exc} = 550 nm); (c) excitation and (d) emission spectra of **4** in ethanol glass at 77 K (λ_{exc} = 420 nm, λ_{det} = 660 nm).

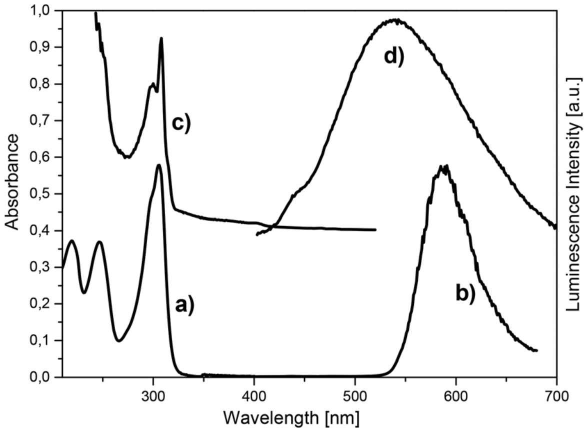


Fig. 9 (a) Absorption spectrum of **5** in ethanol ($c = 6.6 \times 10^{-5}$ mol L^{-1}); (b) emission spectrum of a crystalline sample of **5** at 77 K (λ_{exc} = 300 nm); (c) excitation and (d) emission spectra of **5** in ethanol glass at 77 K (λ_{exc} = 300 nm, λ_{det} = 540 nm).

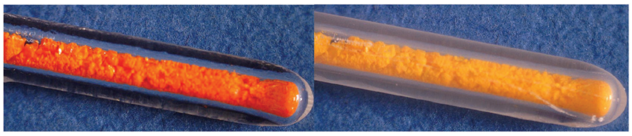


Fig. 10 Digital pictures of crystals of **5** at room temperature (left) and after immersion in liquid nitrogen (right).

absorption, which means that an LMCT excited state might be involved as well. As we had pointed out in a recent publication the lowest energy excited states of Bi(III) compounds are lying very close to each other and one has to expect a mixture of different transitions in this energy range.[52]

Upon measuring the emission spectra of solid **5** at r.t. and 77 K, we noticed thermochromic behaviour. At room temperature, a crystalline sample of **5** is orange and changes its colour to yellow when cooled with liquid nitrogen (Fig. 10). Thermochromism of bismuth compounds is a well-known phenomenon and ascribed to structural changes like phase transitions or alterations of interatomic distances.[53,54]

Conclusion

The two new $[\mathrm{Bb}]^-$ and $[\mathrm{Bt^{Me}}]^-$ ligands expand considerably the range of available disubstituted boron centred soft ligands. They are conveniently prepared in the form of their sodium complexes. Related ligand systems have earlier been used to model the active sites in certain metalloenzymes (*e.g.*, hydrogenases, alcohol dehydrogenases), in the study of sulfur-rich proteins such as metallothioneins and rubredoxins, *etc.*[10b] We have also reported bismuth complexes, $[\mathrm{BiBb_2Cl}]$ (**3**), $[\mathrm{BiBt^{Me}}_3]$ (**4**), $[\mathrm{BiL^1}_4\mathrm{Cl_2}][\mathrm{BiL^1}_2\mathrm{Cl_4}]$ (**5**) and the dimeric complex $[\mathrm{BiL^2}_2\text{-}(\mu\text{-Cl})\mathrm{Cl}]_2$ (**6**). Complex **3** exhibits an interestingly short and unprecedented (B)H⋯Bi interaction of 2.58(10) Å length. Compounds **4** and **5** have been chosen for basic luminescence studies. No emission could be detected in solution at r.t., but they feature emission bands in the solid state at 674 (**4**) and 586 nm (**5**). At 77 K in ethanol glass, the signals are found at 618 and 537 nm, respectively. Compound **5** shows thermochromic behaviour with a conspicuous colour change from orange at r.t. to yellow at 77 K. We are now further extending our work to the synthesis of ternary complexes of bismuth by incorporating some conjugated co-ligands (1,10-phenanthroline, 2,2′-bipyridine, *etc.*) that might have improved photophysical properties.

Experimental

$\mathrm{NaBH_4}$ (Alfa Aesar), 2-mercapto-benzimidazole (Acros Organics), 2-mercapto-4-methylthiazole (Alfa Aesar) and $\mathrm{BiCl_3}$ (Acros Organics) were procured and used without further purification. NMR spectra were measured on Bruker Avance 300, Bruker DRX 500 or Bruker Avance 500 spectrometers and the chemical shifts were referenced to the residual proton signals of the deuterated solvents and are reported in ppm. Elemental analyses were performed on a EuroEA Elemental Analyser. ESI-MS spectra were measured using Esquire 3000 (Bruker Daltonik 2000). IR spectra were recorded using FTIR (Bruker, ALPHA). Melting points were determined using Büchi B 545 melting point apparatus and are uncorrected. Other operations were carried out under nitrogen atmosphere using Schlenk techniques unless otherwise stated. Described methods with certain modifications were followed for the synthesis of disubstituted ligands.[23]

[NaBb] (1)

2-Mercapto-benzimidazole (20.0 mmol, 3.00 g) and $\mathrm{NaBH_4}$ (10.0 mmol, 0.375 g) were intimately ground, mixed and then dissolved in 20 mL of freshly distilled thf. The resulting solution was heated at 55 °C for 8 h. Evolution of hydrogen gas was observed during the course of the reaction through a gas bubbler. The clear solution obtained was filtered, concentrated under vacuum to 7 mL and then cooled to 4 °C. A colourless precipitate formed overnight and was filtered, washed with small amounts of toluene, ether and finally dried under vacuum. The solid obtained is sufficiently pure; however, it can be recrystallized from a mixture of *n*-pentane and thf (1 : 3). Yield: 78%; colourless powder; m.p. 242–244 °C (with decomposition); Anal. calcd for $\mathrm{C_{14}H_{12}BN_4S_2Na{\cdot}2C_4H_8O}$ (found): C 55.23 (54.84), H 5.90 (6.13), N 11.71 (10.81), S 13.40 (12.59); IR (cm^{-1}, KBr pellet), ν(B–H) 2407; ^{1}H NMR (dmso-d_6) δ = 11.01 (br, 2H, HN), 7.38–7.40 (d, 4H, C5H, C9H), 6.84–7.02 (m, 12H, C2H, C3H, C4H, C10H, C11H, C12H), 3.77 (br, 2H, $\mathrm{BH_2}$); ^{13}C NMR (dmso-d_6) δ = 171.72 (C7, C14), 138.79 (C1, C13), 132.48 (C6, C8), 120.91 (C5, C9), 120.64 (C2, C12), 114.54 (C3, C11), 107.77 (C4, C10); ^{13}C NMR (DEPT-135) (dmso-d_6) δ = 122.16 (C5, C9), 120.57 (C2, C12), 114.55 (C3, C11), 107.70 (C4, C10), ^{11}B NMR (dmso-d_6), δ = −10.19 (br); ^{1}H NMR (thf-d_8), δ = 10.99 (br, 2H, HN), 6.84–7.10 (m, 6H, C2H, C3H, C4H, C10H, C11H, C12H), 7.39 (d, 2H, C5H, C9H); ^{13}C NMR (thf-d_8) δ = 171.72 (C7, C14), 138.78 (C1, C13), 132.54 (C6, C8), 120.51 (C5, C9), 120.30 (C2, C12), 113.43 (C3, C11), 107.32 (C4, C10); ^{13}C NMR (DEPT-135) (thf-d_8) δ = 120.05 (C5, C9), 118.65 (C2, C12), 118.44 (C3, C11), 106.64 (C4, C10); ^{11}B NMR (thf-d_8), δ = −14.01 (br), ESI-MS (−), *m/z* [assignment] = 310 $[\mathrm{Bb}]^-$.

$[\mathrm{NaBt^{Me}}]$ (2)

This compound was prepared by the same procedure as that described above by reacting 2-mercapto-4-methylthiazole (20.0 mmol, 2.34 g) and $\mathrm{NaBH_4}$ (10.0 mmol, 0.375 g). The resulting solid was washed with toluene (3 × 20 mL) and ether (2 × 20 mL) and finally recrystallized from thf. Yield: 73%; m.p. 232–234 °C; Anal. calcd for $\mathrm{C_8H_{10}BN_2S_4Na}$ (found): C 32.44 (31.55), H 3.40 (3.40), N 9.46 (9.02); IR (cm^{-1}, KBr pellet), ν(B–H) 2432; ^{1}H NMR (dmso-d_6) δ = 6.22 (s, 2H, HC-ring), 2.36 (s, 6H, $\mathrm{CH_3}$); ^{13}C NMR (dmso-d_6) δ = 189.85 (C═S), 147.69 (C═N), 105.42 ($\mathrm{CCH_3}$), 19.22 ($\mathrm{CH_3}$); ^{11}B NMR (dmso-d_6) δ = −11.37 (br); ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 6.18 (s, 2H, HC-ring), 2.12 (s, 6H, $\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 189.00 (C═S), 144.82 (C–H),

Table 8 X-ray crystallographic data for compounds **1–6**

Compound	**1**	**2**	**3**	**3a**	**4a**	**4b**	**5**	**6**
Empirical formula	$C_{14}H_{12}BN_4NaS_2\cdot 4C_4H_8O$	$C_8H_{10}BN_2NaS_4\cdot C_4H_8O$	$C_{28}H_{24}B_2BiClN_8S_4$	$C_{28}H_{24}B_2Bi_2\text{-}Cl_4N_8S_4\cdot 6H_2O$	$C_{24}H_{30}B_3BiN_6S_{12}\cdot CH_2Cl_2$	$C_{24}H_{30}B_3BiN_6S_{12}\cdot 1.5CHCl_3$	$C_{28}H_{24}BiCl_2N_8S_4$, $C_{14}H_{12}BiCl_4N_4S_2$, $4(C_4H_8O)$	$C_{16}H_{20}Bi_2Cl_6N_4S_8\cdot 2(C_4H_8O)$
M_r	622.61	368.32	866.84	1290.27	1113.60	1207.72	1820.26	1299.71
T (K)	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2/c$	$P2_1/c$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	19.0481(5)	20.9265(1)	10.8600(4)	12.6318(6)	21.1943(8)	20.4370(2)	11.3881(1)	9.7298(2)
b (Å)	20.4629(4)	7.78420(5)	10.0470(3)	24.2019(12)	9.8398(4)	13.2322(1)	12.3760(1)	10.4082(2)
c (Å)	20.5596(5)	22.8130(1)	17.0342(5)	7.3555(3)	21.9999(9)	33.6123(3)	12.5068(1)	10.5641(2)
α (°)	64.0371(9)	90	90	90	90	90	86.3437(5)	95.4432(8)
β (°)	73.6124(9)	113.7167(3)	103.8650(19)	90.001(3)	118. 004(2)	105.7911(5)	89.9873(5)	102.1521(8)
γ (°)	66.0668(9)	90	90	90	90	90	82.1420(4)	95.4020(8)
Z	8	8	2	2	4	8	1	1
V (Å^3)	6532.0(3)	3402.30(3)	1804.45(10)	2248.68(18)	4050.8(3)	8746.61(13)	1742.53(3)	1033.95(4)
F(000)	2656	1536	844	1232	2192	4744	896	620
Cryst. size (mm)	0.30 × 0.28 × 0.20	0.30 × 0.25 × 0.25	0.30 × 0.20 × 0.10	0.15 × 0.11 × 0.05	0.30 × 0.08 × 0.03	0.16 × 0.06 × 0.05	0.30 × 0.27 × 0.20	0.30 × 0.26 × 0.21
Refl. measured	118 678	112 292	29 455	6543	48 513	69 897	79 411	39 228
Unique refl.	29 881	9884	4111	6543	8538	10 024	10 138	6017
(R_{int})	0.057	0.038	0.066	0.0	0.071	0.055	0.039	0.052
No. of param.	1626	409	208	257	472	569	429	211
R ($I > 2\sigma(I)$)	0.0415	0.0251	0.0599	0.0406	0.0388	0.0299	0.0170	0.0243
R_w (all refl.)	0.1068	0.0695	0.1553	0.0820	0.0887	0.0719	0.0419	0.0587
Goodness-of-fit	1.044	1.043	1.075	1.252	1.018	1.021	1.070	1.014
$\rho_{\text{max/min}}$ (e Å^{-3})	0.32/−0.36	0.53/−0.50	5.96/−2.37	2.59/−2.82	1.35/−1.62	1.07/−1.22	0.65/−1.60	2.28/−2.07
CCDC no.	961729	961730	961731	961732	961733	961734	961735	961736

102.96 (C–CH_3), 15.35 (CH_3); ESI-MS (−), *m*/*z* [assignment] = 272 $[Bt^{Me}]^-$.

$[BiBb_2Cl]$ (3)

[Na(Bb)] (0.241 g, 0.720 mmol) and $BiCl_3$ (0.113 g, 0.360 mmol) were dissolved in 20 mL of acetonitrile and then mixed slowly under N_2 atmosphere. Upon mixing, an orange yellow solution formed that was stirred at room temperature for 6 h and then concentrated under vacuum to 4 mL. This resulted in a yellow precipitate upon standing overnight at 4 °C. The collected precipitates were suspended in slightly warm water (10 mL), filtered, washed again with water and finally re-dissolved in small amounts of acetonitrile and filtered. The solvent was removed by a rotary evaporator affording a yellow solid. (After work-up during the synthesis of **3**, a trace amount of crystalline material with a different composition, $[BiBbCl(\mu\text{-}Cl)_2]_2$ (**3a**), was obtained by slow evaporation of the mother liquor; its composition was only determined by X-ray crystallography.) Yield (**3**): 58%; m.p. 228–230 °C; Anal. calcd for $C_{14}H_{12}N_4S_2Cl_2Bi{\cdot}2CH_3CN$ (found), C 32.64 (32.41), H 2.74 (2.55), N 12.69 (11.22); IR (cm^{-1}, KBr pellet), *ν*(B–H) 2449, 2423. ^1H NMR (thf-d_8), δ = 12.15 (br, 4H, HN), 7.04–7.33 (m, 16H, ring), BH_2 (not located); ^{13}C NMR (thf-d_8), δ = not located (C7, C14), 137.49 (C1, C13), 132.53 (C6, C8), 122.54 (C5, C9), 120.33 (C2, C12), 113.37 (C3, C11), 109.88 (C4, C10); ESI-MS (+), *m*/*z* [assignment] = 831$[Bi(Bb)_2 + 2H]^{2+}$.

$[BiBt^{Me}{}_3]$ (4)

This complex was synthesized by the same procedure as that adopted for **3** by reacting $[NaBt^{Me}]$ (0.212 g, 0.720 mmol) and $BiCl_3$ (0.113 g, 0.360 mmol); however, the resulting solid was extracted with and then recrystallized from dichloromethane. Crystals **4** suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2 solution and had the composition of the solvate $[BiBt^{Me}{}_3]{\cdot}CH_2Cl_2$ (**4a**); by cooling a saturated solution of **4** in $CHCl_3$, crystals with a composition $[BiBt^{Me}{}_3]{\cdot}CHCl_3$ (**4b**) were obtained. Physico-analytical characterization was carried out only for **4a** and not for **4b**. Only two single crystals of **4b** were obtained that were used during crystallographic experiments. Yield of **4a**: 63%; m.p. 109 °C; Anal. calcd for $C_{24}H_{30}B_3N_6S_{12}Bi{\cdot}CH_2Cl_2$ (found): C 26.96 (26.17), H 2.90 (2.84), N 7.55 (6.83); ^1H NMR ($CDCl_3$) δ = 6.46 (s, 6H, HC-ring), 2.27 (s, 18H, CH_3); ^{13}C NMR ($CDCl_3$) δ = 187.76 (C=S), 148.24 (CH), 109.02 (C–CH_3), 17.33 (CH_3); ESI-MS (+), *m*/*z* [assignment] = 1050.8 $[Bi(Bt^{Me})_3 + Na]^+$.

$[BiL^1{}_4Cl_2][BiL^1{}_2Cl_4]$ (5)

2-Mercaptobenzimidazole (1.20 g, 8.00 mmol) dissolved in 10 mL of thf was added slowly to a suspension of $BiCl_3$ (0.630 g, 2.00 mmol) in the same solvent. Upon mixing, a clear yellow solution was obtained that was stirred at room temperature for 24 h and then concentrated under vacuum to 7 mL. The resulting solution was kept at room temperature for five weeks resulting in the precipitation of red crystals. These were filtered, washed with small amounts of thf and methanol and dried. Yield: 65%; m.p. 218–220 °C; Anal. calcd for $C_{42}H_{36}Cl_6N_{12}S_6Bi_2{\cdot}4C_4H_8O$ (found): C 38.27 (38.17), H 3.77 (3.83), N 9.23 (9.02), S, 10.53 (10.51); ^1H NMR (thf-d_8) δ = 11.64 (br, 12H, HN), 7.09–7.19 (m, 24H, ring); ^{13}C NMR (thf-d_8) δ = 164.83 (C7), 130.79 (C1, C6), 120.56 (C2, C5), 107.77 (C3, C4).

$[BiL^2{}_2Cl_2(\mu\text{-}Cl)_2]$ (6)

2-Mercapto-4-methylthiazole (0.938 g, 8.00 mmol) and $BiCl_3$ (0.630 g, 2.00 mmol) was reacted in the same way as described for **5**. The resulting yellow solution was kept at room temperature for one week to afford red crystals. Yield: 71%; m.p. 148–151 °C; Anal. calcd for $C_{16}H_{20}Cl_6N_4S_8Bi_2{\cdot}2C_4H_8O$ (found): C 22.18 (21.62), H 2.79 (2.64), N 4.31 (4.29), S 19.76 (19.95); ^1H NMR (thf-d_8) δ = 11.92 (br, 4H, HN), 6.30 (s, 4H, CH-ring), 2.18 (s, 12H, CH_3); ^{13}C NMR (thf-d_8) δ = 189.86 (C=S), 137.73 (C–CH_3), 107.17 (S–CH), 12.40 (CH_3); ESI-MS (+), *m*/*z* [assignment] = 468.9 $[L_2Bi]^+$, 621.8 $[L_3Bi - Na]^{2+}$.

Electronic spectroscopy

For photophysical characterization, spectroscopic-grade solvents were used throughout all measurements. Absorption spectra were recorded with a Varian Cary 300 double beam spectrometer. Emission spectra at 300 and at 77 K were measured with a steady-state fluorescence spectrometer (Jobin Yvon Fluorolog 3).

X-ray crystallographic experiments

X-ray data set were collected using crystals obtained by slow cooling of saturated solution (thf) (**1**), slow diffusion of *n*-pentane into thf solution of (**2**), slow evaporation of saturated solution (CH_3OH) (**3**), slow evaporation of mother liquor (**3a**), slow evaporation of CH_2Cl_2 solution (**4a**), cooling of saturated solution ($CHCl_3$) (**4b**), and slow diffusion of *n*-pentane into thf solution (**5** and **6**). Single-crystals suitable for X-ray diffraction measurements were picked and mounted on a glass fibre using paratone oil and transferred onto the goniometer of the diffractometer.

Hydrogen atoms at boron were placed at calculated positions except for **1**, **2**, **3** and **4a** for which they were located and refined isotropically. A summary of data collection and structure refinement is reported in Table 8. The structures were solved by direct methods and refined by full-matrix least squares cycles (program SHELXS-97 or SHELXL-97).[54] In compound **3** the contributions of disordered solvent molecules were corrected for using the SQUEEZE procedure of PLATON.[55] CCDC 961729–961736 contain the supplementary crystallographic data for this paper.

Acknowledgements

We are thankful to Klaus-Peter Mester for recording NMR spectra and to Brigitte Michel (both Bielefeld) for elemental analyses. M. I. acknowledges with special thanks the Deutscher Akademischer Austausch Dienst (DAAD) for providing a PhD stipend.

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ARTICLE TYPE

Structural chemistry of hemi and holo directed lead(II) complexes in soft environment

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

To investigate the geometries and stereo chemical activity of the lone pair at the lead (Pb) atom, lead(II) complexes (**1** – **10**) with one tripodal (L^1), one dipodal (L^2) boron substituted soft ligands and eight other small soft hetrocyclic ligands, 2-mercaptobenzimidazole (L^3), 2-mercapto-5-methylbenzimidazole (L^4), 3-mercapto-1,2,4-triazole (L^5H), 3-mercapto-4-methyl-1,2,4-triazole (L^6), 2-mercapto-1,3,4-thiadiazole (L^7H), 2-mercapto-5-methyl-1,3,4-thiadiazole (L^8H), 5-mercapto-1-methyltetrazole (L^9H) and 2-mercapto-4-phenylthiazole ($L^{10}H$) were prepared. The structures of these complexes were elucidated on the basis of X-ray crystallography, elemental analyses as well as ^1H NMR, ^1H DOSY, ^{13}C NMR and ^{207}Pb NMR spectroscopy. The coordination number of these complexes vary from 4 – 8. Majority of the complexes are polymeric and possesses hemidirected environment around lead centres. Solution studies revealed that most of the complexes are dissociated in high polar solvents. 'Photophysics to come'

Introduction

Lead(II) has electronic configuration [Xe] $4f^{14}5d^{10}6s^2$ and is classified as a borderline soft metal ion in the hard and soft acid–base concept of Pearson.[1-2] Lead is well known to be toxic for the growth of organisms and its most preferred target in organism are the sulphur rich proteins that have zinc binding sites. The replacement of zinc by lead disrupts the structures of these proteins making them dysfunctional.[3-6]

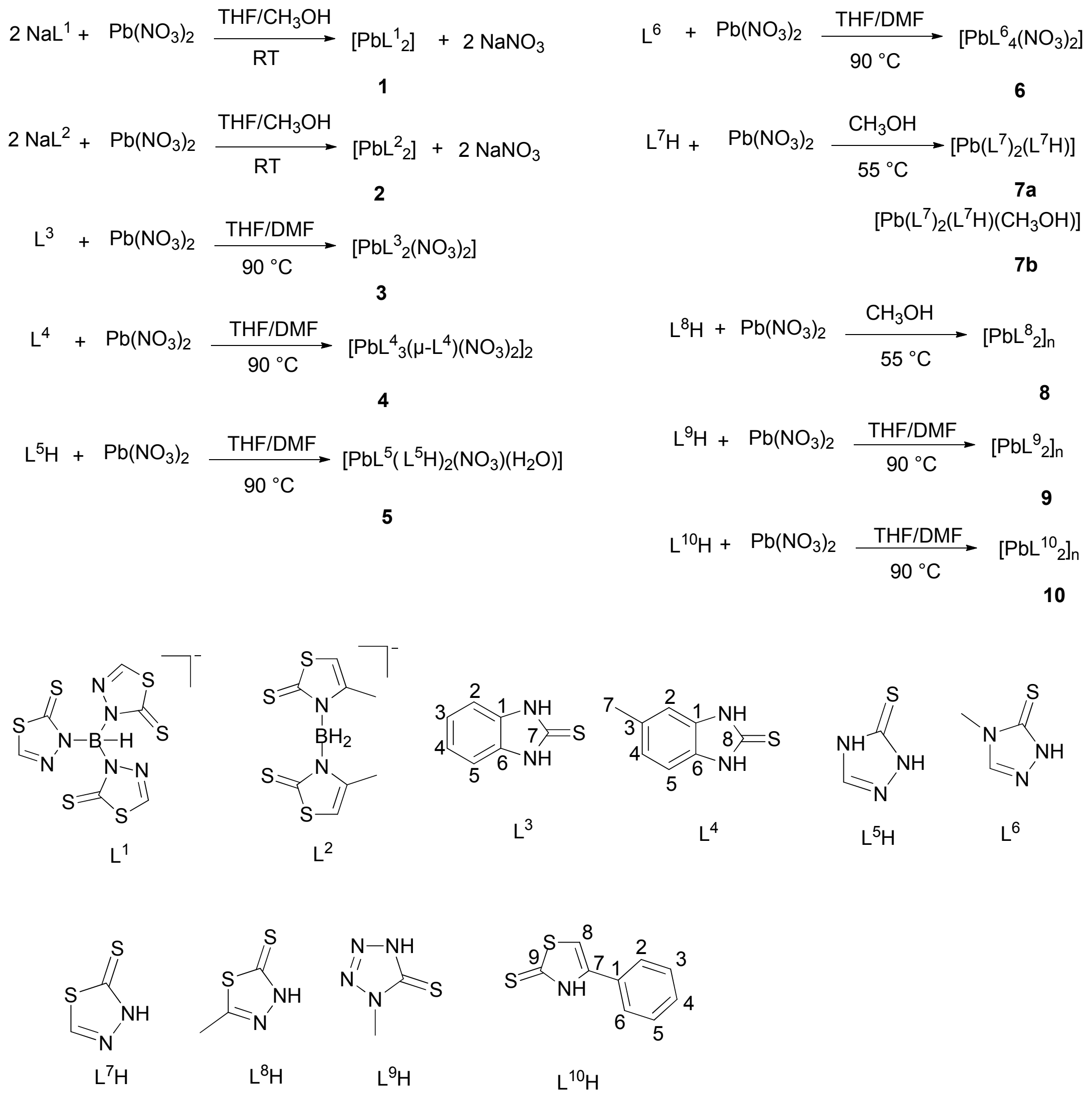
During the last few decades, coordination chemistry of lead(II) with hetero donor ligands remained an active area of research due to their interesting mode of bonding. A wide range of coordination numbers (1 – 12) for Pb(II) in such complexes has been reported.[7-12] Lead(II) complexes have not only bio-relevant importance but have also been employed as precursors for bulk or nanostructured PbS and PbSe materials.[13] It has been reported that 6s electron pair and several other factors such as the hard or soft nature of ligands, attractive or repulsive forces etc affect the geometries around lead(II) centres.[14] Depending upon the influence of lone pair in determining the geometries of lead(II) complexes, the terms holo and hemi-directed have been employed in the literature.[15] Despite great efforts in the past for the coordination chemistry of Pb(II) with S donor ligands, rational design and tuning of the the ligand structure to satisfy the coordination preferences and requirements of the Pb(II) atom is still a challenging task. Our growing interest in the field of coordination chemistry of bismuth complexes with analogous sulfur donor ligands[16,17] has prompted us to synthesize and study the coordination pattern of lead(II) complexes with such ligands. For this purpose, we report here the synthesis of ten lead complexes with two boron centered and eight other small heterocyclic ligands. Preliminary photo-physical investigations of selected lead complexes are also part of this manuscript.

Results and discussion

Synthesis

Sodium salt of the tripodal (L^1)[18] and dipodal (L^2)[17] boron substituted ligands were synthesised according to a literature protocols. These two ligands (L^1, L^2) along with the other eight commercially available heterocyclic soft ligands (L^3 – $L^{10}H$) were reacted with lead(II) nitrate to yield lead(II) complexes (**1** – **10**) under different conditions (Scheme-1).

The reaction of $PbNO_3$ with the tripodal boron centred soft ligand (L^1) in a 1:2 ratio afforded complex **1** as yellow precipitates which were found only to be soluble in DMF and 1-methyl pyrrolidinone. The elemental analysis data support the composition of PbL^1. Crystallization of **1** was carried out by slow diffusion of *n*-pentane into 1-methyl-2-pyrrolidinone solution that resulted yellow crystals of **1a**. The free heterocycle coordinated to lead atom is expected to come from impure ligand that contains trace amount of free heterocycle. Majority of the complexes 1 – 10 have poor solubility and are freely soluble only in DMSO and moderately soluble in DMF. Good yields (above 65 %) of these complexes have been obtained. These complexes 1 – 10 were characterised by ^1H NMR, ^1H DOSY NMR, ^{13}C NMR, ^{207}Pb NMR, elemental analyses and finally by single crystal X-ray diffraction.



Scheme 1. Synthesis of lead(II) complexes (**1 – 10**) and labelling schemes of the ligands

Solid state structures

Single X-ray crystallography revealed molecular structures of complexes **1 – 10** with compositions of $[Pb(L^1)_2(L^7H)_2L']$ **1a** (where L′ is 1-methyl-2-pyrrolidinone), $[PbL^2_2]$ **2**, $[PbL^3_2(NO_3)_2]$ **3**, $[PbL^4_3(\mu\text{-}L^4)(NO_3)_2]_2$ **4**, $[Pb(L^5)(L^5H)_2(NO_3)(H_2O)]_n$ **5**, $[PbL^6_4(NO_3)_2]$ **6**, $[Pb(L^7)_2(L^7H)]_n$ **7a**, $[Pb(L^7)_2(L^7H)(CH_3OH)]_n$ **7b**, $[PbL^8_2]_n$ **8**, $[PbL^9_2]_n$ **9**, $[PbL^{10}_2]_n$ **10**. Selected bond lengths and angles are presented in Tables 1 – 6 and their molecular structures are shown in Figures 1 – 10.

Molecular structure of **1a** is shown in Figure 1 and exhibit coordination number six accomplished by three sulphur atoms {S(1) from one tripodal ligand, S(3) from second tripodal ligand, S(7) from thiadiazole unit}, one oxygen atom O(1) from 1-methyl-2-pyrrolidinone, two nitrogen atoms {N(7) from one thiadiazole and N(8) from another thiadiazole moiety}. The important bond lengths and angles are listed in Table 1 which are comparable with $[(Tm^{Ph})_2]Pb$,[19] $\{[(Tm^{Ph})_2]Tl\}^+$,[20] $\{[(Tm^{Me})_2]Bi\}^+$,[21] $\{[(Tm^{Me})_2]Tl\}^+$ [22] (where Tm = hydrotris(methimazolyl)borate). The structure **1a** can also be compared with polymeric structure of its thallium analogue $[HB(mtda)_3]_2Tl$[23] (where $HB(mtda)_3$ = L^1) having TlS_6 core with octahedral geometry. Polymeric chain for **1a** can be generated by centre of inversion and translation along *a* axis.

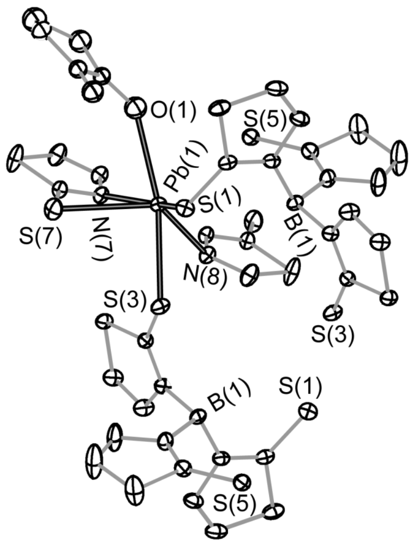


Figure 1. Molecular structure of [Pb(L^1)$_2$(L^{7}H)$_2$L′] **1a**. Hydrogen atoms have been omitted for clarity; displacement ellipsoids are drawn at the 50% level.

Table 1. Selected bond lengths [Å] and angles [deg] of lead(II) complexes **1** and **2**

1a		**2**	
Pb(1)–S(7)	2.843(2)	Pb(1)–S(1)	2.954(2)
Pb(1)–S(3)	2.921(2)	Pb(1)–S(3)	2.713(2)
Pb(1) –S(1)	3.095(2)	Pb(1)–S(5)	2.813(2)
Pb(1)–N(8)	2.746(2)	Pb(1)–S(7)	2.969(2)
Pb(1)–N(7)	2.638(2)	H(1A)–Pb(1)	2.66(2)
Pb(1)–O(1)	2.674(2)	B(1)–Pb(1)	3.609(2)
S(1)–C(1)	1.687(2)	S(1)–Pb(1)–S(7)	168.3(2)
S(3)–Pb(1)–S(1)	68.9(2)	S(3)–Pb(1)–S(1)	89.6(2)
S(7)–Pb(1)–S(1)	99.8(2)	S(3)–Pb(1)–S(5)	76.9(2)
S(7)–Pb(1)–S(3)	87.5(2)	S(3)–Pb(1)–S(7)	78.7(2)
N(7)–Pb(1)–N(8)	75.6(1)	S(5)–Pb(1)–S(7)	97.2(2)
N(8)–Pb(1)–S(3)	76.4(2)	H(1A)–Pb(1)–S(5)	128.2(5)
O(1)–Pb(1)–S(1)	97.3(2)		
O(1)–Pb(1)–S(3)	159.1(2)		
N(7)–Pb(1)–S(1)	157.1(2)		

The molecular structure of complex **2** is shown in Figure 2 and its important bond lengths and angles are given in Table 1. In this complex the lead atom is coordinated by four sulphur atoms and a hydrogen atom of an –BH$_2$ unit (B(1)–H(1A)···Pb interaction). This defines two six-membered and one eight-membered rings. Overall the coordination geometry can be described as distorted octahedron with a stereochemical active lone pair. The interesting feature of the complex is, B(1)–H(1A)···Pb interaction at a distance of 2.66(2) Å (Pb···B(1), 3.609(2) Å) by one –BH$_2$ unit. The second –BH$_2$ unit has a distance of B(2)–H(2A)···Pb 3.02 Å which is too large. However it makes a weaker contact of 2.84 Å with lead atom of neighbouring molecule forming a dimer at centre of inversion. B(1)–H(1A)···Pb interaction can be compared with a related distance in [Tl(Bm^{Me})]$_x$ (B–H···Tl distance of 2.69 Å (Tl–B, 3.50 Å).[24] Such an interaction provides a characteristic feature to soft borate ligands that makes them flexible and inserts stabilizing effects.[25,26] The complex **2** when compared with its bismuth analogue [Bi(Bt^{Me})$_3$] (where Bt^{Me} (dihydrobis(2-mercapto-4-methylthiazolyl)borate) = L^2) reported by us[17] reveals significant differences. [Bi(Bt^{Me})$_3$] is monomeric with no B–H···Bi interaction[17]. To best of our knowledge, B–H···Pb interaction in complex **2** with dipodal boron centred soft ligand is unprecedented. However a similar interaction with one BH unit has been observed for a lead complex [Tm^{Ph}]$_2$Pb with a tripodal boron centred soft ligand.[19]

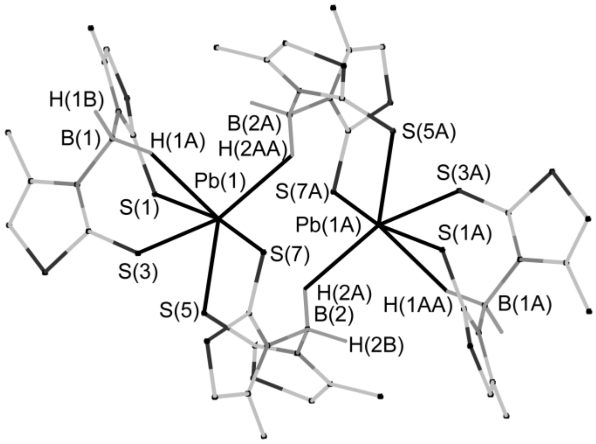
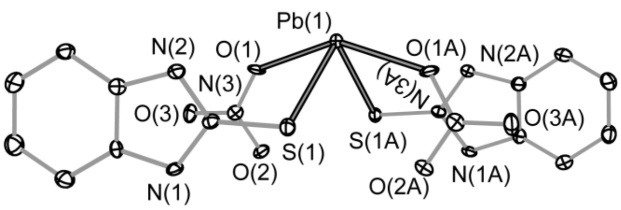
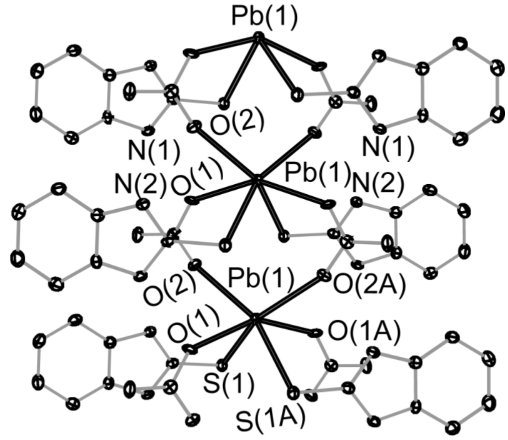


Figure 2. Solid state structure of [PbL$^2_2$] **2**. Hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 50% level.

Complex 3 possesses C$_2$-symmetry. The lead atom is four coordinated, to two sulfur atoms of benzimidazole ligands and two oxygen atoms of two nitrate ions and can be referred as hemidirected (Figure 3a). Both the benzimidazole and nitrate behave as monodentate. The bond lengths and angles are listed in Table 2. The interesting feature of this complex is the presence of significant secondary interactions (Pb(1)–O(2) 2.925(3) Å }, which are shorter than the sum of the van der Waals' radii (3.10).[27] The hemidirected tetrahedron (Figure 3a) with a stereo-chemically active lone-pair of electrons on the lead atom leaves space for bonding of O atom of nitrate ligand of adjacent complex resulting polymeric structure along glide plane c perpendicular to a (Figure 3b). Such secondary interactions have also been reported at a distance of (Pb–O 2.989(10) Å for [Pb$_2$(ins)$_2$(CH$_3$CH$_2$OH)]$_n$ (ins = *N*-isonicotinamidosalicylailead dimine).[27] There are also weak N–H···O hydrogen-bond intermolecular interactions where the donor-acceptor distance for N(1)–H(1)···O(1) and N(2)–H(2)···O(2) are 1.95(2) Å and 1.97(2) Å respectively.



(a)



(b)

Figure 3. (a) Coordination environment around Pb(II) in $[PbL^3_2(NO_3)_2]_n$ **3** and (b) its coordination polymer, hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 50% level.

Complex **4** crystallizes in the monoclinic space group C_2/c. It forms discrete dimeric units $[\{Pb(L^4)_3(\mu\text{-}L^4)Pb(NO_3)_2\}_2$ at centre of inversion (Figure 4). The double bridging mode of sulphur is similar as reported for $[(mimt)(NO_3)_2Pb(\mu\text{-}mimt)_2Pb(NO_3)_2(mimt)_2]$ where mimt = 1-methylimidazoline-2(3H)-thione.[28] The distances between lead and the bridging sulphur atoms are Pb(1)–S(1A) 3.098(2) Å, Pb(1)–S(1) 2.830(2) Å while the S–Pb–S angles are Pb(1)–S(1)–Pb(1A) 102.2 SD and S(1)-Pb-S(1A) 77.8 SD resulting a Pb···Pb distance of 4.617 Å. As expected, the Pb–S bond lengths to the non-bridging L^4 ligands are shorter than those to the bridging ligands (Table 2) and are comparable with those of the discussed complex **3**. Furthermore, two monodentate nitrate ligands also coordinate to each lead atom resulting an overall coordination number seven. The relatively longer Pb–O bonds (Table 2) can be compared with $[Pb_2(phen)_2(mbtfa)_4]$ and $[Pb_2(dmp)_2(mbtfa)_4]$ (phen, dmp and mbtfa are 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline and 4-methoxybenzoyltrifluoroacetonate,[31] (Pb–O distances: 2.829(5)–2.918(5) Å respectively). It is also important to note that such distances have been overlooked in the past.[29-30] The important bond angles are listed in Table 2 and the complex can be classified as hemidirected. It is somewhat surprising with coordination number 7 for a complex to be hemidirected because of possible ligand crowd. However, Glusker *et al.* [17] noticed that a relatively large number of lead(II) complexes were hemidirected for coordination number 7 (21 out of 31) searched in CSD.

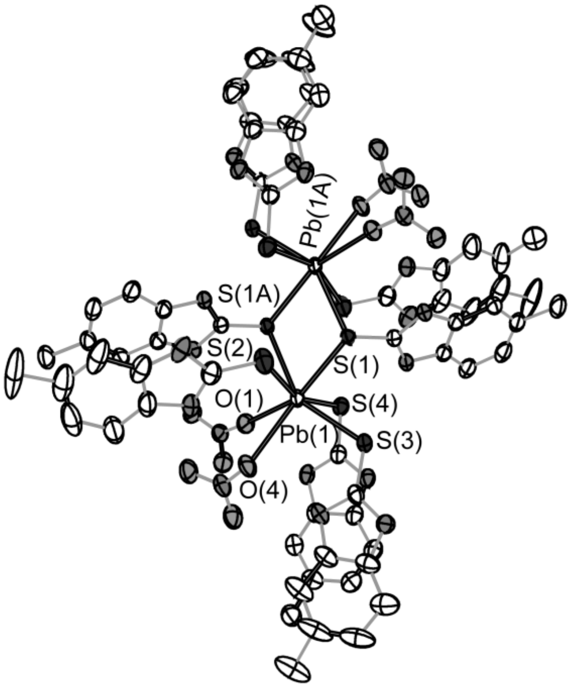


Figure 4. Solid state structure of $[PbL^4_3(\mu\text{-}L^4)(NO_3)_2]_2$ **4**. Hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 50% level.

Table 2. Selected bond lengths [Å] and angles [deg] of complexes **3** and **4**

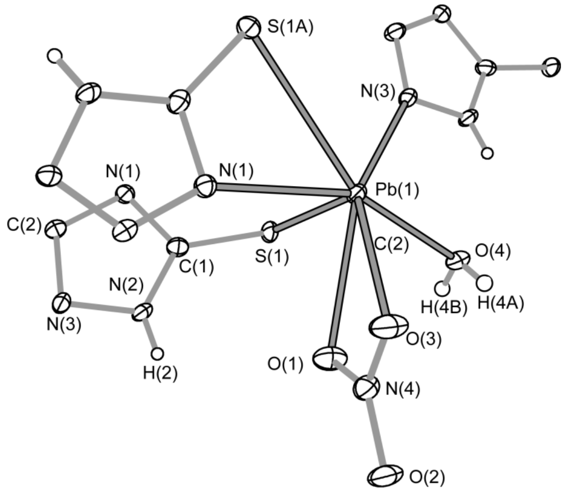
3		**4**	
Pb(1)–S(1)	2.886(2)	Pb(1)–S(1) Pb(1)–S(1A)	2.830(2), 3.098(2)
Pb(1)–S(1A)	2.886(2)	Pb(1)–S(3)	2.859(2)
Pb(1)–O(1)	2.574(3)	Pb(1)–S(2)	2.953(2)
Pb(1)–O(1A)	2.574(3)	Pb(1)–S(4)	2.985(2)
Pb(1)–O(2)	2.925(3)	Pb(1)–O(4)	2.887(3)
Pb(1)–O(2A)	2.925(3)	Pb(1)–O(1)	2.938(2)
N(1)–H(1)···O(1)	1.95(2)	S(1)–Pb(1)–S(3)	76.5(2)
S(1)–C(1)	1.719(5)	S(1)–Pb(1)–S(2)	67.9(2)
O(1)–Pb(1)–S(1)	78.1(2)	S(3)–Pb(1)–S(2)	99.7(2)
O(1)–Pb(1)–O(1A)	147.9(2)	S(3)–Pb(1)–S(4)	81.4(2)
S(1)–Pb(1)–S(1A)	95.4(2)	S(2)–Pb(1)–S(4)	160.2(2)
		S(3)–Pb(1)–S(1)	148.9(2)
		S(2)–Pb(1)–S(1)	86.5(2)
		S(4)-Pb(1)-S(1)	83.0(2)

Lead complex 5 crystallizes in the form of a sheet-like structure perpendicular to a, formed by the glide plane b and the 2 fold screw axis along c of *Pbcn* (Figure 5). In this complex, each Pb atom is in hemidirected environment by coordinating one water molecule and a bidentate nitrate ligand as well as three monodentate triazole ligands. Two of the three bind with their nitrogen site and one through sulphur. The important feature of the structure is bridging nature of S(1) that results sheet like structure. The affinity of lead towards both soft and hard donor sites support its borderline placement in HSAB concept. The important bond lengths and angles of 5 are given in Table 3 which can be compared with a closely reported structure of [Pb(trzS)]$_n$ (Where trzS = 1,2,4-triazole-3-thiol).[32] The latter complex was in-situ synthesised by heating ahtrzSH (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole) and possesses square pyramidal environment (N_3S_2) with coordination number 5.

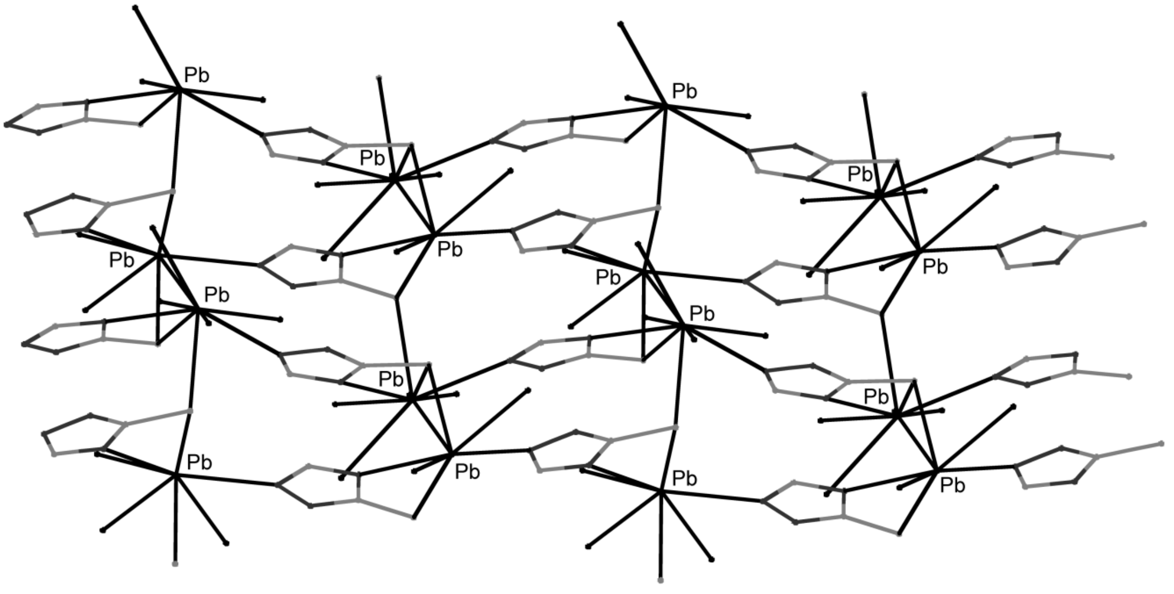
Table 3. Selected bond lengths [Å] and angles [deg] of complexes **5** and **6**

5		6	
Pb(1)–S(1)	2.817(2)	Pb–S	3.020(2)
Pb(1)–S(1A)	3.13(2)		
Pb(1)–N(1)	2.540(4)	Pb–O	2.726(2)
Pb(1)–N(3)	2.764(4)	S(1)–C(1)	1.694(3)
Pb(1)–O(1)	2.632(3)	O–Pb(1)–O *cis*	46.8(2)
Pb(1)–O(3)	2.856(3)	O–Pb–O *trans*	147.4(2)
Pb(1)–O(4)	2.716(3)	S–Pb(1)–S *trans*	153.4(2)
O(1)–Pb(1)–S(1)	76.2(2)	S–Pb(1)–S *cis*	93.0(2)
O(4)–Pb(1)–S(1)	77.1(2)		
O(1)–Pb(1)–O(4)	75.9(2)		
N(1A)–Pb(1)–S(1)	83.0(2)		
N(3)–Pb(1)–S(1)	77.9(2)		
O(1)–Pb(1)–N(3)	138.7(2)		
O(3)–Pb(1)–S(1)	121.5(2)		
O(3)–Pb(1)–O(4)	95.6(2)		

Complex 6 was synthesised using a methyl substituted 1,2,4-triazole under similar conditions as for complex **5**. The solid state structure of 6 reveals a remarkable contrast to **5** and is monomeric with coordination number 8 and S4 symmetry. The Pb atom is coordinated by four 3-mercapto-4-methyl-1,2,4-triazole (L^6) ligands via their sulphur donor atoms and by two bidentate nitrate ligands. The Pb–S and Pb–O bond lengths are 3.020(2) Å and 2.726(2) Å respectively. The complex is holodirected compared to 5. Glusker et al.[17] have found the majority of lead(II) complexes in CSD with coordination number 8 to be holodirected.



(a)



(b)

Figure 5. (a) Coordination environment around Pb centre of [Pb(L^5)(L^{5}H)$_2$(NO$_3$)(H$_2$O)]$_n$ **5**, (b) part of sheet like structure of [Pb(L^5)(L^{5}H)$_2$(NO$_3$)(H$_2$O)]$_n$ **5**. Hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 50% level.

Complex **6** was synthesised using a methyl substituted 1,2,4-triazole under similar conditions as for complex **5**. The solid state structure of **6** reveals a remarkable contrast to **5** and is monomeric with coordination number 8 and S_4 symmetry. The Pb atom is coordinated by four 3-mercapto-4-methyl-1,2,4-triazole (L^6) ligands via their sulphur donor atoms and by two bidentate nitrate ligands. The Pb–S and Pb–O bond lengths are 3.020(2) Å and 2.726(2) Å respectively. The complex is holodirected compared to **5**. Glusker *et al* .[17] have found the majority of lead(II) complexes in CSD with coordination number 8 to be holodirected.

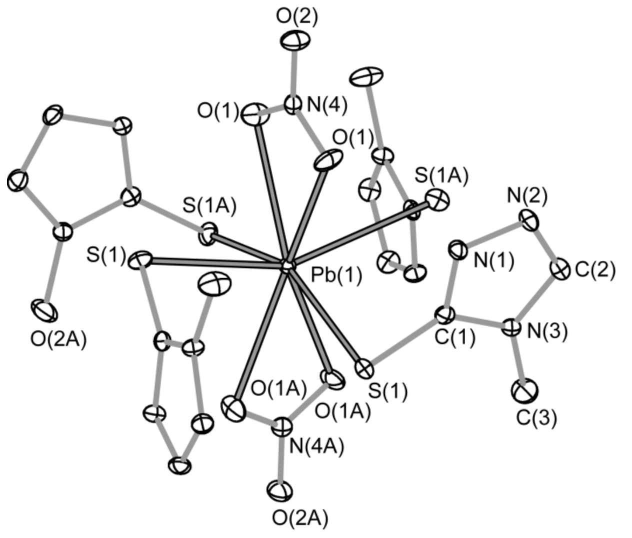
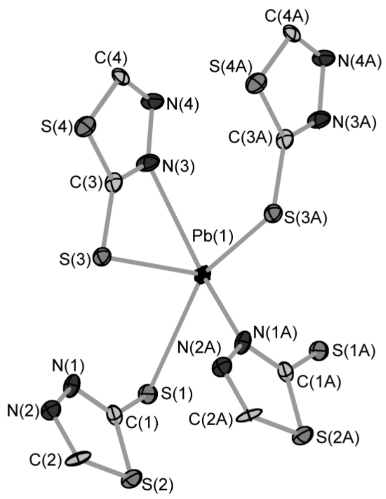


Figure 6. Solid state structure of $[PbL^6_4(NO_3)_2]$ **6**. Hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 50% level.

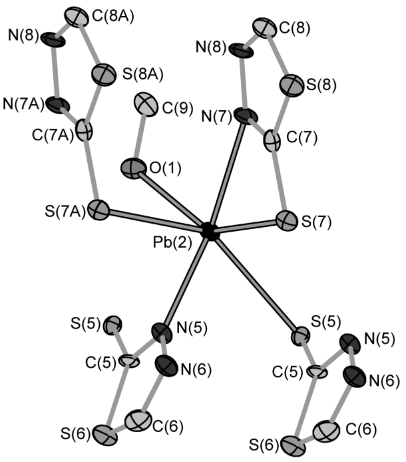
The molecular structure of complex **7** is shown in Figure 7. This complex in solid state represent two 1D coordination polymers a and b. The two coordination polymers are linked through S(5) and run along the a axis. The two ligands (L^7H) at each Pb atom in both molecules a and b have different coordination modes (Figure 7a,b). For example, in molecule a, one of the ligand (L^7H) behaves bidentate and coordinate via S(3) [Pb(1)–S(3) 2.852(3) Å] and N(3) [Pb(1)–N(3) 2.864(13) Å] donor atoms, however S(3) is bridging and coordinates further to the next lead atom at a distance of Pb(1)–S(3) 3.016(3) Å. The second heterocyclic ligand (L^7H) coordinates to Pb(1) only via N(1) (Pb(1)–N(1) 2.534(9) Å) and uses its S(1) donor site to coordinate to a lead atom of the neighbouring monomeric unit. The coordination number around each lead atom of **a** is five with a distorted square pyramidal geometry. The presence of stereochemically active lone pair is identifiable from a void as well as from bond angles (Table 4). In polymer chain of b (Figure 7d), the coordination number at each lead atom is six with an additional Pb–O bond to a methanol solvent. The important bond lengths and angles are depicted in Table 4 and are slightly different from molecule **a**. Moreover, one bridging atom S(3) in molecule **a** compared to two bridging atoms (S(7) and O(1)) also make another difference in the structures of both **a** and **b** molecules.

Table 4. Selected bond lengths [Å] and angles [deg] of complexes **7a** and **7b**

7a		**7b**	
Pb(1)–S(3)	2.852(3),	Pb(2)–S(7)	2.847(3)
Pb(1)–S(3A)	3.016(3)	Pb(2)–S(7A)	2.950(3)
Pb(1)–S(1)	3.086(3)	Pb(2)–S(5)	3.058(3)
Pb(1)–N(1)	2.534(9)	Pb(2)–N(7)	2.791(9)
Pb(1)–N(3)	2.864(13)	Pb(2)–N(5)	2.595(9)
N(1)–Pb(1)–S(3)	88.5(2)	Pb(2)–O(1)	2.865 SD
		Pb(2)–O(1A)	2.943 SD
N(1)–Pb(1)–S(3A)	65.7(2)	N(5)–Pb(2)–N(7)	133.2(3)
S(3)–Pb(1)–S(3)	87.3(2)	N(5)–Pb(2)–S(7)	88.5(2)
N(1)–Pb(1)–S(1)	77.5(2)	N(7)–Pb(2)–S(7)	56.8(2)
S(3)–Pb(1)–S(1)	86.6(2)	N(5)–Pb(2)–S(7A)	65.7(2)
N(1)–Pb(1)–N(3)	126.8(4)	N(7)–Pb(2)–S(7A)	81.7(2)
		S(7)–Pb(2)–S(7A)	88.6(2)
		N(7)–Pb(2)–S(5A)	125.0(2)
		Pb(2)–O(1)–Pb(2A)	88.4(3)
		Pb(2)–S(7)–Pb(2A)	88.7(2)



(a)



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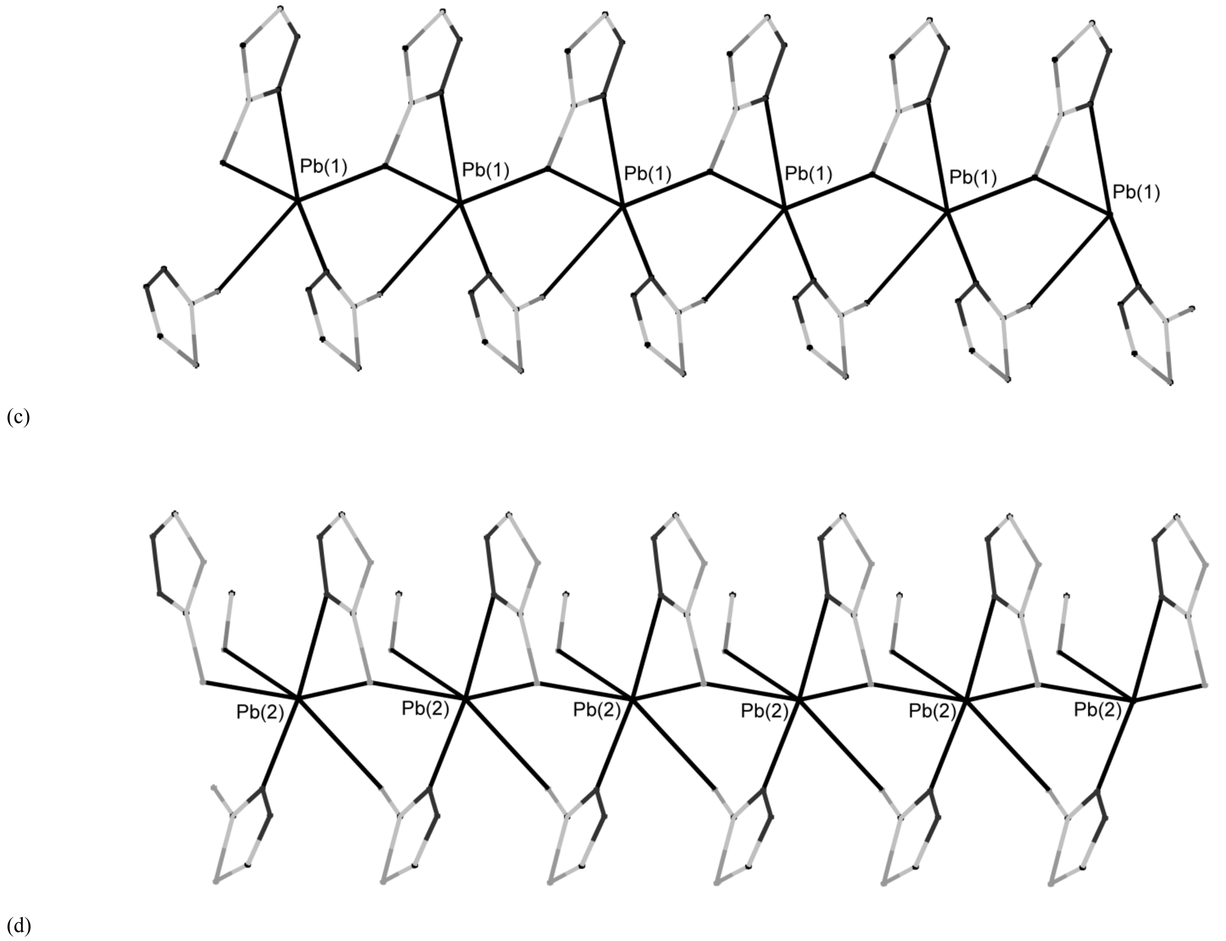


Figure 7. (a) Monomeric unit of $[Pb(L^7)_2(L^7H)]_n$ **7a**, (b) monomeric unit of $[Pb(L^7)_2(L^7H)(CH_3OH)]_n$ **7b**, (c) part of polymeric structure of $[Pb(L^7)_2(L^7H)]_n$ **7a**, (d) part of polymeric structure of $[Pb(L^7)_2(L^7H)(CH_3OH)]_n$ **7b**. Hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 50% level.

X-ray diffraction analysis for complex **8** shows that it also possesses a polymeric structure assembled via the S(1) atom that bridge two lead atom in the chain (Figure 8). The coordination geometry of each lead atom in this polymeric chain (running along *c* axis build by glide plane *c* of *P2₁/C* is irregular five-coordinated with a hemidirected environment and can be best described as distorted square pyramidal. The significant bond lengths and angles are tabulated in Table 4. These are comparable with complex **5** discussed above as well as with reported structure of $[Pb(trzS)]_n$ (Where trzS = 1,2,4-triazole-3-thiol).[32]

In complex **9**, each Pb(II) ion is five-coordinated (similar to complex **8**) by three S atoms and two N atoms from three tetrazole ligands (L^9H) forming a distorted square pyramidal coordination geometry (Figure 9). One tetrazole ligand (L^9H) acts as bridging bidentae via N(4) and S(1) forming a chain by two fold screw axis along *b*, where as the the second (L^9H) acts as tridentate via N(8) and S(2). S(2) act as bridging and coordinate to symmetry generated Pb(1A) of the second chain, thereby forming a double chain (running along *b* axis). The bond lengths and angles (Table 5) can be compared with related lead complexes based on diffrent substituted tetrazole ligands.[33-34]

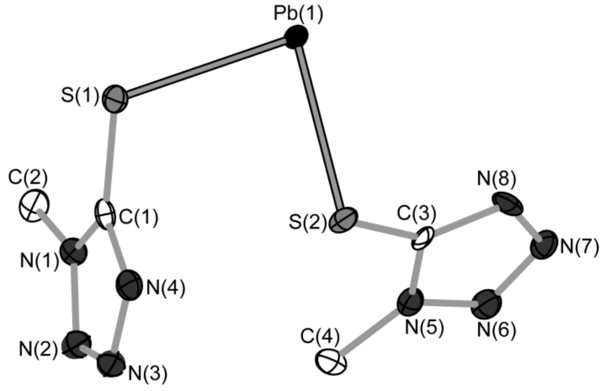
Table 5. Selected bond lengths [Å] and angles [deg] of complex **8**

	8
Pb(1)–S(1)	2.778(3)
Pb(1)–S(1A)	2.993(3)
Pb(1)–S(3)	2.922(3)
Pb(1)–N(3)	2.473(8)
Pb(1)–N(1)	2.827(9)
S(3)–Pb(1)–S(1)	91.0(2)
S(1)–Pb(1)–S(1A)	84.3(2)
N(1)–Pb(1)–N(3)	131.1(3)
N(3)–Pb(1)–S(1A)	81.3(2)
N(3)–Pb(1)–S(1)	76.5(2)
N(3)–Pb(1)–S(3)	79.8(2)
N(1)–Pb(1)–S(3)	86.4(2)

The lead complex **10** with 2-mercapto-4-phenylthiazole ($L^{10}H$) exhibit polymeric structure (running along *b* axis created by glide plane *b* of *Pbca*) (Figure 10). Each lead atom has distorted octahedral geometry with hemidirected environment defined by four sulphur and two nitrogen atoms of 2-mercapto-4-phenylthiazole ($L^{10}H$). Both ligands ($L^{10}H$) chelate the lead(II) ion and the sulphur atoms form bridges. Bond distances and angles are listed in Table 6. The Pb–S are similar to those observed for complex n **4** and can be also compared with [(mimt)$(NO_3)_2$Pb(μ-mimt)$_2$Pb$(NO_3)_2$(mimt)$_2$] where mimt = 1-methylimidazoline-2(3H)-thione. [28]

Table 6. Selected bond lengths [Å] and angles [deg] of complexes **9** and **10**

9		**10**	
Pb(1)–S(1)	2.810 (2)	Pb(1)–S(1)	2.788(2)
Pb(1)–S(2A)	3.108(2)	Pb(1)–S(1A)	3.097(2)
Pb(1)–S(2)	2.745(2)	Pb(1)–S(3)	2.818(2)
Pb(1)–N(8)	2.749(7)	Pb(1)–S(3A)	2.980(2)
Pb(1)–N(4)	2.589(8)	Pb(1)–N(1)	2.742(3)
S(1)–Pb(1)–S(2)	154.2(2)	Pb(1)–N(2)	2.731(3)
S(1)–Pb(1)–S(2A)	84.9(2)	S(1)–Pb(1)–S(3)	87.0(2)
S(2)–Pb(1)–S(2A)	86.3(2)	S(1)–Pb(1)–S(3A)	87.3(2)
N(8)–Pb(1)–N(4)	163.2(2)	S(1A)–Pb(1)–S(3A)	173.5(2)
N(8)–Pb(1)–S(2A)	82.8(2)	S(1)–Pb(1)–N(1)	58.2(2)
Pb(1)–S(2)–Pb(1A)	114.1(2)	S(3)–Pb(1)–N(2)	57.8(2)
Pb(1)–S(2A)–Pb(1A)	114.1(2)	N(2)–Pb(1)–N(1)	155.4(2)
		Pb(1)–S(1A)–Pb(1)	92.8(2)
		Pb(1)–S(3A)–Pb(1)	94.8(2)



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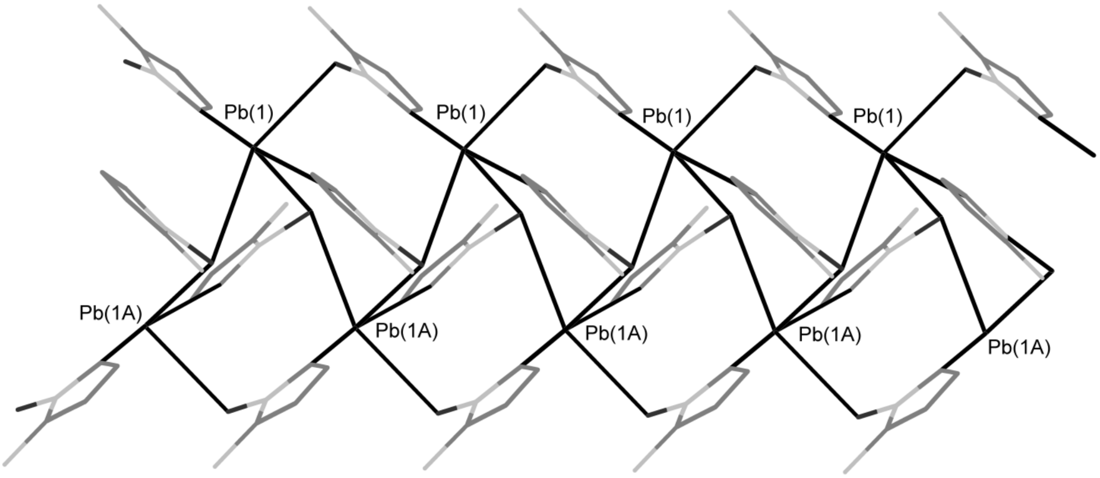
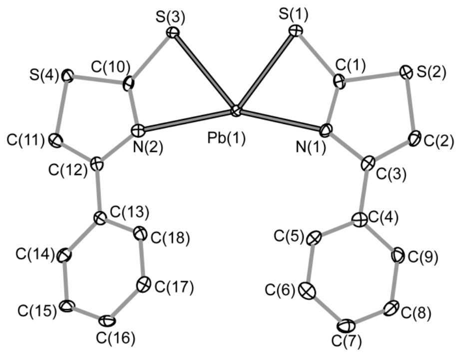
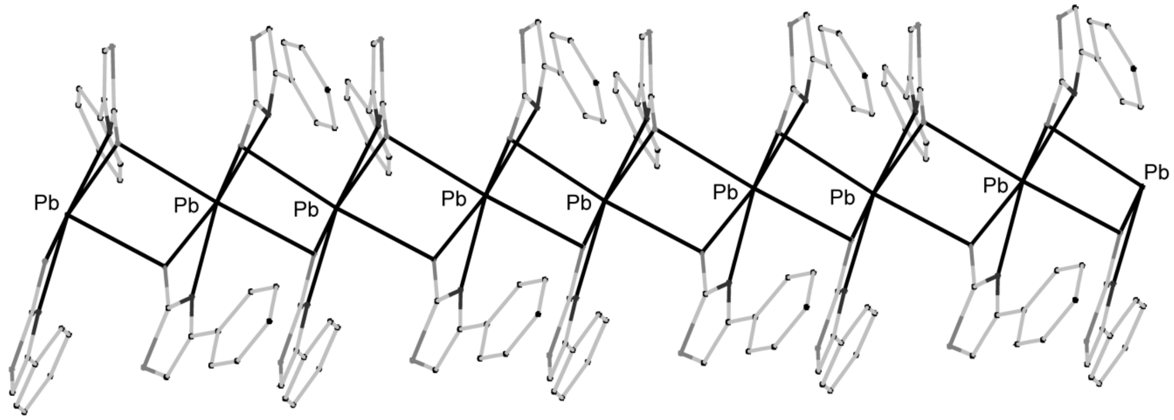


(b)

Figure 9. (a) Assymetric unit of [PbL^9]$_n$ **9** with labelling of all atoms for clarity, (b) Part of double chain of [PbL^9]$_n$ **9**. Hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 50% level.



(a)



(b)

Figure 10. (a) Asymmetric unit of [PbL$^{10}_2$] (**10**) with labelling of all atoms for clarity, (b) A part of extended structure of [PbL$^{10}_2$]$_n$ (**10**). Hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 50% level.

Solution studies

^{1}H NMR spectra of the complexes were recorded in dmf-d7 and dmso-d6 depending upon solubility of the respective complex (see experimental section). The ^{1}H NMR and ^{13}C NMR spectra of complexes (**1** – **10**) were compared with those of free ligand compounds (L^1 – L^{10}H). The ^{1}H NMR spectra of complexes **1**, **3**, **4**, **6**, **7** shows slight variations in chemical shift when compared with those of the respective free ligand compounds, indicating a significant dissociation of these complexes. However, for complexes **2**, **5**, **8**, **9** and, **10**, the protons of the groups $-C_6H_5$, $-CH_3$ and –CH protons exhibit a notable chemical shift (see experimental section). For example, the ^{1}H NMR spectrum complex **2**, exhibit two signals at 6.34 and 2.13 ppm for HC–ring and CH_3 protons, respectively, but 6.22 (HC-ring) and 2.37 ppm (CH_3) for free ligand compound L^2. Moreover, in this spectrum no $-BH_2$ signals were observed at room temperature; a similar observation has also been reported.[35] Interestingly in the ^{11}B NMR of this complex, two different signals at –14.25 ppm and –1.96 ppm were observed indicating different environments of B atoms (Figure 11). This might be due to monomeric nature of the complex in solution keeping interaction with only one BH unit (the stronger one at a distance of 2.66 Å). However, in complex 1 no such interaction can be established.

^{1}H DOSY experiments for **2**, **3** and **6** were also performed and the diffusion co-efficent were compared with their respective free ligand compounds (Table 7). On the basis of diffusion co-efficient data it can be argued that complexes **3** and **4** are highly dissociated as the diffusion co-efficient are almost same within experimental error. However the CH proton of complex 2 have significantly different diffusion co-efficient 2.34 × 10^{-10} m^{2}s^{-1} compared to free ligand compound (2.62 × 10^{-10} m^{2}s^{-1}) which reveals that the complex 2 is not dissociated in solution. The obtained further support the conclusion derived from ^{1}H NMR and ^{13}C NMR about dissociation of these complexes.

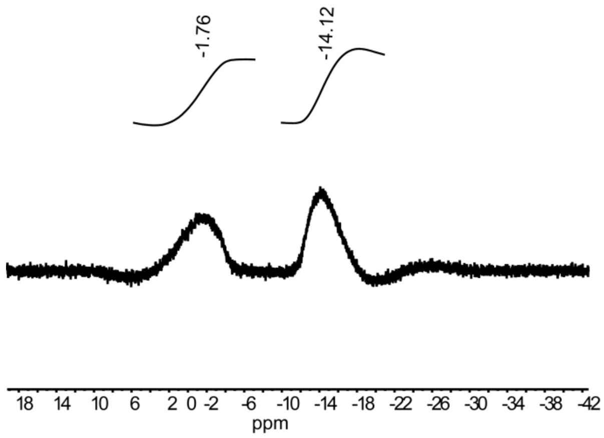


Figure 11. ^{11}B NMR spectrum of complex **2**

Table 7. Diffusion co-efficient of complexes **2**, **3** and **6**

Compound	Diffusion co-efficient (m^{2}s^{-1})
2	CH (2.34 × 10^{-10})
FLC	CH (2.62 × 10^{-10})
3	C_6H_5 (2.79 × 10^{-10})
FLC	C_6H_5 (2.83 × 10^{-10})
4	CH (3.44 × 10^{-10})
FLC	CH (3.59 × 10^{-10})

Where FLC is free ligand compound of respective complex

Similar to the ^{1}H NMR spectra described above, the ^{13}C NMR chemicals shifts of the free ligand compounds in complexes **1**, **3**, **4**, **6**, **7** and **8** are very similar, supporting dissociation phenomenon. However, the ^{13}C NMR spectra of **2**, **5**, **9** and **10** show significant chemical shifts differences for carbon signals compared to their free ligand compounds. The most important feature of these ^{13}C NMR spectra is the up-field shift (ca. 4 – 15 ppm, see experimental section) of the C=S unit in these complexes indicating thione-sulphur coordination.

In ^{207}Pb NMR spectral data of the metal complexes (see experimental section), the broad variation in chemical shifts makes it rather difficult to assign and discuss solution structures of these complexes. Majority of the complexes do not exhibit signals at room temperature. Morover the signals have low intensity. This can be attributed to a different degree of dissociation of these complexes in the highly polar solvent as is also evident from ^1H, ^1H DOSY and ^{13}C NMR spectra. Another experiment was also performed with pure lead nitrate solution. A sharp signal for Pb was observed which upon addition of ligand solution broadens and ultimately disappear.

Conclusion:

Ten novel lead(II) complexes in sulphuriched environment have been structurally characterized. Majority of them have hemidirected environment around lead atoms with coordination numbers in the range 4 – 8. The X-ray crystallography further revealed that most of them have extended structures (ID polymeric chains, double chains or sheet like structures). Complex 2a has a B–H···Pb interaction which makes it an unique example in the chemistry of lead with dipodal boron centred soft ligands. All the complexes are almost insoluble in common organic solvents except dmf or dmso, however in these high polar solvents most of them exhibit dissociation. We have also observed that despite of equal opportunity of hard and soft donor sites in the ligands **1** – **10**, the lead ions exhibit affinity only for sulphur donor sites in complexes **2**, **3**, **4** and **6** while in all other cases it coordinates both nitrogen and sulphur donor sites simultaneously.
'Photophysics to come'

Experimental work

All the solvents used during this work were dried and distilled before use. 2-mercaptobenzimidazole(L^3) , 2-mercapto-5-methylbenzimidazole(L^4), 3-mercapto-1,2,4-triazole (L^5H), 3-mercapto-4-methyl-1,2,4-triazole (L^6), 2-mercapto-1,3,4-thiadiazole (L^7H), 2-mercapto-5-methyl-1,3,4-thiadiazole (L^8H), 5-mercapto-1-methyltetrazole (L^9H), 2-mercapto-4-phenyltetrazole ($L^{10}H$) and $Pb(NO_3)_2$ were procured from Alfa Aesar, Sigma Aldrich or Acros Organic and used without further purification. Tripodal boron substituted ligands (L^1) and dipodal boron substituted ligand (L^2) were synthesised according to literature procedures.[18] NMR spectra were recorded on Bruker Avance 300, Bruker DRX 500 or Bruker Avance 500 spectrometers and the chemical shifts of ^1H NMR and ^{13}C NMR were referenced to the residual proton (^1H) or the carbon signals of the deuterated solvents and are reported in ppm. Elemental analyses were performed using a EuroEA Elemental Analyser. Melting points were determined using a Büchi B 545 melting point apparatus and are uncorrected. All operations were carried out in inert atmosphere of nitrogen using Schlenk and glove box techniques.

*Syntheses of complexes **1-2***

Ligand (L^1/L^2) 0.720 mmol and lead(II) nitrate (0.360 mmol) were dissolved and stirred separately in 20 mL of THF and methanol, respectively. The solution of ligand was slowly added to that of lead(II) nitrate solution under N_2 atmosphere. The resulting solution was stirred at room temperature for 2 – 3 h and then filtered. The volume of the sample was reduced under vacuum. Yellow coloured solids were obtained, which were washed with small amount of THF, methanol, then dried.

$[PbL^1_2]$ ***1*:** Crystals suitable for diffraction were obtained by slow diffusion of n-pentane into 1-methyl-2-pyrrolidinone solution of the complex *$[Pb(L^1)_2(L^7H)_2L']$* ***1a***; Yield 76 %; m.p. 236 – 239 °C (with decomposition); Anal. calcd. for $C_6H_4BN_6PbS_6$ (found): C 12.63 (12.85), H 0.71 (1.04), N 14.73 (14.75), S 33.72 (34.90); ^1H NMR (dmf-d7) δ = 8.07 (s, 6H, HC=N), ^1H NMR (dmso-d6) δ = 8.54 (s, 6H, HC=N), ^{13}C NMR (dmso-d6) δ = 189.2 (C=S), 144.4 (C=N)
Free ligand compound (L^1) = (d mso-d6) δ = 8.57 (s, 3H, HC=N); ^{13}C NMR (dmso-d6) δ = 189.3 (C=S), 145.4 (C=N); ^{11}B NMR (dmso-d6) δ = –2.36 ppm

$[PbL^2_2]$ ***2*:** Crystals were obtained by slow evaporation of DMF solution of complex **2**; Yield 81 %; m.p. 247 °C (with decomposition); Anal. calcd. for $C_{16}H_{20}B_2N_4PbS_8$ (found): C 20.00 (20.72), H 2.10 (1.75), N 5.83 (5.98); ^1H NMR (dmso-d6) δ = 6.34 (s, 4H, HC=N), not observed (BH_2), 2.13 (s, 12H, H_3C); ^{13}C NMR (dmso-d6) δ = 175.9 (C=S), 149.6 (C=N), 109.8 (C-CH_3), 17.0 (H_3C); ^{11}B NMR (dmso-d6) δ = –14.1, -1.76 ppm; ^{207}Pb NMR (dmf-d7) δ = –461 ppm
Free ligand compound (L^2): ^1H NMR (dmso-d6), δ = 6.22, (s, 2H, HC-ring), 3.17 (br, 2, BH_2), 2.37 (s, 6H, CH_3); ^{13}C NMR (dmso-d6), δ = 189.9 (C=S), 147.7 (C=N), 105.4 (C–CH_3), 19.2 (CH_3); ^{11}BNMR = –11.25 ppm

*Syntheses of complexes **3** – **8**:*

Solution of the heterocyclic ligands L^3, L^4, L^5H, L^6, L^9H and $L^{10}H$ (4.00 mmol) in 10 mL of THF was added drop-wise to a solution of lead(II) nitrate (2.00 mmol) in 10 mL of DMF, stirred at room temperature and finally heated to 90 °C for 3 – 4 h. The resulting clear solutions were concentrated under vacuum resulting precipitation. The precipitates were filtered off, washed with small amounts of THF, then with acetone and finally dried.

$[PbL^3_2(NO_3)_2]$ **3**: Single crystals were obtained by slow cooling of a warm solution of complex **3** in DMF/methanol; Yield 78 %; m.p. 190 °C; Anal. calcd. for $C_{14}H_{12}N_6O_6PbS_2$ (found): C 26.62 (27.09), H 1.91 (1.90), N 13.31 (13.15), S 10.15 (10.69); ^1H NMR (dmso-d6) δ = 11.52 (s, 4, NH), 7.11 – 7.16 (m, 8H, H_5C_6-ring); ^{13}C NMR (dmso-d6) δ = 168.5 (C7), 132.7 (C1; C6), 122.7 (C2; C5), 109.8 (C3; C4).
Free ligand compound (L^3) = ^1H NMR (dmso-d6) δ = 12.52 (s, 1, NH), 7.09 – 7.16 (m, 4H, H_5C_6-ring); ^{13}C NMR (dmso-d6) δ = 168.6 (C7), 132.7 (C1; C6), 122.8 (C2; C5), 110.0 (C3; C4).

$[PbL^4_3(\mu\text{-}L^4)(NO_3)_2]$ ***4*** : Single crystals were obtained by slowly cooling of a warm solution of complex **4** in DMF/THF; Yield 65 %; m.p. 226 – 229 °C (with decomposition); Anal. calcd. for $C_{72}H_{80}N_{20}O_{16}Pb_2S_8$ (found): C 40.18 (39.65), H 3.75 (3.80), N 13.01 (13.01), S 11.92 (11.99); ^1H NMR (dmso-d6) δ = 12.40 (s, 2, NH), 6.91 – 7.06 (m, 4H, H_5C_6-ring), 2.33 (s, 3H, CH_3); ^{13}C NMR (dmso-d6) δ = ^{13}C NMR (dmso-d6) δ = 168.2 (C8), 133.0 (C1), 132.0 (C6), 130.7 (C2), 123.5 (C5), 110.1(C3), 109.6 (C4), 21.4 (C7);
Free ligand compound (L^4) = ^1H NMR (dmso-d6) δ = 12.40 (s, 2, NH), 6.92 – 7.06 (m, 4H, H_5C_6-ring), 2.33 (s, 3H, CH_3); ^{13}C NMR (dmso-d6) δ = 168.2 (C8), 132.7 (C1), 132.0 (C6), 130.6 (C2), 123.5 (C5), 110.1 (C3), 109.6 (C4), 21.4 (C7).

[Pb(L^5)(L^{5}H)$_2$(NO$_3$)(H$_2$O)] **5**: Single crystals were obtained by cooling the solution of complex **5** in DMF/THF in refrigerator; Yield 74 %; m.p. 207 – 210 °C (with decomposition); Anal. calcd. for $C_6H_5N_{10}O_4PbS_3$ (found): C 12.33 (12.50), H 0.86 (1.49), N 23.96 (24.10), S 16.46 (16.88); ^{1}H NMR (dmso-d6) δ = 14.12 (br, 2H, NH), 8.56 (s, 1H, HC═N); ^{13}C NMR = 156.6 (C═S), 147.0 (C═N)
Free ligand compound (L^{5}H) = ^{1}H NMR (dmso-d6) δ = 13.38 (br, 2H, NH), 8.25 (s, 1H, HC═N); DMSO-d6) δ = 166.0 (C═S), 141.0 (C═N)

[PbL$^6_4$(NO$_3$)$_2$] **6:** Single crystals were obtained by cooling the solution of complex **6** in DMF/THF in refrigerator; Yield 87 %; m.p. 140 – 142 °C (with decomposition); Anal. calcd. for $C_{12}H_{20}N_{14}O_6PbS_4$ (found): C 18.20 (17.94), H 2.55 (2.60), N 24.76 (23.92); S 16.20 (16.64); ^{1}H NMR (dmso-d6) δ = 13.66 (br, 4H, NH), 8.42 (s, 4H, CH), 3.43 (s, 12H, H$_3$C-); ^{13}C NMR (dmso-d6) δ = 166.6 (C═S), 143.3 (C═N), 31.7 (H$_3$C)
Free ligand compound (L^6) = ^{1}H NMR (dmso-d6) δ C= 13.63 (s, 1H, NH) 8.39 (s, 1H, HC═N), 3.43 (s, 3H, H$_3$C-); ^{13}C NMR (dmso-d6) δ = 166.7 (C═S), 143.1 (C═N), 31.7 (H$_3$C)

[PbL$^9_2$H]$_n$ ***9***: Single crystals were obtained by low evaporation of the solution of complex **9** in DMF/THF; Yield 87 %; m.p. 203 – 206 °C (with decomposition); Anal. calcd. for $C_4H_6N_8PbS_2$ (found): C 10.98 (11.01), H 1.38 (1.32), N 25.61 (25.09); ^{1}H NMR (dmso-d6) δ = 3.76 (s, 3H, H$_3$C-), ^{13}C NMR (dmso-d6) δ = 161.7 (C═S), 33.5 (H$_3$C); ^{207}Pb NMR (dmf-d7) δ = –2628 ppm;
Free ligand compound L^{9}H = ^{1}H NMR (dmso-d6) δ = 3.78 (s, 3H, H$_3$C-), ^{13}C NMR (dmso-d6) δ = 164.6 (C═S), 33.8 (H$_3$C)

[PbL$^{10}_2$H]$_n$ ***10***: Single crystals were obtained by slow evaporation of a solution of complex **10** in DMF/THF; Yield 87 %; m.p. 266 – 269 °C (with decomposition); Anal. calcd. for $C_{18}H_{12}N_2PbS_4$ (found): C 36.53 (37.35), H 2.10 (2.57), N 4.73 (6.05), S 21.67 (21.69); ^{1}H NMR (dmso-d6) δ = 7.83 – 7.86 (dd, 2H, C2H, C6H), 7.23 – 7.37 (m, 3H, C3H–C5H), overlapped in aryl region (CH–thiazole ring); ^{13}C NMR (dmso-d6) δ = not measured due to limited solubility;
Free ligand compound (L^{10}H):^{1}H NMR (dmso-d6) δ = 13.66 (br, 1H, NH), 7.75 – 7.77(dd, 2H, C2H, C6H), 7.40 – 7.48(m, 3H, C3H–C5H), 7.32 (CH–thiazole ring).

Synthesis of complexes 7 & 8
The **7** and **8** were synthesised by the branched tube method: 1.0 mmol of heterocyclic ligand (L^{7}H or L^{8}H) and 0.5 mmol of lead(II) nitrate were placed in a separate arm of a branched tube. Methanol was then carefully added under N$_2$ atmosphere to fill both arms. The tube was stoppered and the ligand-containing arm was immersed in a bath held at 55 ℃, while the other was left at room temperature. After 2 days, crystals were formed in the room temperature arm. These crystals were then filtered off, washed with acetone, dried and stored under an atmosphere of N$_2$.

[Pb(L^7)$_2$(L^{7}H)(CH$_3$OH)]$_n$ *7*: Single crystals for this complex were obtained by branch tube method, Yield 76 %; m.p. 196 – 198 °C (with decomposition); Anal. calcd. for $C_9H_7N_8OPb_2S_8$ (found): C 11.83 (10.72), H 0.77 (0.76), N 12.26 (12.69), S 28.06 (27.38); ^{1}H NMR (dmso-d6) δ = 8.91 (s, 4H, HC═N); ^{13}C NMR (dmso-d6) δ = not observed (C═S), 150.3 (C═N); ^{207}Pb NMR (dmf-d7) δ = –2811 ppm
Free ligand compound (L^{7}H) = ^{1}H NMR (dmso-d6) δ = 14.63 (s, 1H, NH), 8.87 (s, 1H, HC═N); ^{13}C NMR (dmso-d6) δ = 188.2 (C═S), 150.1 (C═N)
[PbL$^8_2$H(NO$_3$)$_2$]$_n$ ***8***: Single crystals for this complex were obtained by branch tube method; Yield 69 %; m.p. 238 – 240 °C (with decomposition); Anal. calcd. for $C_{12}H_{16}N_8S_8Pb$ (found): C 19.58 (19.31), H 2.19 (1.97), N 15.22 (13.93), S 34.85 (32.77); ^{1}H NMR (dmso-d6) δ = 2.55 (s, 3H, CH$_3$), ^{13}C NMR (dmso-d6) δ = 190.1 (C═S), 154.3 (C═N), 16.4 (CH$_3$); ^{207}Pb NMR (dmf-d7) δ = –2585 ppm
Free ligand compound (L^{8}H) = ^{1}H NMR (dmso-d6) δ = 2.45 (s, 3H, CH$_3$), ^{13}C NMR (dmso-d6) δ = 189.2 (C═S), 160.1 (C═N), 16.2 (CH$_3$)

Luminescence activity

For luminescence activity, compounds are under measurements in co-operation with Dr. Uwe Monkowius, Linz, Austria.

X-ray Crystallographic Analyses. X-ray diffraction data were collected from single crystals of **1a**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9** and **10**. Crystals suitable for X-ray diffraction were picked under inert paratone oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a cold gas stream. The data for **3**, **4**, **6** and **7** were collected on a Bruker Nonius Kappa CCD diffractometer with radiation source Mo-K$_\alpha$, while the data for compounds **1a** (with Mo--K$_\alpha$ radiation source) and **5** (with Cu-K$_\alpha$ radiation source) were collected using Bruker AXS Kappa with APEX II. Similarly crystal data of complexes **2** **8**, **9** and **10** (all with Mo-K$_\alpha$ except **2** with Cu radiaton source) were collected using Super Nova, Dual, atlas diffractometer. A summary of data collections and structure refinements is reported in Tables 7 and 8. The structures were solved by direct methods and refined by full-matrix least squares cycles (programs SHELXS-97 or SHELXL-97)[36] and Olex2.[37]

Table 7. X-ray crystallographic data for compounds **1** – **5**

Compound	**1a**	**2**	**3**	**4**	**5**
Empirical formula	$C_{13}H_{14}BN_9OPbS_8$	$C_{16}H_{20}B_2N_4PbS_8$	$C_{14}H_{12}N_6O_6PbS_2$	$C_{72}H_{80}N_{20}O_{16}Pb_2S_8$	$C_2H_4N_4O_4PbS$
M_r	786.81	753.65	631.61	2152.42	387.34
T (K)	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K
Crystal system	triclinic	triclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pccn*	*C*2/*c*	*Pbcn*
a (Å)	10.1258(9)	9.93379(19)	12.354(5)	25.8252(2)	17.9942(7)
b (Å)	11.5049(11)	12.2627(3)	16.814(6)	20.7570(2)	6.3605(2)
c (Å)	12.7990(19)	12.4372(3)	9.0073(18)	15.8960(2)	13.1333(5)
α (°)	111.827(6)	65.316(2)	90	90	90
β (°)	108.210(6)	83.1389(17)	90	90.0600(6)	90
γ (°)	95.805(5)	66.8959(19)	90	90	90
Z	2	2	4	4	8
V (Å^3)	1274.3(3)	1264.40(5)	1870.9(11)	8521.10(15)	1503.13(9)
F(000)	756	728	1200	4288	1392
Cryst. size (mm)	0.38 x 0.24 x 0.14	0.35 × 0.21 × 0.15	0.30 x 0.09 x 0.03	0.26 x 0.14 x 0.10	0.33 x 0.05 x 0.03
Refl. measure*d*	87623	74818	19912	163344	27266
Unique refl. (R_{int})	7414(0.0263)	7372(0.0459)	2139(0.0662)	12428(0.077)	1418(0.0453)
No. of param.	293	300	132	566	122
R ($I > 2\sigma(I)$)	0.0150	0.0146	0.0270	0.0319	0.0195
R_w (all refl.)	0.0354	0.0327	0.0515	0.0825	0.0553
Goodness-of-fit	1.047	1.085	1.016	1.039	1.195
ρmax/min (e Å^{-3})	1.333/-1.166	0.52/-0.70	2.454/-0.681	1.777/-0.661	1.357/-0.840

Table 8. X-ray crystallographic data for compounds **6** – **10**

Compound	**6**	**7**	**8**	**9**	**10**
Empirical formula	$C_{12}H_{20}N_{14}O_6PbS_4$	$C_9H_7N_8OPb_2S_8$	$C_6H_6N_4S_4Pb$	$C_4H_6N_8PbS_2$	$C_{18}H_{12}N_2PbS_4$
M_r	791.85	914.09	469.58	437.48	591.73
T (K)	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K
Crystal system	tetragonal	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$I\bar{4}$	$P2_1$	$P2_1/c$	$P2_1/n$	*Pbca*
a (Å)	10.5430(11)	4.05170(10)	13.3192(4)	8.94447(19)	19.9345(3)
b (Å)	10.5430(11)	24.3412(7)	11.7420(4)	4.92209(8)	7.34785(13)
c (Å)	11.7670(6)	10.7681(4)	7.72600(19)	23.5863(5)	24.3982(4)
α (°)	90	90	90	90	90
β (°)	90	93.9769(17)	93.931(2)	92.5552(18)	90
γ (°)	90	90	90	90	90
Z	2	2	4	4	8
V (Å^3)	1308.0(3)	1059.43(6)	1205.46(6)	1037.36(4)	3573.75(11)
F(000)	768	834	864	800	2240
Cryst. size (mm)	0.30 x 0.28 x 0.28	0.20 x 0.03 x 0.03	0.20 × 0.06 × 0.02	0.49 × 0.09 × 0.03	0.18 × 0.05 × 0.04
Refl. measure*d*	13152	22633	44530	77856	31790
Unique refl. (R_{int})	1804(0.0373)	4808(0.097)	4649(0.0392)	1819(0.0894)	3150(0.0370)
No. of param.	105	254	139	138	226
R ($I > 2\sigma(I)$)	0.0130	0.0195	0.0404	0.0357	0.0208
R_w (all refl.)	0.0284	0.0550	0.1131	0.0943	0.0444
Goodness-of-fit	0.965	1.013	1.095	1.121	1.187
ρmax/min(e Å^{-3})	0.780/-0.739	2.178/-2.082	1.48/-1.80	3.32/-3.08	0.78/-0.68

Notes and references

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Manuscript-4

Cite this: DOI: 10.1039/x0xx00000x

Received 00th XXXX,
Accepted 00th XXXX

DOI: 10.1039/x0xx00000x

www.rsc.org/

Synthesis, structural and photo-physical studies of bismuth(III) complexes with a Janus scorpionate and co-ligands

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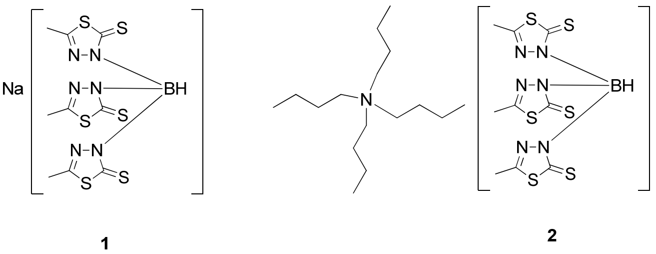
Some novel complexes of bismuth(III) with the Janus scorpionate ligand $[HB(mtda^{Me})_3]^-$ ($mtda^{Me}$ = 2-mercapto-5-methyl-1,3,4-thiadiazolyl) were synthesized. $Na[HB(mtda^{Me})_3]$ (**1**) was reacted with BiX_3 (X = Cl, I, NO_3) in molar ratio 2:1 to afford the bismuth complexes $[\{HB(mtda^{Me})_3\}_2BiCl]$ (**3**), $Na[\{HB(mtda^{Me})_3\}_2BiI_2]$ (**4**) and $[\{HB(mtda^{Me})_3\}_2Bi(NO_3)]_n$ (**5**). Two mixed complexes $[\{HB(mtda^{Me})_3\}Bi(phen)Cl_2]$ (**6**) and$[\{HB(mtda^{Me})_3\}Bi(bipy)Cl_2]$ (**7**) were obtained using Janus scorpionate as primary ligand in the presence of 1,10-phenanthroline and 2,2′-bipyridyl, respectively, as co-ligands in 1:1 ratio. The obtained complexes were characterized by ^1H, ^{13}C and diffusion NMR (DOSY), elemental analyses and mass spectrometry. Structures of the compounds $NBu_4[HB(mtda^{Me})_3]$ (**2**), **3**, **4**, **5**, **6** and **7** were determined by single crystal X-ray diffraction. The molecular dynamic processes and methyl group exchange in complex **3** was also studied by variable temperature NMR measurements. All bismuth complexes, except the polymeric **5**, are monomeric. Complexes **6** and **7** exhibit (B)H···Bi interactions of 2.76(3) and 2.71(2) Å length, respectively. Compounds **2**, **3**, **4**, **5**, **6** and **7** were screened for their luminescent activity. >>>to come<<<.

Introduction

Since the first synthesis of soft scorpionate ligands namely (hydrotris(methimazolyl)borate (Tm)[1] a large number of contributions in this research area have appeared in the literature. This is because these soft ligands have been used successfully for stabilization of low-valent, electron-rich metal ions.[2-3] Such complexes also demonstrate susceptibility for oxidation and thus give access to unusual oxidation states. Furthermore such soft ligands also exert weaker field strengths compared to hard ligands as has been established for the examples $[Fe(Tm^{Me})_2]$[4] and $[Fe(Tp^{Me})_2]$.[5] Compared to their hard analogues, these ligands have twisting and flexibility capabilities to accommodate metal ions of larger ionic radii and show variable coordination behaviour including monodentate (κ^1-*S*), bidentate (κ^2-*S,S'*or κ^2-*S,H*) and tridentate (κ^3-*S,S',S''*or κ^3-*S,S',H*) binding modes.[6-7] Janus scorpionates are a subclass of soft scorpionate ligands with a simultaneous ability to coordinate through hard and soft donor sites; the term is borrowed from Roman mythology, where Janus, god of gates and doors, is a bifrons representing this disambiguation.[8-9] These ligands are known as hybrid of Trofimenko's tris(pyrazolyl)borates[10-11] and Reglinski's tris(mercaptoimidazolyl)borates[1] and are also closely related to Bailey's [12] and Marchiò's ambidentate thioxotriazolylborates.[13]



Scheme 1. Sodium and tetra-*n*-butyl derivatives of the Janus scorpionate ligand $[HB(mtda^{Me})_3]^-$ (**1**,**2**)

The anion $[HB(mtda^{Me})_3]^-$ ($mtda^{Me}$ = 2-mercapto-5-methyl-1,3,4-thiadiazolyl) is a typical Janus scorpionate ligand with conjoined (*N,N,N*-) and (*S,S,S*-) donor faces; it was first reported by Silva and co-workers in 2008 (Scheme 1).[9] They have described its polymeric alkali metal and monomeric iron complexes. The ligand is referred to as second generation Janus scorpionate ligand and differs from first generation ligands only by methyl substitution at position 5 of the heterocycle.

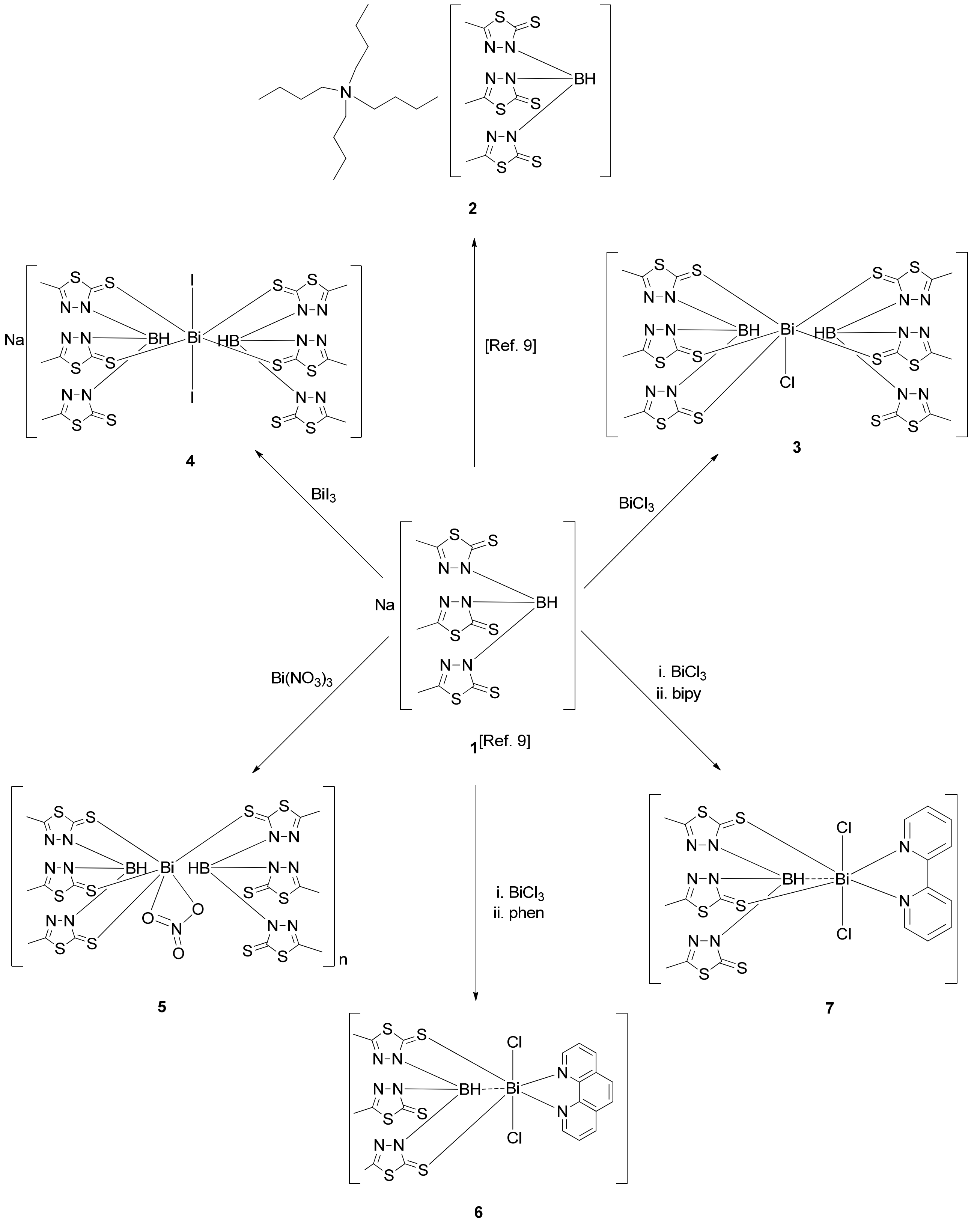
Recently we have reported a novel Janus scorpionate ligand along with its bismuth complexes.[14] In continuation of our growing interest in bismuth chemistry based on soft scorpionates, we present here bismuth complexes of $[HB(mtda^{Me})_3]^-$. For this purpose, we have utilized different bismuth sources such as $BiCl_3$, $Bi(NO_3)_3$ and BiI_3 to explore the effect of halide and halide free anions on the coordination geometry of the bismuth complexes. The idea was to see, whether these ions (with variable sizes and nature) permit Janus scorpionate ligands to adopt the κ^3-coordination mode, consequently resulting in cationic sandwich complexes of bismuth. Furthermore, the co-ligands (1,10-phenanthroline and 2,2′-bipyridyl) were employed to prepare mixed complexes of bismuth while keeping $[HB(mtda^{Me})_3]^-$ as primary ligand. Mixed complexes involving 2,2′-bipyridine and 1,10-phenanthroline have found considerable attention because of their favourable absorption and excited state properties.[15] However, such exploration towards bismuth has, despite strong spin-orbit coupling constant and less expensive nature, been less explored. This contribution provides besides the structural and bonding aspects of several novel bismuth complexes also information on their photo-physical properties.

Results and discussion

Recently we have reported bismuth complexes with a novel Janus scorpionate ligand namely $[Bi(Tr^{Me})Cl(\mu\text{-}Cl)_2]_2$ and $[Bi(Tr^{Me})Cl_2(\mu\text{-}Cl)]_n$ (Tr^{Me} = $[HBL_3]^-$ with L = 3-mercapto-4-methyl-1,2,4-triazole).[14] Extending the same methodology we present here the synthesis of some bismuth complexes with the known second generation Janus scorpionate ligand $[HB(mtda^{Me})_3]^-$ ($mtda^{Me}$ = 2-mercapto-5-methyl-1,3,4-thiadiazolyl). Syntheses of its sodium and tetrabutylammonium salts, $Na[HB(mtda^{Me})_3]$ (**1**) and $NBu_4[HB(mtda^{Me})_3]$ (**2**), were carried out according to literature protocols.[9] Additionally we report here the crystal structure of $NBu_4[HB(mtda^{Me})_3]$ (**2**). The tetrabutylammonium derivative was synthesized due to its favourable solubility properties and use during luminescence measurements. However, after various experiments $Na[HB(mtda^{Me})_3]$ (**1**) was found to be a more advantageous reagent for the synthesis of bismuth complexes (Scheme 2), because $NBu_4[HB(mtda^{Me})_3]$ (**2**) resulted in products which were difficult to purify and led to smaller yields. The same observation was made during the synthesis of $[Bi(Tr^{Me})Cl(\mu\text{-}Cl)_2]_2$.[14] Different bismuth salts such as $BiCl_3$, BiI_3 and the halide free $Bi(NO_3)_3$ were reacted in an M:L ratio of 1:2 with the intention to achieve octahedral geometry (Scheme 2). Bismuth complexes **3** – **5** are coloured solids (**3** red, **4** orange, **5** red). Compared to other bismuth complexes, **3** is better soluble in dichloromethane, chloroform, acetonitrile, tetrahydrofuran and methanol. However, in highly polar solvents like dmf and dmso it dissociates. Compound **4** does not dissociate in dmf and dmso, while complex **5** dissociates in dmso but does not dissociate in dmf (see section "Solution NMR studies"). The synthetic chemistry was further extended with co-ligands such as 1,10-phenanthroline and 2,2'-bipyridyl (Scheme 2) to see the effect on (a) structural aspects of bismuth geometries upon introduction of these neutral bidentate ligands, (b) luminescence properties of these complexes due to their inherently conjugated nature. Complexes **6** and **7** were synthesized at room temperature and are also coloured (**6** yellow, **7** orange red) solids. They have poor solubilities in common organic solvents. In dmf and dmso, they lose their identity as mixed complexes, instead complexation occurs only between co-ligands and bismuth (see section "Solution NMR studies"). After workup, the yields of all complexes **3** – **7** range between 55 – 73 %.

Solid state characterization

Single crystal X-ray crystallography revealed molecular structures of the bismuth complexes with the compositions $[\{HB(mtda^{Me})_3\}_2BiCl]\cdot 2CH_3CN$ (**3**), $Na[\{HB(mtda^{Me})_3\}_2BiI_2]\cdot CH_3CN\cdot H_2O$ (**4**) $[\{HB(mtda^{Me})_3\}_2Bi(NO_3)]_n\cdot CH_3OH$ (**5**), $[\{HB(mtda^{Me})_3\}Bi(phen)Cl_2]\cdot 2.1CHCl_3$ and (**6**) $[\{HB(mtda^{Me})_3\}Bi(bipy)Cl_2]\cdot CH_3CN$ (**7**). Selected bond lengths and angles are presented in Tables 1 – 4 and their molecular structures are shown in Figures1 – 6.



Scheme-2: Synthesis of bismuth complexes **3** – **7**

The ionic molecular structure of **2** is shown in Figure 1. Important bond lengths and angles are listed in Table 1 and are within the normal range. The bond lengths and angles can be compared with the closely related salts Na[HB(mtda^{Me})$_3$], K[HB(mtda^{Me})$_3$] and (K,Na)[HB(mtda^{Me})$_3$], whose molecular structures have been earlier reported.[9] The N–B–N angles range from 106.5(2) to 110.5(2)°, i.e. they slightly deviate from regular tetrahedral angles.

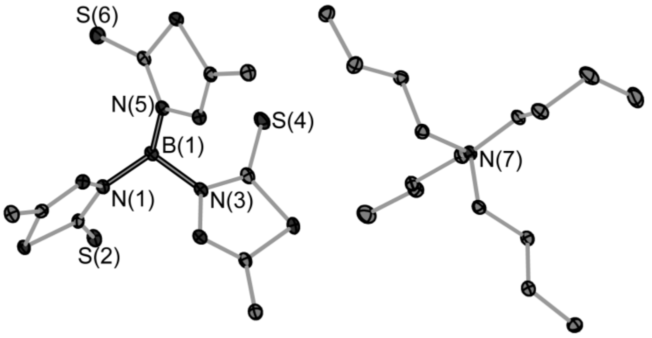


Figure 1. Molecular structure of NBu$_4$[HB(mtda^{Me})$_3$] (**2**). Hydrogen atoms and solvent molecules have been omitted for clarity, displacement ellipsoids are drawn at the 30% level.

Table 1. Selected bond lengths [Å] and angles [deg] of compound **2**

C–S (thione)	1.668(2) – 1.676(2)
N(1)–B(1)	1.556(2)
N(3)–B(1)	1.548(2)
N(5)–B(1)	1.561(2)
B(1)–H(1)	1.05(2)
N(1)–B(1)–N(3)	108.3(2)
N(1)–B(1)–N(5)	110.5(2)
N(3)–B(1)–N(5)	106.5(2)

Complex **3** crystallizes in the orthorhombic space group $P2_12_12_1$. Its molecular structure is shown in Figure 2; selected structural parameters are listed in Table 2. Two acetonitrile molecules of the solvent required for crystallization are present in the crystal lattice. The central bismuth atom has a distorted octahedral geometry accomplished by two [HB(mtda^{Me})$_3$]$^-$ ligands with different coordination modes, (κ^3-*S,S',S''*) and (κ^2-*S,S'*). The sixth position is occupied by a chloro ligand. The Bi–S bond lengths for the (κ^3-*S,S',S''*) coordinate ligand cover the range between 2.717(2) and 2.905(2) Å, while for the (κ^2-*S,S'*) coordinate ligand the values are 2.907(2) and 2.978(2) Å. The chloride ligand is terminally bound to the bismuth atom with a distance of 2.586(1) Å and is in agreement with related literature Bi–Cl terminal distances.[16] One B–H units is oriented away from the bismuth, the other one is reasonably orientated toward the bismuth atom, but the resulting H(1) – Bi(1) distance is above 3 Å and not considered as a (B)H···Bi interaction. It is important to mention that the S–Bi–S bond angles involving the ligand with κ^3 mode are close to 90° (range: 85.4(2) – 89.1(2)°) while the S–Bi–S angle involving the κ^2-mode ligand deviates significantly at 117.9°. The Cl–Bi–S (*cis*) angles (Table 2) also show deviations from a regular octahedral arrangement of binding atoms. This distorted octahedral distribution of bond angles indicates the presence of a stereo-chemically active lone pair of electrons at bismuth. The binding situation in complex **3** is thus different to that in the closely related compound [Bi(Tt)$_2$]Cl (Tt = hydrotris(thioxotriazolyl)borate),[12] where both ligands coordinate in a (κ^3-*S,S',S''*) mode resulting in a regular octahedral geometry. The structural parameters can also be compared with our recently reported [Bi(Tr^{Me})Cl(μ-Cl)$_2$]$_2$ (Tr^{Me} is a soft scorpionate based on triazole) as well as with [Tm^{Me}BiCl(μ-Cl)$_2$]$_2$ [17] and [Tm$^{t\text{-}Bu}$BiCl(μ-Cl)$_2$]$_2$[18] (Tm^R is a soft scorpionate based on imidazole units). However, these complexes are dimeric and bridged by chloro ligands.

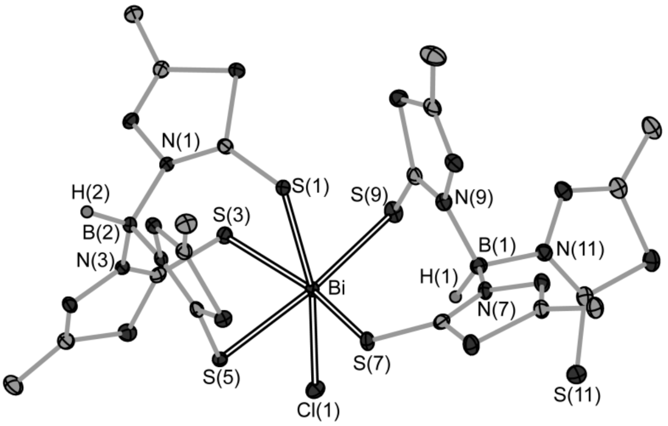


Figure 2. Molecular structure of [{HB(mtda^{Me})$_3$}$_2$BiCl] (**3**) in the crystal. Hydrogen atoms except B–H and solvent molecules have been omitted for clarity, displacement ellipsoids are drawn at the 30% level.

The molecular structure of complex **4a** is shown in Figure 3. The asymmetric complex possesses a crystallographic centre of inversion leading to a disorder of the sodium atom and its coordination sphere, these occupies only every second hard donor side of the complex, whereas the bismuth atom and its coordination sphere shows the appropriate center of inversion symmetry. In contrast to complex **3** it displays only slight deviation from a regular octahedral geometry at bismuth. The bismuth atom binds to four sulphur atoms of two symmetric ligands with (κ^2-*S,S'*) coordination mode and iodo ligands placed *trans* to each other. Important bond lengths and angles are listed in Table 2. The Bi–S bond have lengths of 2.819(2) (S(1)) and 2.859(2) Å (S(3)) and are comparable to those in **3**. The monomeric as well as regular octahedral nature despite of halide presence is contrasting previous reports on [Bi(Tr^{Me})Cl(μ-Cl)$_2$]$_2$,[14] [Bi(Tr^{Me})Cl$_2$(μ-Cl)]$_n$[14] [Tm^{Me}BiCl-(μ-Cl)$_2$]$_2$,[17] [Tm$^{t\text{-}Bu}$BiCl(μ-Cl)$_2$]$_2$,[18] (where Tr^{Me} and Tm^{Me} are soft scorpionate ligands based on imidazole and triazole units). The (κ^2-*S,S'*) coordination mode of the ligand in complex **4a** also differs from that of the related bismuth complex [Bi(κ^3-Tm^{Me})(κ^1-Tm^{Me})I].[19] Spicer et al. reported that a regular S$_6$ coordination sphere would be unattainable in bismuth complexes in the presence of halide ions; they pointed out that by the presence of halide ions the balance of orbital energies is sufficiently changed to allow a directional lone pair to be observed.[19,20] Furthermore, the sodium ion is coordinated – as expected by the HSAB concept – to the three hard nitrogen donor sites of one ligand with coordination mode (κ3-*N,N',N''*). Its octahedral coordination environment is completed by one methanol and two acetonitrile ligands. The Na–N distances to [HB(mtda^{Me})$_3$]$^-$ are in the range between 2.450(3) and 2.677(3) Å; this is in agreement with the related structure of Na[HB(mtda^{Me})$_3$].[9] There are disordered acetonitrile and water molecules (ratio 77:23) on hard donor site of second ligand. The water molecule makes hydrogen bonding contacts with N(4A) of the ligand at a distance of 2.23Å and with acetonitrile N(7A) at a distance of 2.22 Å. So in essence the most salient features of the molecular structure of **4** in the light of previous results are the almost octahedral geometry at bismuth and the real Janus-type behaviour of the ligand [HB(mtda^{Me})$_3$]$^-$ towards Bi on the soft and Na on hard side. In this sense it is related to reports of Reglinski et al.[17] on the unusual salt [Tm$_2$Bi]-[Tp$_2$Na] (Tp = hydrotris(pyrazolyl)borate), with regular octahedral coordination geometry at bismuth, but with the difference that only one sort of ligand in **4** is capable of taking over the role of two different in this case.

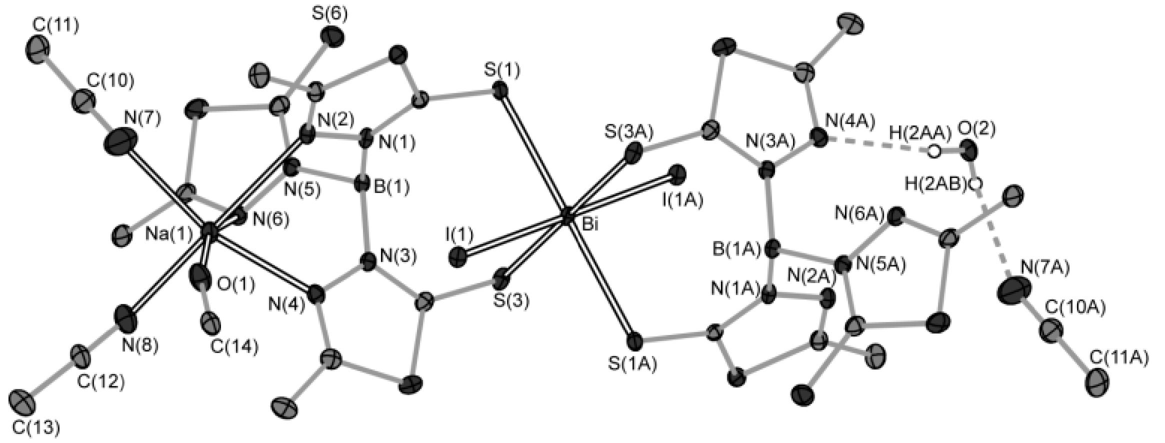


Figure 3. Molecular structure of [{[(CH$_3$CN)$_2$(CH$_3$OH)Na]μ-[Naκ^3-*N,N′,N″*:Biκ^2-*S,S′*-{HB(mtda^{Me})$_3$]}$_2$BiI$_2$]·CH$_3$CN.H$_2$O (**4a**) in the crystal. Hydrogen atoms have been omitted for clarity, displacement ellipsoids are drawn at the 30% level. CH$_3$CN and H$_2$O are included to show H-bonding contacts.

Table 2. Selected bond lengths [Å] and angles [deg] of complexes **3** and **4**

3		**4**	
Bi–S(1)	2.905(2)	Bi–S(1)	2.819(2)
Bi–S(3)	2.749(2)	Bi–S(3)	2.859(2)
Bi–S(5)	2.717(2)	Bi–I(1)	3.002(1)
Bi–S(7)	2.907(2)	Na(1)–O(1)	2.309(4)
Bi–S(9)	2.978(2)	Na(1)–N(2)	2.677(3)
Bi–Cl(1)	2.586(1)	Na(1)–N(4)	2.450(3)
S–Bi–S (*cis*)	75.2(1)–117.5(2)	Na(1)–N(6)	2.599(3)
S–Bi–S (*trans*)	159.3(2)–167.1(2)	Na(1)–N(7)	2.440(4)
Cl–Bi–S (*cis*)	78.6(2) – 98.4(2)	Na(1)–N(8)	2.394(6)
Cl–Bi–S(1) (*trans*)	167.8(2)	S(1)–Bi–S(1A)	180.0
		S(1)–Bi–S(3)	88.1(2)
		S(3)–Bi–S(3A)	180.0
		S(1)–Bi–S(3A)	91.9(2)
		I(1)–Bi–I(1A)	180.0
		S(3)–Bi–I(1)	95.8(2)
		S(1)–Bi–I(1)	93.5(2)

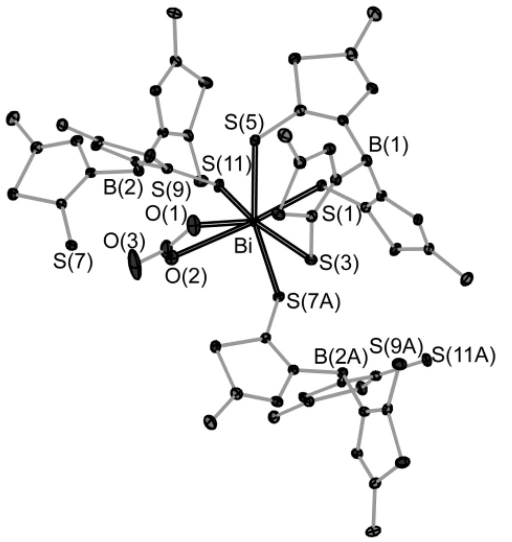
Complex **5** crystallizes in the monoclinic space group $P2_1c$. Its molecular structure is shown in Figure 4. This complex is of polymeric nature and is different in constitution compared to the related reported structures of [Bi(Tr^{Et,Me})]NO$_3$[21], [Bi(Tr^{Ph,Me})]NO$_3$[22] and [Bi(Tr^{Ph,Ph})]NO$_3$.[23]

These three bismuth complexes are monomeric and show regular octahedral geometry with the nitrate being a non-coordinate counter ion. The Bi–S bond lengths (Table 3) (except Bi–S(11) 2.86 Å, slightly longer) lie within the range found in the CCSD data base for bismuth complexes with soft scorpionate ligands.[24] Furthermore, the coordination number around each bismuth ion is 7 with three [HB(mtda^{Me})$_3$]$^-$ ligands surrounding it. One of them coordinate is bound in the tridentate mode (κ3-*S,S',S''*), while the other two coordinate in (κ2-*S,S*') modes and of these uses its remaining sulphur atom to bind the next bismuth atom resulting a polymeric chain. Additionally, a nitrate ion also coordinates to the bismuth atom in a bidentate manner with distances Bi–O(1) 2.708(3) and Bi–O(2) 2.747(2) Å. Selected bond angles are listed in Table 3; they reveal a distorted geometry for this complex.

The molecular structure of complex **6** is shown in Figure 5. This complex crystallizes with disordered molecules of chloroform in the unit cell. Complex **6** is monomeric and the bismuth atom is chelated by a tridentate Janus scorpionate ligand (κ3-*H,S,S'*) ligand, and a bidentate co-ligand (phenanthroline). Two chloro ligands complete the coordination sphere resulting in coordination number 7. Some notable examples of mixed complexes with scorpionate ligands includes *cis*-L$_2$Ru(Z)$^{n+}$ [(L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen), Z= bis-coordinated scorpionate)[15] [YCl$_2$(Tp^{Me2})(phen)] (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate).[25] To best of our knowledge, complex **6** is the first mixed complex of bismuth based on soft scorpionate ligands. The bond lengths of Bi–S (range 2.943(2) – 2.966(2) Å) and Bi–Cl (range 2.558(2) – 2.613(2) Å) compares well with those of complex **3**. A (B)H···Bi interaction at 2.76(3) Å is also present; it can be compared with literature values reported for $[BiBb_2Cl]$[26], $[Tm^{Ph}]_2Pb$[27] and $[Tl(Bm^{Me})]_x$[28] complexes. The structural parameters can also be compared with a mixed complex $[Bi(S_2CNC_5H_{10})_2(NO_3)(phen)(S_2CNC_5H_{10})$ = pyrrolinedithiocarbamate)] having a sulphur donor ligand and phenanthroline ligand.[29]

Table 3. Selected bond lengths [Å] and angles [deg] of complex **5**

Bi–S(1)	2.693(2)
Bi–S(3)	2.771(2)
Bi–S(5)	2.803(2)
Bi–S(7)	2.801(2)
Bi–S(11)	2.866(2)
Bi–O(1)	2.708(3)
Bi–O(2)	2.747(2)
S–Bi–S (*cis*)	72.7(1) – 94.3(2)
S–Bi–S (*trans*)	161.5(2) – 163.3(2)
O–Bi–S (*cis*)	72.4(2) – 121.4(2)
O–Bi–S(1) (*trans*)	153.0(2) – 154.9(2)
O(1)–Bi–O(2)	46.9(2)



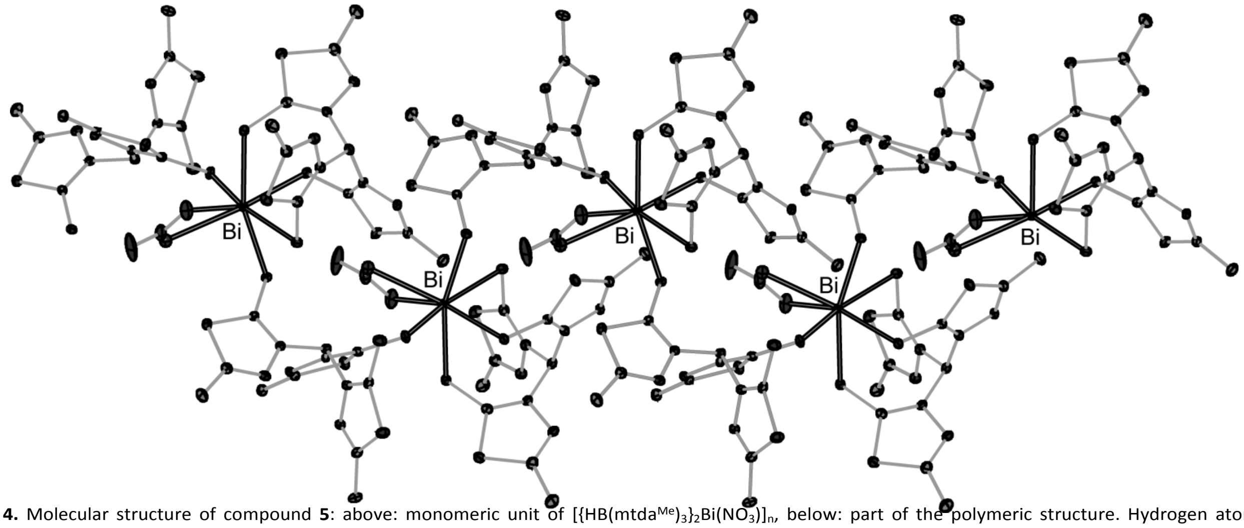


Figure 4. Molecular structure of compound **5**: above: monomeric unit of $[\{HB(mtda^{Me})_3\}_2Bi(NO_3)]_n$, below: part of the polymeric structure. Hydrogen atoms and solvent molecules have been omitted for clarity, displacement ellipsoids are drawn at the 30% level.

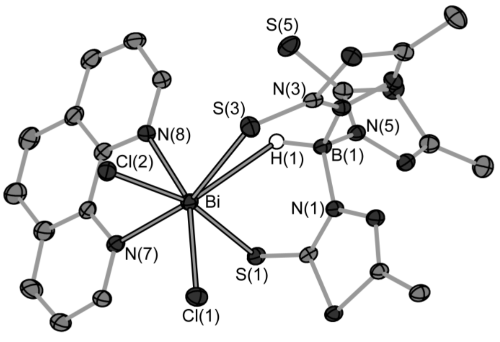


Figure 5. Molecular structure of $[\{HB(mtda^{Me})_3\}Bi(phen)Cl_2]$ (**6**). Hydrogen atoms except B–H and solvent molecules have been omitted for clarity, displacement ellipsoids are drawn at the 30% level.

The reported complex has coordination number eight with shorter Bi–S (2.641(2), 2.824(2)) and longer Bi–N (2.713(6), 2.794(5) Å) bonds compared to **6**. The bond angles listed in Table 4 indicate a distorted octahedral geometry of the complex.

The molecular structure of complex **7** in the solid state is shown in Figure 6. The constitution of complex **7** is similar to that of complex **6** and is accomplished by a Janus scorpionate ligand $[HB(mtda^{Me})_3]^-$, two terminally bound chloro ligands and a bidentate bipyridyl ligand. The complex adopts distorted octahedral geometry as revealed from its bond angles (Table 4). S(1)–Bi–S(3) exhibit maximum deviation at 118°. The distances Bi–S (2.965(2) – 3.002(2) Å), Bi–N (2.435(2) – 2.513(2) Å), Bi–Cl (2.549(2) – 2.566(2) Å) compare well to those of complex **6**. The (B)H···Bi interaction at 2.71(2) Å is of the same length as in **6** within experimental error. The distances Bi–N and Bi–Cl in **6** are shorter when compared with a related mixed complex [$LaCl_2(Tp^{Me2})$(bipy)] (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) (mean La–N 2.699(5) Å, mean La–Cl 2.748(2) Å).[25]

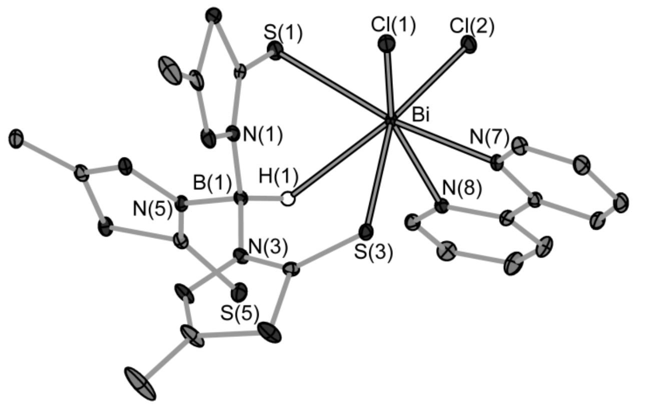


Figure 6. Molecular structure of [{$HB(mtda^{Me})_3$}Bi(Bipy)Cl_2] (**7**). Hydrogen atomsexcept B–H and solvent molecules have been omitted for clarity, displacement ellipsoids are drawn at the 30% level.

Table 4. Selected bond lengths [Å] and angles [deg] of complexes **6** and **7**

6		**7**	
Bi–S(1)	2.966(2)	Bi–S(1)	3.003(2)
Bi–S(3)	2.943(2)	Bi–S(3)	2.965(2)
Bi–N(7)	2.445(3)	Bi–N(7)	2.435(2)
Bi–N(8)	2.490(3)	Bi–N(8)	2.512(2)
Bi–Cl(1)	2.613(2)	Bi–Cl(1)	2.566(2)
Bi–Cl(2)	2.558(2)	Bi–Cl(2)	2.549(2)
(B)H···Bi	2.76(3)	(B)H···Bi	2.71(2)
S(1)–Bi–S(3)	117.1(2)	S(1)–Bi–S(3)	118.7(2)
S(1)–Bi–N(7)	78.1(2)	S(1)–Bi–N(7)	170.3(2)
S(1)–Bi–N(8)	92.5(2)	S(1)–Bi–N(8)	113.3(2)
S(3)–Bi–N(7)	162.3(2)	S(3)–Bi–N(7)	71.0(2)
S(3)–Bi–N(8)	101.5(2)	S(3)–Bi–N(8)	84.8(2)
Cl–Bi–S (*cis*)	80.5(2) – 100.0(2)	Cl–Bi–S (*cis*)	87.8(2) – 90.9(2)
Cl–Bi–S (*trans*)	162.4(2)	Cl–Bi–S (*trans*)	152.0(2)
Cl(1)–Bi–Cl (2)	90.3(2)	Cl(1)–Bi–Cl (2)	93.9(2)

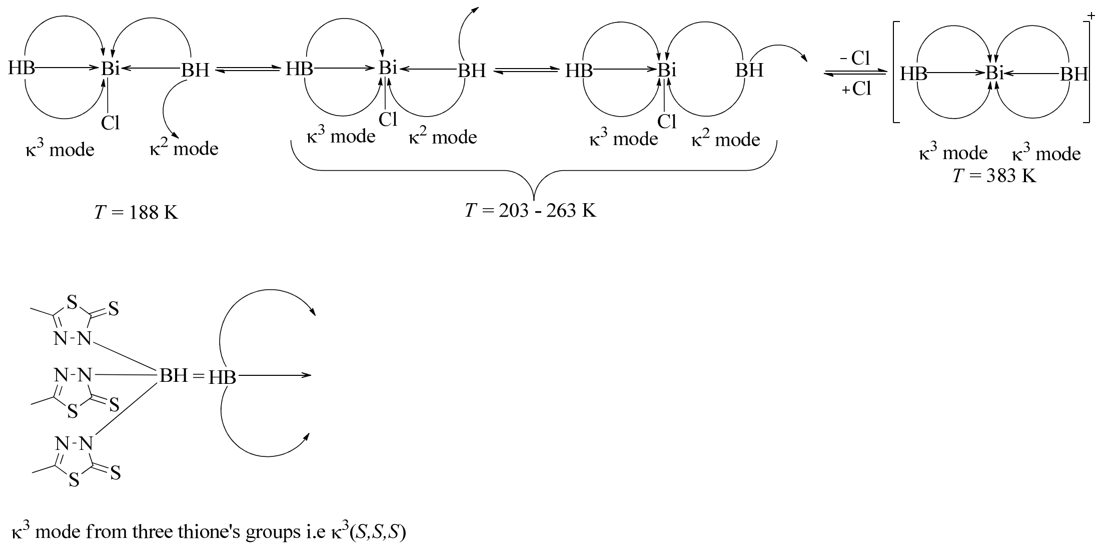
Solution NMR studies

The ^1H NMR spectra of complexes **3** – **5** were recorded. The resonances of the methyl protons show a significant chemical shift relative to that of the free ligand $[HB(mtda^{Me})_3]^-$. The three complexes **3**, **4** and **5** exhibit a broad singlet for methyl protons at 2.52, 2.57 and 2.52 ppm, respectively, compared to δ = 2.37 ppm for free ligand $[HB(mtda^{Me})_3]^-$ indicating a fluxional coordination behavior. The dynamics have been studied exemplarily on compound **3** by VT in the range of 188 to 383 K using CD_2Cl_2 and $C_2D_2Cl_4$ as solvents (Figures 7 and 8). Two methyl resonances were observable (Figure 7). At lower temperature their shifts are about 2.47 and 2.73 ppm. At 188 K one of these methyl resonances starts to split, so it possibly belongs to a ligand with coordination mode (κ^2-*S,S'*) (Scheme 3). At 203 K two signals at $\delta = 2.46$ and 2.67 ppm are obtained for the methyl groups. We assume that at lower temperature one of the scorpionate ligands coordinates in κ^3 mode while the other one is coordinated dynamically to the bismuth centre in κ^2 fashion according to Scheme 3. At 293 K the signals of the methyl groups coalesce to give one broad resonance.

Surprisingly the broad singlet splits into two signals again when raising the temperature above 333 K. We conclude that at higher temperature the chloride ligand is split off to give a cationic bismuth complex exhibiting both scorpionate ligands to coordinate in κ^3-*S,S',S''* mode. Confirmation of this working hypothesis was obtained from molar conductance measurements. With increasing temperature of an acetonitrile solution of complex **3** its molar conductance was also found to increase: from 34 $\Omega^{-1}cm^2mol^{-1}$ (at RT) to 75 $\Omega^{-1}cm^2mol^{-1}$ at 70 °C. The non-equivalence of the ligands may be due to a stereochemically active lone pair at bismuth. Spicer et al. have also observed dynamics at low temperature for an antimony complex based on a soft scorpionate ligand [Sb(κ^3-Tm^{Me})(κ^1-Tm^{Me})Br] (Tm^{Me} = hydrotris(methimazolyl)borate).[12]

The most important feature of the ^{13}C NMR spectra of complexes **3** – **5** is an up-field shift for the C═S resonance compared to that of the free ligand (see experimental section). This can be attributed to the coordination of the thione unit to the bismuth atom. The resulting spectrum exhibited a broad peak for the methyl carbon atoms supporting the possibility of different environments of methyl groups in this complex. ^1H NMR spectra of complexes **3**, **6** and **7** were also recorded in dmf-*d*7 and then compared to those of $[HB(mtda^{Me})_3]^-$ and the co-ligands. This comparison reveals that these complexes are significantly dissociated in dmf (see experimental section).

The dissociation was further proven by ^1H diffusion NMR experiments. Diffusion coefficients were determined using the proton resonance of the methyl groups of $[HB(mtda^{Me})_3]^-$ and complex **3**, respectively. As shown in Table 5, the diffusion coefficient of complex **3** is slightly smaller (4.76×10^{-10} m^2 s^{-1}) than that of the free ligand $[HB(mtda^{Me})_3]^-$in form of its sodium salt (4.57×10^{-10} m^2 s^{-1}). This indicates that complex **3** is at least partially dissociated in dmf (Equation 1).



Scheme 3. Schematic illustration for the possible dynamics of complex **3** in solution

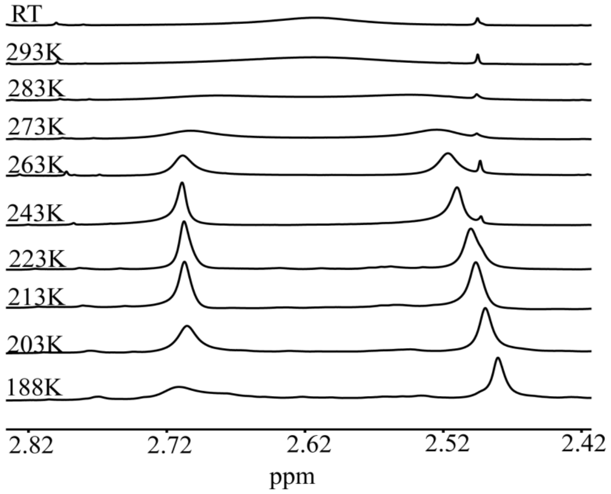


Figure 7. Variable temperature ^1H NMR spectra of complex **3** in CD_2Cl_2 solution

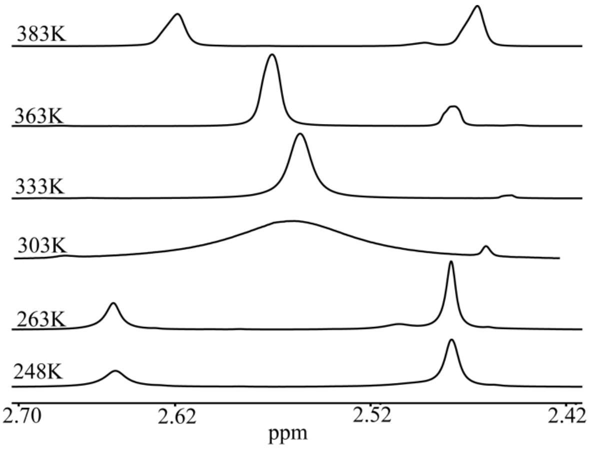


Figure 8. Variable temperature ^1H NMR spectra of complex **3** in $C_2D_2Cl_4$ solution

Similarly the diffusion coefficients of complexes **6** and **7** were determined using the proton resonance of the methyl group of $[HB(mtda^{Me})_3]^-$and that of the aromatic amine i.e. the co-ligands. Table 5 shows that the diffusion coefficients of the complexes **6** and **7** differ from the diffusion coefficients of their free co-ligands (phen and bipy), but are close to that of $[HB(mtda^{Me})_3]^-$. This indicates that in dmf complexes **6** and **7** are also dissociated (Equation 2).

$$[\{HB(mtda^{Me})_3\}_2BiCl] \underset{-dmf}{\overset{+dmf}{\rightleftharpoons}} [\{HB(mtda^{Me})_3\}BiCl]^+ + [HB(mtda^{Me})_3]^-$$

Equation 1. Dissociation of complex **3** in dmf

$$[\{HB(mtda^{Me})_3\}Bi(phen)Cl_2] \underset{-dmf}{\overset{+dmf}{\rightleftharpoons}} [(phen)BiCl_2]^+ + [HB(mtda^{Me})_3]^-$$

$$[\{HB(mtda^{Me})_3\}Bi(bipy)Cl_2] \underset{-dmf}{\overset{+dmf}{\rightleftharpoons}} [(bipy)BiCl_2]^+ + [HB(mtda^{Me})_3]^-$$

Equation 2. Dissociation of complexes **6** and **7** in dmf

Attempts to determine a reliable value for diffusion co-efficient for complex **4** were hampered by the width of the singlet of the methyl protons.

Table 5. Diffusion coefficients of complexes **3**, **7** and **8** and the free ligand compounds of the corresponding respective complexes

Compound	Diffusion coefficient ($m^2\ s^{-1}$)
3	4.76×10^{-10}
$[HB(mtda^{Me})_3]^-$	4.57×10^{-10}
6	5.04×10^{-10} (phen), 4.93×10^{-10} $[HB(mtda^{Me})_3]^-$
phen	CH (8.73×10^{-10})
7	8.60×10^{-10} (bipy), 4.54×10^{-10} $[HB(mtda^{Me})_3]^-$
bipy	1.01×10^{-10}

Mass spectra

The ESI-MS spectrum of complex **3** reveals the presence of a single molecular ion peak *m/z* = 1018.8 and can be assigned to $[BiL_2]^+$ (L = $HB(mtda^{Me})_3$). It further indicates that chloride is labile and has been removed. Similar single molecular ion peaks have been observed and reported in the literature for $[Bi(Tr^{Et,Me})_2]^+$[21] and $[Bi(Tr^{Me})_2]^+$.[14] Complex **4** exhibits different ion peaks attributed to *m/z* = 403.1 $[HB(mtda^{Me})_3^-]$ (free ligand),1018.9 $[Bi(L)_2]^+$ (L = $HB(mtda^{Me})_3$), 915.5 $[Na_2BiLI_2]^+$ and 871.7 $[Bi(LH)I_2]^+$. Such fragmentation has also been previously observed for related complex $[Cu(Tr^{Et,Me})]_2$.[21] The mass spectrum of **5** exhibits the presence of only two peaks which can be assigned to *m/z* = 1018.8 $[Bi(L)_2]^+$ (L = $HB(mtda^{Me})_3^-$) and 612.8 $[Bi(LH)]^{2+}$ species. Similar to complex **3**, the mass spectrum of **6** also exhibits the presence of different ion peaks that can be assigned as follow: *m/z* = 1018.8 $[BiL_2]^+$, 828.9 $[Bi(L)(phen)Cl]^+$, 612.9 $[Bi(LH)]^+$. The mass spectrum of complex **7** shows different peaks as observed in above cases. These are assigned and given in experimental section.

Conclusions

We have successfully prepared and characterized bismuth complexes with the known second generation Janus ligand $[HB(mtda^{Me})_3]^-$. We have observed that in the presence of different counter anions such as chloride, iodide and nitrate, $[HB(mtda^{Me})_3]^-$ exhibits different coordination modes towards bismuth ions. Furthermore, two mixed metal complexes were also prepared and characterized. In both these mixed complexes, an interesting feature of (B)H···Bi interaction (at 2.76(3) Å for **6** and 2.71(2) Å for **7**) was observed. This is in contrast to **3**, **4** and **5** where such interactions are absent. All the resulting complexes are monomeric except **5** which is polymeric in nature. Previously it has been established in the literature that the general preference of coordination mode of the scorpionate ligand is κ^3, resulting in the dominant structural motif of cationic sandwich complexes.[19] However, in this present investigation, none of the complexes possesses a sandwich structure with κ^3 coordinate mode from both sides of the Janus scorpionate ligands. This demonstrates greater flexibility in binding than anticipated from previous results.

Photophysics

Acknowledgements

We are thankful to Klaus-Peter Mester for recording NMR spectra and to Brigitte Michel for elemental analyses. M. I. acknowledges with special thanks the Deutscher Akademischer Austausch Dienst (DAAD) for providing a PhD stipend.

Experimental work

All the solvents used during this work were dried and distilled before use. $BiCl_3$, BiI_3, $BiNO_3{\cdot}5H_2O$, 2,2′-bipyridyine and 10-phenanthroline were procured from Alfa Aesar and Acros Organics and used without further purification. NMR spectra were recorded on Bruker Advance 300, Bruker DRX 500 or Bruker Advance 600 spectrometers and the chemical shifts were referenced to the residual proton (^1H) or the carbon signals of the deuterated solvents and are reported in ppm. Diffusion NMR measurements have been performed by using the LED sequence with bipolar gradients (ledbpgp2s) delivered by the manufacturer. The probe was disconnected from the gas supply and the sample has been allowed to equilibrate for four hours within the probe/magnet prior to data recording. The duration of the gradients was incremented linearly in 16 steps. The diffusion coefficients have been calculated by using the relaxation module of the Bruker software TOPSPIN®. Elemental analyses were performed using a EuroEA Elemental Analyser. ESI-MS and MALDI-TOF spectra were measured using Esquire 3000 (Bruker Daltonik 2000) and Voyager DE PE Bio-system 2000 spectrometers. Melting points were determined using a Büchi B 545 melting point apparatus and are uncorrected. Values of molar conductance ($\Omega^{-1}\ cm^2\ mol^{-1}$) were determined at room temperature in acetonitrile solution (1 mmol L^{-1}) using a CG 853 conductometer (Schott GmbH, Germany). However for complex **3**, molar conductance was also measured at 70 °C.

$Na[HB(mtda^{Me})_3]$(1)

Compound **1** was synthesized according to literature procedure.[9] ^1H NMR (dmso-*d6*) δ = 2.30 (s, 9H, CH_3); ^{13}C NMR (dmso-*d6*) δ = 190.1 (C═S), 154.3 (C═N), 16.3 (H_3C); ^{11}B NMR (dmso-*d6*) δ= –4.12 (br); ^1H NMR (dmf-*d7*) δ = 2.30 (s, 9H, CH_3); ^{13}C NMR (dmf-*d7*) δ = 191.1 (C═S), 154.3 (C═N), 15.9 (H_3C).

$NBu_4[HB(mtda^{Me})_3]$ (2)

A sample was prepared according to a literature protocol.[9] Crystals suitable for diffraction were grown by slowly allowing a dichloromethane solution of **2** to evaporate in a refrigerator. ^1H NMR (CD_2Cl_2) 3.24 (m, 8H, NCH_2), 2.37 (s, 9H, mtda-CH_3), 1.64 (m, 8H, CH_2), 1.41 (m, 8H, CH_2), 0.98 (m, 12H, CH_3); ^{13}C NMR (CD_2Cl_2) 190.9 (C═S), 155.2 (HC═N), 58.9 (CH_3), 23.9 (CH_2), 19.7 (CH_2), 16.1 (CH_2), 13.3 (CH_3).

$[\{HB(mtda^{Me})_3\}_2BiCl]$ (3)

A solution of $Na[(mtda^{Me})_3]$ (**1**) (0.493 g, 1.15 mmol) in 50 mL of acetonitrile was slowly added to one of $BiCl_3$ (0.180 g, 0.574 mmol) in 50 mL of acetonitrile under N_2 atmosphere. The resulting orange yellow solution was stirred at room temperature for 4 h and then filtered. The volume of the sample was removed under vacuum and then dried. An orange solid was obtained, which was washed with small amount of methanol and then *n*-pentane. The product was recrystallized from acetonitrile. Single crystals with composition $[\{HB(mtda^{Me})_3\}_2BiCl]\cdot 2CH_3CN$ (**3**) were obtained by slow diffusion of *n*-pentane into an acetonitrile solution of the complex. These crystals were dried under vacuum and analysed as follows. Yield 68%; m.p. 191 – 193 °C (with decomposition); Molar conductance 34 Ω^{-1} cm^2 mol^{-1} at RT; 75 Ω^{-1}cm^2 at 70 °C; Anal. calcd. for $C_{18}H_{20}B_2N_{12}S_{12}ClBi\cdot CH_3CN$ (found): C 21.91 (22.59), H 2.11 (2.18), N 16.61 (16.45); ^{1}H NMR ($C_2D_2Cl_4$), δ = 2.52 (s, 18H, H_3C); ^{13}C NMR ($C_2D_2Cl_4$) δ = 187.5 (C=S), 156.6 (C=N), 16.03 (H_3C); ^{1}H NMR (dmf-*d7*), δ = 2.32 (s, 18H, H_3C); ^{13}C NMR (dmf-*d7*) δ = 190.91 (C=S), 154.0 (C=N), 15.03 (H_3C); ESI-MS *m*/*z* [assignment] = 1018.8 $[Bi(L)_2]^+$ (L = $HB(mtda^{Me})_3^-$).

$[\{HB(mtda^{Me})_3\}_2BiI]$(4)

This complex was prepared according to the same procedure as described above by reacting an acetonitrile solution of $Na[HB(mtda^{Me})_3]$ (0.493 g, 1.15 mmol) and a methanol solution of BiI_3 (0.338 g, 0.574 mmol) respectively. The following analytical data were obtained for the bulk solid of **4**. Yield, 63 %; m.p. 111 °C; Molar conductance at RT: 42 Ω^{-1}cm^{2}mol^{-1}; Anal. calcd. for $C_{18}H_{20}N_{12}S_{12}B_2BiI$ (found): C 18.85 (18.21), H 1.75 (1.98), N 14.53 (14.66); ^{1}H NMR(dmf-*d7*), δ = 2.46 (s, br, 18H, H_3C); ^{1}H NMR (dmso-*d6*), δ = 2.76 (s br, 18H, H_3C); ^{13}C NMR (dmso-*d6*) δ = 170.1 (C=S), 154.7 (C=N), 16.4 (H_3C); ^{1}H NMR ($CDCl_3$), δ = 2.57 (s, br, 18H, H_3C);^{13}C NMR ($CDCl_3$) δ = 187.5 (C=S), 163.4 (C=N), 16.5 (H_3C); ESI-MS *m*/*z* [assignment] = 1018.9 $[Bi(L)_2]^+$, 915.5 $[Na_2Bi(L)_2(I)_2]^+$, 871.7 $[Bi(LH)_2(I)_2]^+$.

Crystals were obtained by slow evaporation of an acetonitrile solution of complex **4**; this resulted only in two single crystals after several weeks. Their composition $Na[\{HB(mtda^{Me})_3\}_2Bi\text{-}I_2]\cdot CH_3CN.H_2O$ (**4a**) was determined by crystallography.

$[\{HB(mtda^{Me})_3\}_2BiNO_3]_n$ (5)

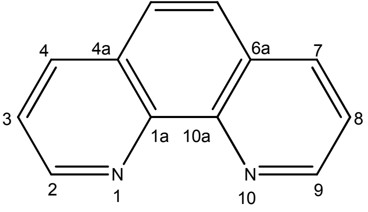
This complex was prepared according to same procedure as described above by reacting an acetonitrile solution of $Na[HB(mtda^{Me})_3]$ (0.493 g, 1.15 mmol) with a methanol solution of $Bi(NO_3)_3\cdot 5H_2O$ (0.278 g, 0.574 mmol). It was recrystallized similar to **3**. The following analysis was carried out on bulk solid obtained after recrystallization from acetonitrile. Yield 73%; colour red; m.p. 125°C (decompose); Molar conductance at RT: 38 Ω^{-1} cm^2 mol^{-1}; ^{1}H NMR (dmso-*d6*), δ = 2.76 (s, 18H, H_3C), 1.99 (s, H_3C-acetonitrile); ^{13}C NMR (dmso-*d6*) δ = 188.8 (C=S), 154.3 (C=N), 16.4 (H_3C); ^{1}H NMR ($CDCl_3$), δ = 2.52 (s, br, 18H, H_3C), 2.08 (s, 3H, H_3C-acetonitrile); ^{13}C NMR ($CDCl_3$) δ = 169.0 (C=S), 158.8 (C=N), 16.0 (H_3C); ESI-MS *m*/*z* [assignment] = 1018.8 $[Bi(L)_2]^+$, 612.8 $[Bi(LH)]^{2+}$. HRMS: calculated for $C_{18}H_{20}N_{12}S_{12}B_2Bi^+$ (found): 1018.85971, (1018.85668) (dev. 2.97 ppm).

Single crystals with composition $[\{HB(mtda^{Me})_3\}_2Bi\text{-}(NO_3)]_n\cdot CH_3OH$ were obtained by cooling the methanol solution of complex **5** in a refrigerator for several weeks.

$[\{HB(mtda^{Me})_3\}_2Bi(Phen)(Cl)_2]$ (6)

Equimolar solutions of $Na[HB(mtda^{Me})_3]$ (0.493 g, 1.15 mmol) and $BiCl_3$ (0.362 g, 1.15 mmol) in 30 mL of anhydrous acetonitrile were prepared and mixed. The reaction mixture was stirred for 1 h at room temperature, and then the solution of 1,10-phenanthroline (0.207 g, 1.15 mmol) in 10 mL acetonitrile was added dropwise over a period of 45 minutes. The mixture was stirred for 6 h and the resulting precipitate were filtered, washed with small amounts of acetonitrile and methanol and dried in vacuum. The orange yellow solid was extracted three times with anhydrous chloroform (30 mL each). Removal of the solvent afforded compound **6** as a residue which was further washed with *n*-pentane and diethyl ether and again dried in vacuum. Single crystals of the composition $[\{HB(mtda^{Me})_3\}_2Bi(phen)Cl_2]\cdot 2.1CHCl_3$ were obtained by slow evaporation of a chloroform solution of complex **6**. Below analysis was carried out on bulk solid. Yield 61 %; m.p. 206 – 208 °C (with decomposition); Molar conductance at RT: 16 Ω^{-1} cm^2 mol^{-1}; Anal. calcd. for $C_{21}H_{20}N_8S_6BBiCl_2$ (found): C 29.07 (29.52), H 2.32 (2.07), N 12.92 (10.83); ^{1}H NMR (dmf-*d7*) δ = 9.77 (4H, dd, H(2,9), 8.97 (4H, dd, H(4,7)), 8.30 (4H, s, H(5,6)); 8.18 (4H, dd, H(3,8)), 2.32 (s, 9H, H_3C); ^{13}C NMR (dmf-*d7*) δ = 190.6 (C=S), 153.8 (C=N), 150.6 (C2, C9), 143.6 (C1a, C10a), 139.6 (C4, C7), 130.4 (C4a, C6a), 127.4 (C5, C6), 125.1 (C3, C8), 15.0 (H_3C-mtda); ^{1}H NMR (dmso-*d6*) δ = 9.19 (6H, dd, H(2,9)), 8.58 (6H, d, H(4,7)), 8.05 (6H, s, H(5,6)); 7.84 (6H, dd, H(3,8)), 2.30 (s, 9H, H_3C), ^{13}C NMR (dmso-*d6*) δ = 190.1 (C=S), 154.3 (C=N), 150.6 (C2, C9), 145.4 (C1a, C10a), 137.5 (C4, C7), 129.0 (C4a, C6a), 127.2(C5, C6), 124.2 (C3, C8), 16.3 (H_3C-mtda); ESI-MS *m*/*z* [assignment] = 1018.8 $[Bi(L)_2]^+$, 828.9 $[Bi(L)(phen)(Cl)]^+$, 612.9 $[Bi(LH)]^+$

Free co-ligand (1,10-phenanthroline): ^{1}H NMR (dmf-*d7*) δ = 9.77 (2H, dd, H(2,9), 8.97 (2H, dd, H(4,7)), 8.30 (2H, s, H(5,6)); 8.18 (2H, dd, H(3,8)), 2.32 (s, 9H, H_3C); ^{13}C NMR (dmf-*d7*) δ = 150.1 (C2, C9), 146.2 (C1a, C10a), 136.2 (C4, C7), 129.0 (C4a, C6a), 126.7 (C5, C6), 123.5 (C3, C8).

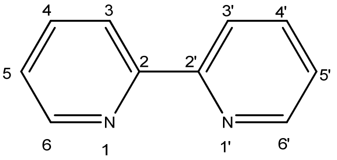


Labelling scheme of 1,10-phenanthroline

$[\{HB(mtda^{Me})_3\}_2Bi(Bipy)Cl_2]$ (7)

This complex was prepared using $Na[HB(mtda^{Me})_3$ (0.493 g, 1.15 mmol) and $BiCl_3$ (0.362 g, 1.15 mmol) and 2,2′-bipyrdyl (0.180 g, 1.15 mmol) in a similar way to that described for **7**. Crystals were grown by slow evaporation of acetonitrile solution of the complex **7** at room temperature with composition $[\{HB(mtda^{Me})_3\}Bi(bipy)Cl]\cdot CH_3CN$ (**7**). Below analysis was carried out on bulk solid. Yield 55 %; m.p. 161 – 164 °C (with decomposition); Molar conductance (Ω^{-1} cm^2 mol^{-1}) 23 at RT; Anal. calcd. for $C_{19}H_{18}N_8S_6BBiCl_2$ (found): C 27.12 (27.10), H 2.16 (1.95), N 13.32 (13.04); ^{1}H NMR (dmf-*d7*) δ = 8.80 (3H, d, (6, 6′)), 8.49 (3H, d, H9) 8.05 (6H, m, (3, 3′)), 7.49 (3H, dd, (5, 5′)),2.32 (s, 9H, H_3C-mtda), ^{13}C NMR (dmf-*d7*) δ = 190.6 (C═S), 155.6 (C═N), 153.8 (C2, C2′), 149.6 (C3, C3′), 137.4 (C5, C5′), 124.3 (C4, C4′), 120.6 (C6, C6′), 15.03 (H_3C-mtda); ^{1}H NMR (dmso-*d6*) δ = 8.69 (2H, dd, H(6, 6′), 8.38 (2H, d, H(3, 3′), 7.96 (2H, dt, H(4, 4′), 7.47 (2H, dd, H(5, 5′), 2.30 (s, 9H, H_3C-mtda), ^{13}C NMR (dmso-*d6*) δ = 190.1 (C═S), 155.6 (C═N), 154.3 (C2,C2′), 149.8 (C3, C3′), 137.7 (C5, C5′), 124.6 (C4, C4′), 121.3 (C6, C6′), 16.4 (H_3C-mtda); ESI-MS *m*/*z* [assignment] = 767.3 $[BiL(bipy)]^+$, 685.5 $[BiLCl_2]^+$, 711.5 $[Bi(bipy)_3Cl]^+$.

Free co-ligand (2,2′-bipyridine): ^{1}H NMR (dmf-*d7*) δ = 8.90 (2H, dd, (6, 6′)), 8.66 (2H, d, H9) 8.15 (2H, m, (3, 3′)), 7.69 (2H, dd, (5, 5′).



Labelling scheme of 2,2′-bipyridine

Luminescence activity

For luminescence activity, compounds are under measurements in co-operation with Dr. Uwe Monkowius, Linz, Austria

X-ray Crystallographic Analysis. X-ray diffraction data were collected from **2**, **3**, **4a**, **5**, **6** and **7**. Single-crystals suitable for X-ray diffraction were picked under inert paratone oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer. Data sets for **5** and **6** were collected on a Bruker Nonius Kappa CCD diffractometer using Mo-K_α radiation, while data sets for compounds **2** and **3** were collected using a Bruker AXS Kappa (APEX II) with Cu-K_α radiation. Data sets for **4** and **7** were collected on a Super Nova using Mo-K_α radiation. A summary of data collection and structure refinement is reported in Table 6. The structures were solved by Direct Methods and refined by full-matrix least squares cycles (programs SHELXS-97 or SHELXL-97).[30] CCDC contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table 6. X-ray crystallographic data for compounds **2**, **3**, **4a**, **5**, **6** and **7**

Compound	**2**	**3**	**4a**	**5**	**6**	**7**
Empirical formula	$C_{16}H_{36}N$, $C_9H_{10}BN_6S_6\cdot 0.25H_2O$	$C_{18}H_{20}B_2BiClN_{12}S_{12}\cdot 2CH_3CN$	$C_{25}H_{35}B_2BiI_2N_{15}NaO_2S_{12}$	$C_{18}H_{20}B_2BiN_{12}O_3S_{12}\cdot CH_3OH$	$C_{21}H_{18}BBiC_{l2}N_8S_6\cdot 2.31(CHCl_3)$	$C_{21}H_{21}BBiCl_2N_9S_6$
M_r	652.36	1137.34	1469.79	1113.83	1140.63	882.52
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$C2/c$	$P3_1c$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.2030(4)	9.5033(2)	14.92021(15)	14.0818(11)	9.3244(2)	8.98994(20)
b (Å)	12.2363(4)	15.4993(4)	17.08670(14)	12.7834(11)	15.4392(4)	11.7912(3)
c (Å)	13.4489(5)	28.4071(7)	20.8514(2)	22.436(3)	16.1384(4)	15.1964(4)
α (°)	69.855(1)	90	90	90	116.5277(11)	93.4539(19)
β (°)	65.230(1)	90	107.7276(11)	97.836(9)	92.9132(15)	99.5573(19)
γ (°)	69.921(1)	90	90	90	91.2053(14)	99.4185(18)
Z	2	4	4	4	2	2
V (Å^3)	1664.57(10)	4184.21(17)	5063.37(9)	4001.1(7)	2073.53(9)	1560.74(6)
F(000)	697	2232	2832	2184	1103	856
Crystal size (mm)	0.35 x 0.23 x 0.09	0.17 x 0.07 x 0.02	0.17 × 0.11 × 0.09	0.19 x 0.16 x 0.04	0.21 x 0.06 x 0.04	0.15 × 0.13 × 0.06
Reflections measured	39938	126049	136600	56524	47674	36667
Unique reflections (R_{int})	5956 (0.0281)	7791 (0.0388)	7384 (0.0344)	9179 (0.0540)	9473 (0.066)	9107 (0.0351)
No. of parameters	547	477	373	468	490	369
R (I>2σ(I))	0.0254	0.0145	0.0210	0.0307	0.0314	0.0197
R_w(all reflections)	0.0681	0.0361	0.0494	0.0557	0.0693	0.0414
Goodness-of-fit	1.031	1.004	1.211	1.058	1.027	1.024
$\rho_{max/min}$(e Å^{-3})	0.37/–0.28	0.65/–0.83	0.98/–0.55	0.88/–0.79	1.16/–1.52	0.76/–0.85
CCDC no.	970797	970798	970799	970800	970801	970802

Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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TOC entry

Synthesis, structural and photo-physical studies of bismuth(III) complexes with a Janus scorpionate and co-ligands

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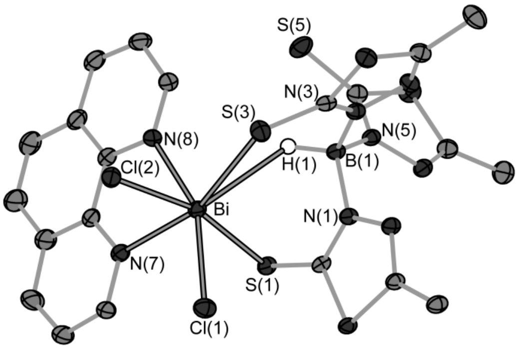
A bismuth complex with almost octahedral geometry despite of halide ions and two mixed bismuth complexes that feature (B)H···Bi interactions at distances of 2.76 (3) and 2.71(2) Å are presented.



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ARTICLE TYPE

Boron-centred soft ligands based on tetrazole units and their complexes with sodium, potassium and bismuth ions

Muhammad Imran,[a] Andreas Mix,[a] Beate Neumann,[a] Hans-Georg Stammler,[a] Uwe Monkowius,[b] XXX[b] and Norbert W. Mitzel[a,]*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The syntheses of Na(ttt^{Me}) (**1**), K(ttt^{Me}) (**2a**), K(btt^{Me}) (**2b**), KNa(ttt^{Me})$_2$ (**3**) and Na(btt^{Ph}) (**4**) are reported, where (ttt^{Me})$^{-}$ and (btt^{R})$^{-}$ (R = Me, Ph) are tri- and di-substituted boron-centred soft ligands; they were produced by the reaction of NaBH$_4$ and KBH$_4$ with the corresponding tetrazole heterocycles: 1-methyl-5-thiotetrazole (L^{1}H) and 1-phenyl-5-thiotetrazole (L^{2}H). The syntheses of Na(ttt^{Me}) (**1**) and K(ttt^{Me}) (**2a**) were carried out following Trofimenko's protocol. The anion (ttt^{Me})$^{-}$ is a typical Janus scorpionate ligand. Na(ttt^{Me}) (**1**) and Na(btt^{Ph}) (**4**) were reacted with Bi(CH$_3$COO)$_3$ to observe the coordination pattern of these ligands towards bismuth ions. These reactions afforded the complexes [Bi(ttt^{Me})$_2$(CH$_3$COO)] (**5**), [Bi(L^2)$_2$]$_2$ (**6a**, **6b**) and [Bi(L^2)$_3$] (**7**). The products were characterized by NMR spectroscopy, by elemental analyses and by mass spectrometry. Solid state structures were determined by X-ray diffraction of single crystals of **1**, **2a**, **2b**, **4**, **5**, **6a**, **6b** and **7**. M(ttt^{Me}) (M = Na (**1**), K (**2a**)) and K(btt^{Me}) (**2b**) exhibit sheet-like structures. The alkali metal complexes **1** – **4** dissociate in solution as observed in ^{1}H, ^{13}C NMR and ^{1}H diffusion NMR experiments. Negative mode ESI-MS data also indicate the presence of monomers.

<<A part on photo-physical measurement has to be included here>>

Introduction

Tri-substituted boron-centred anionic soft ligands, based on methimazole units hydrotris(methimazolyl)borate (tm^{Me}) have first been prepared in 1996 by Silva et al.[1] Later on, a large number of modifications using a number of different alkyl/aryl groups have been made.[2] Another class of tri-substituted boron-centred soft ligands has been reported in 2006 and was classified as Janus scorpionates.[3,4] Closely related to Bailey's[5] and Marchiò's[6] ambidentate thioxotriazolylborate these ligands are also described as hybrids of Trofimenko's tris(pyrazolyl)borate [7] and Reglinski's hydrotris(methimazolyl)borate (tm^{Me}).[1] After the first report of a tri-substituted soft ligand, hydrotris(methimazolyl)borate (tm^{Me}), a di-substituted analogue hydrobis(methimazolyl)borate (bm)[8] has been reported. Other examples of di-substituted boron-centred soft ligands include dihydrobis(2-thiopyridone)borate (bmp),[9] dihydrobis(thioxotriazolyl)borate (bt)[10,11] and dihydrobis(1-methyl-5-thiotetrazolyl)borate (btt^{Me}).[12] These ligands are considered to be soft congeners of their hard analogues, the tris- (tp) and bis(pyrazolyl)borates (bp).[7] However, the soft systems are considered to be advantageous over their hard analogues in the stabilization of low-valent, electron-rich metal ions.[13,14] Their complexes demonstrate susceptibility for oxidation thus giving rise to metal complexes with unusual oxidation states. Established literature knowledge is that these soft ligands exert weaker field strengths compared to hard ligands.[15,16] They show variable coordination modes such as κ^1-*S*, κ^2-*S*,*S* or κ^2-*S*,*H* and κ^3-*S*,*S*,*S* or κ^3-*S*,*S*,*H*.[17,18]

Prior to this work, only Na(btt^{Me}) (btt^{Me} = dihydrobis(1-methyl-5-thiotetrazolyl)borate anion) has been synthesized and complexed to cobalt and nickel ions resulting in the complexes [Co(btt^{Me})$_2$] and [Ni(btt^{Me})$_2$].[12] However, no related work involving 1-phenyl-5-thiotetrazole (L^{2}H) has been reported. Recently we have synthesized alkali metal and bismuth complexes of the Janus scorpionate ligand (tr^{Me})$^{-}$ ([HBR$_3$]$^{-}$ with R = 3-mercapto-4-methyl-1,2,4-triazole).[19] We have also reported the preparations of two ligands di-substituted at boron, (bb)$^{-}$ = dihydrobis(2-mercapto-benzimidazolyl)borate and (bt^{Me}) = dihydrobis(2-mercapto-4-methylthiazolyl)borate, and their complexation behaviour towards sodium and bismuth(III) ions.[20] In continuation of our ongoing efforts in this area, we report here another tri-substituted (Janus scorpionate (ttt^{Me})$^{-}$) (hydrotris(1-methyl-5-thiotetrazolyl)-borate) and a di-substituted (btt^{Ph})$^{-}$ (dihydrobis(1-phenyl-5-thiotetrazolyl)borate) boron-centred soft ligand. We describe their coordination behaviour towards alkali metals and bismuth(III) ions as well as their preliminary photo-physical studies.

Results and discussion

Synthesis

Alkali metal salts $Na(ttt^{Me})$ (**1**), $K(ttt^{Me})$ (**2a**) were synthesized by reacting together MBH_4 and 1-methyl-5-thiotetrazole (L^1H) according to Trofimenko's protocol (Scheme 1). The ligand $(ttt^{Me})^-$ is a typical Janus scorpionate ligand with N and S donor sites. These (crude) ttt^{Me} salts were of sufficient purity to be used for further reactions (see below) and for NMR spectroscopic characterization.

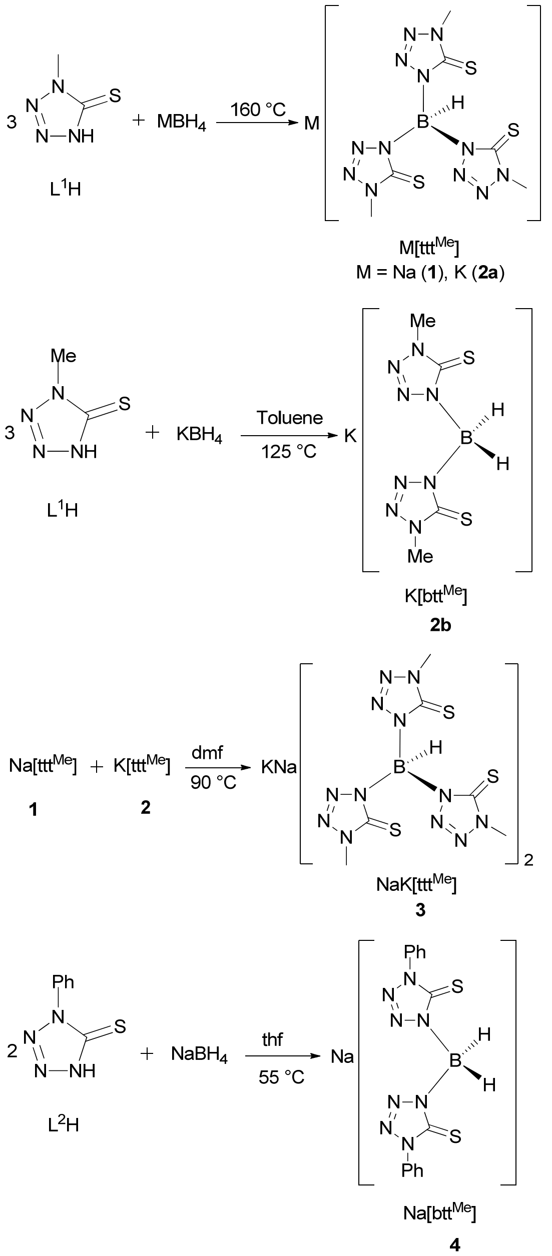
The mixed metal compound $KNa(ttt^{Me})_2$ (**3**) was prepared (Scheme 1) with the intention to observe the preferential binding of sodium and potassium ions towards the hard and soft sites. Apparently, a crystalline sample of $KNa(ttt^{Me})_2$ (**3**) could be isolated, but attempts to determine its crystal structure was not possible due to the crystals being weakly diffracting.

Recently we have reported a similar mixed metal compound $KNa(tr^{Me})_2$ [19] (where tr^{Me} = Janus scorpionate ligand based on triazole units). $Na(ttt^{Me})$ (**1**), $K(ttt^{Me})$ (**2**) are pretty stable compounds, but for long-time storage an inert atmosphere is necessary. Compounds **1** and **2a** are freely soluble in thf, H_2O, CH_3CN, dmf and dmso; this makes a difference to the related sparingly soluble compounds $M(tr^{Me})$[19] and $M[HB(mtda^R)_3]$[3,4] (where M = Na, K; tr^{Me} and $HB(mtda^R)_3$ are Janus scorpionate ligands based on triazole and thiadiazole units). In order to increase the solubility and thus synthetic utility, their tetrabutylammonium derivatives have been reported $NBu_4(tr^{Me})$[19] and $NBu_4[HB(mda^R)]$[3,4], respectively. The improved solubility of **1** and **2a** compared to that of $M(tr^{Me})$[19] and $M[HB(mtda^R)_3]$[3,4] in protic solvents might be fruitful for green chemistry applications in water and alcoholic solvents.

Recrystallization of **1** and **2a** was performed from solvent mixtures water/thf/toluene (ratio 1:5:4), because only addition of water led to completely clear solutions allowing to grow well-crystalline material. These recrystallized products, however, contain water and have the formulae $\mathbf{1}\cdot 6H_2O$ and $\mathbf{2a}\cdot 2H_2O$.

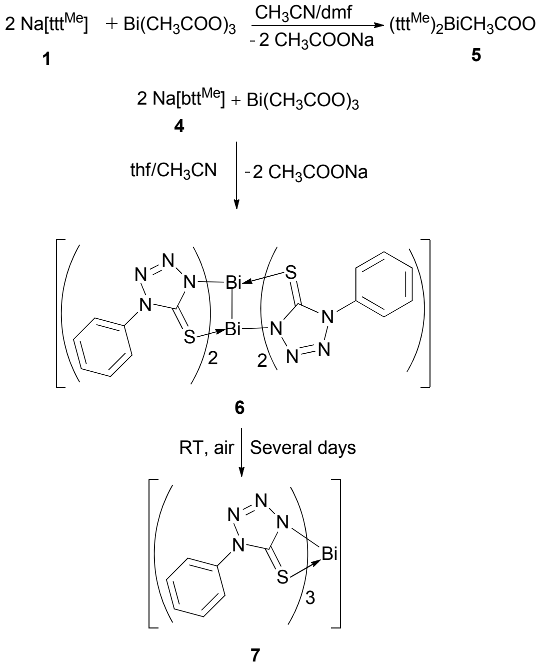
It is important to mention that the yield of product **2a** using the classical protocol is diminished during workup to 32 %, because the raw product contains larger amounts of impurities (free heterocycle, mono and di-substituted species) making the isolation process more laborious. An improved protocol employs the high boiling solvent toluene; the crude reaction mixture contains again a mixture of mono-, di- and tri-substituted species, however, with major abundance of the di-substituted species **2b** and very small contribution of tri- and mono-substituted species. After workup the obtained yield of **2b** was 63 %.

The tri-substituted thiotetrazolatoborate $Na(ttt^{Ph})$ was obtained by reacting 1-phenyl-5-thiotetrazole with $NaBH_4$ via Trofimenko's protocol. By heating the mixture up to 160 °C, a mixture of free heterocycle, mono-, bis-, and tris-substituted borates were obtainned with maximum abundance of the di-substituted species $Na(btt^{Ph})$. Heating to above 200 °C leads to decomposition of the mixture. In analogy to our recently reported bis-substituted boron-centred soft ligands $(bb)^-$ and $(bt^{Me})^-$ [20] the sodium complex of the disubstituted thiotetrazolatoborate $Na(btt^{Ph})$ (**4**) was prepared by reacting 1-phenyl-5-thiotetrazole (L^2H) and $NaBH_4$ in a 2: 1 ratio (Scheme 1). Compound **4** was obtained in 66 % yield and is a colourless pretty stable solid.



Scheme 1. Synthesis of the alkali metal $(ttt^{Me})^-$ and $(btt^{Ph})^-$ complexes **1** – **4**.

Bismuth complexes **5** – **7** were obtained as outlined in Scheme 2. Complexes **5** and **6** require storage under inert atmosphere. Complex **5** is orange. Compound **6** is a complex of Bi(II) with a Bi–Bi bond. Obviously the di-substituted ligand compound $Na(btt^{Ph})$ (**4**) with B–H functions acted as reducing agent and was decomposed so that the resulting 1-phenyl-5-thiotetrazolyl ions could act as ligands. The reaction was conducted in two different solvents, thf and CH_3CN, and the resulting crystalline material contains solvent molecules included into the crystals; the resulting solids are denoted **6a** and **6b**, respectively; both are red. Similarly, Reglinski et al. observed ligand degradation and the reductive ability of $(Tm^{Me})^-$ (hydrotris(methimazolyl)borate) upon reaction with $CuCl_2$ to produce $[Cu^ICl(mtH)(\mu\text{-}mtH)]_2$ (mtH = free heterocyclic methimazole, a decomposition product of $(Tm^{Me})^-$).[14] Compound **7** was obtained by air oxidation of compound **6** and is yellow.



Scheme 2. Syntheses of bismuth complexes **5**, **6** and **7**.

Solid state characterization

The solid state structures of the sodium, potassium and bismuth complexes **1**·6H$_2$O, **2a**, **2b**, **4**, **5**, **6a**, **6b** and **7** were determined by single crystal X-ray diffraction. These structures are shown in Figures 1 – 7. Selected bond lengths and angles are listed in Tables 1 – 6. The three alkali metal complexes **1**, **2a** and **2b** form sheet-like structures in their crystals contrasting the related non-polar polymeric chains of [M(tr^{Me})]$_n$[19] and M[HB{mtda^R}$_3$]$_n$.[3,4]

The molecular structure **1** is shown in Figure 1 and demonstrates a sheet-like structure perpendicular to 011. The compound crystallizes in triclinic system with space group $P\bar{1}$. There are three different types of sodium atoms in the sheet with differently surrounded cores Na(1)O$_3$S$_3$, Na(2)O$_4$S$_2$ and Na(3)O$_4$N$_2$. In all three cases, sodium adopts octahedral coordination geometry with variable degree of distortion. Compared to Na(1) and Na(2), Na(3) has the least distorted environment as revealed from the bond angles listed in Table 1. Na(1) displays a Na(1)O$_3$S$_3$ surrounding constituted by three water molecules and three sulphur atoms of three different Janus scorpionate ligands (ligand coordination mode κ^1-*S*). It is bridged to a symmetry equivalent of itself (about a centre of inversion) by two oxygen atoms, O(1) and O(1A), of two water molecules, and to the neighbouring sodium atom Na(2) via the atoms S(4) and O(2). The result is an endless chain. The Na(2)O$_4$S$_2$ unit contains four water molecules and two sulphur atoms (ligand coordination mode κ^1-*S*); it shares S(4) and O(2) with Na(1). The third sodium atom links the described chains (running along axis *a*) by coordination through the hard donor site of the Janus scorpionate ligand N(7).

Important bond lengths are given in Table 1. The Na–S and Na–N bond lengths are within the ranges described by Silva et al.[3,4] for related alkali metal scorpionates: Na–N 2.30 – 3.15 Å, Na–S 2.68 – 3.25 Å. Moreover, the Na–S bonds in **1** are shorter than the mean value of the above mentioned range; however, the Na–N distance is slightly longer than the mean value of above said range. The Na–O distances in **1** are in the range 2.329(2) – 2.432(2) Å and can be compared with Na–O distances found in [Na(H$_2$O)$_6$][Na(tt)$_2$] ((tt)$^-$ = hydridotris(thioxotriazolyl)borate).[5] No B–H···Na interactions have been found in crystals of **1**, contrasting the situation in related compounds [M(tr^{Me})]$_n$[19] and M[{HB(mtda^R)$_3$}]$_n$.[3,4]

Table 1. Selected bond lengths [Å] and angles [deg] of compound **1**.

Na(1)–S(1)	2.817(2)	Na(2)–S(4)–Na(1)	81.7(1)
Na(1)–S(4)	3.061(2)	O(1)–Na(1)–O(2)	91.9(1)
Na(2) –S(4)	2.867(1)	O(1)–Na(1)–S(1)	108.9(1)
Na(1)–S(5)	2.925(2)	O(2)–Na(1)–S(1)	88.4(1)
Na(1)–O(1)*	2.329(2), 2.405(2)	O(1)–Na(1)–S(4)	166.7(1)
Na(2)–O(2)	2.395(2)	O(2)–Na(1)–S(4	82.9(1)
Na(1)–O(2)	2.432(2)	S(1)–Na(1)–S(4)	83.3(1)
Na(2)–O(3)	2.399(2)	O(2)–Na(2)–S(4)	87.9(1)
Na(3)–N(7)	2.627(2)	O(3)–Na(2)–S(4)	103.6(1)
Na(3)–O(4)	2.382(2)	O(4)–Na(3)–O(5)	86.0(1)
Na(3)–O(5)	2.424(2)	O(4)–Na(3)–N(7)	90.2(1)
		O(5)–Na(3)–N(7)	93.2(1)
		N(7)–Na(3)–N(7A)	180.0

*bridging function

The molecular structure of **2a** is shown in Figure 2. The compound crystallizes in the monoclinic space group $P2_1$. In contrast to **1**, there is only one potassium atom per asymmetric unit with the coordination environment KHN$_2$S$_2$O$_2$. Pairs of potassium ions are linked via bridging water ligands leading to K$_2$O$_2$ rhombi arranged about inversion centres, these rhombi are arranged about the glide plane *n* to a coordination polymer. Each Janus scorpionate ligand (ttt^{Me})$^-$ coordinates to three potassium atoms: to one in the coordination mode κ^3-*H,S,S* via H(1), S(1) and S(2), to the second in κ^2-*N,N* mode via N(2) and N(10), and to the third in κ^1-*N* mode via N(11). This linkage results in a sheet-like structure. The sheets are perpendicular to the axis $10\bar{1}$. Additionally there is a solvent water molecule present. Overall hydrogen contacts perform within the sheet: H1(A)···N(6) (2.16(2) Å), H(1B)···O(2) (1.95(2) Å), and between H(2D)···S(2) (2.48(2) Å) and H(2E)···S(3) (2.56(2) Å).

Table 2. Selected bond lengths [Å] and angles [deg] of compound **2a**.

K(1)–O(1)*	2.749(1), 2.736(1)	O(1)–K(1)–O(1A)	82.9(1)
K(1)–S(1)	3.344(1)	O(1)–K(1)–S(2)	148.1(1)
K(1)–S(2)	3.299(1)	H(1)–K(1)–S(2)	59.9(3)
K(1)–H(1)	2.79(2)	H(1)–K(1)–S(1)	55.6(3)
K(1)–N(2)	2.970(2)	S(1)–K(1)–S(2)	77.4(1)
K(1)–N(10)	3.070(1)	O(1)–K(1)–S(1)	71.7(2)
K(1)–N(11)	3.433(2)	N(2)–K(1)–N(10)	63.9(2)
		N(2)–K(1)–S(2)	74.1(2)
		N(2)–K(1)–S(1)	139.8(1)
		N(10)–K(1)–S(2)	136.7(2)
		N(10)–K(1)–S(1)	143.8(2)

*bridging function

In contrast to **1**, a B–H···K interaction with a distance of 2.79(2) Å was found. The K–S and K–N bond lengths are provided in Table 2 and are within the range found for related K–S (3.05 – 3.73 Å) and K–N distances (2.31– 3.58 Å), respectively.[3] The same applies for the B–H···K distance, which is shorter than the average value reported for related interactions (range 2.43 – 3.34

Å).[3] The typical Janus behaviour of the ligand can be further compared with our recent report on M(tr^{Me}).[19] The anion (tr^{Me})$^-$ is a Janus scorpionate ligand based on triazole units with similar methyl substituent. In contrast, M(tr^{Me}) exhibits a non-polar polymeric structure in variance to the sheet-like structure of **2a**.

Compound **2b** crystallizes in the orthorhombic space group *Pccn*. Similar to compound **2a** it exhibits a sheet-structure perpendicular to the *b* axis. There are B–H···K interactions with a H···K distance of 2.71 Å, i.e. slightly stronger than in **2a**. Each potassium ion in the sheet has the coordination number 8 (compared to CN = 7 found in **2a**) with a coordination sphere comprising $KH_2S_4N_2$. The four ligands surrounding each potassium ion adopt two times κ^3-*H,N,S* and two times κ^1-*S* coordination modes. In turn, each ligand is connected to four potassium atoms. A slight disorder of 7 % of the molecules describes a change of the coordination mode from κ^3-*H,N,S* to κ^1-*S* and vice versa. Both sulphur atoms function as bridges to the next potassium ion resulting in the described sheet aggregation. The K–S and K–N bond lengths are in the range between 3.290(5) and 3.377(5) Å and between 3.021(2) and 3.033(16) Å, respectively. These bond lengths are comparable with those in 2a. Important bond angles are listed in Table 3; they reveal a distorted environment about the potassium ion.

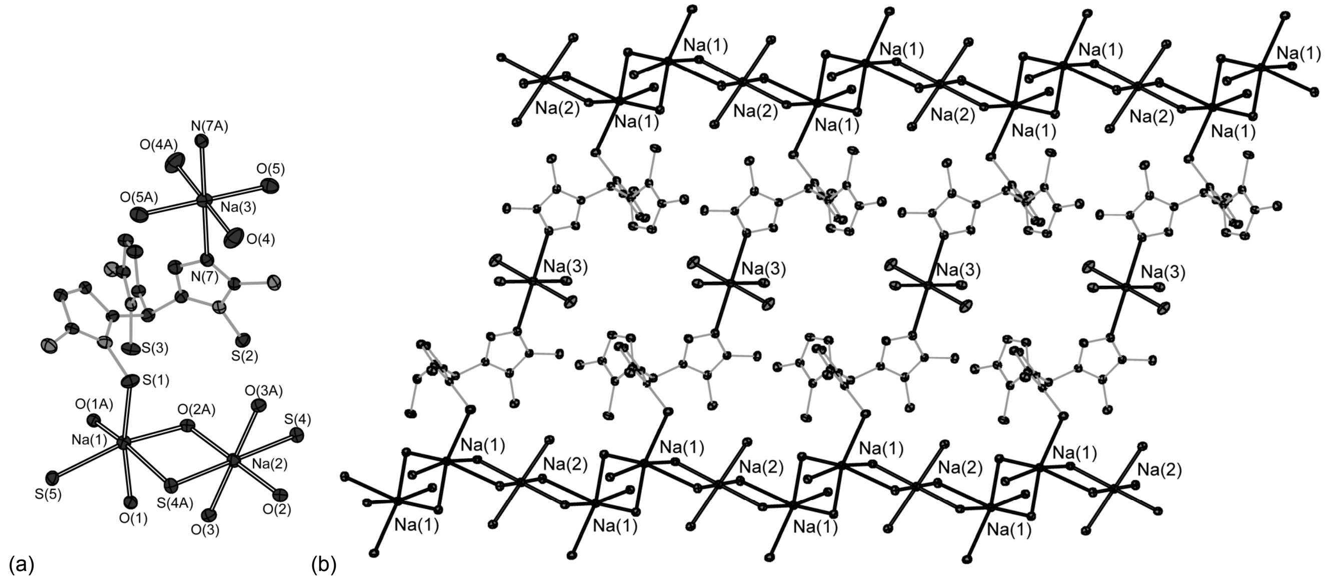


Figure 1. (a) Part of the sheet structure of Na(ttt^{Me})·6H_2O (**1**·6H_2O), displacement ellipsoids drawn at 50 % level (b) sheet structure of Na(ttt^{Me})·6H_2O (**1**·6H_2O), displacement ellipsoids drawn at 30 % level for clarity.

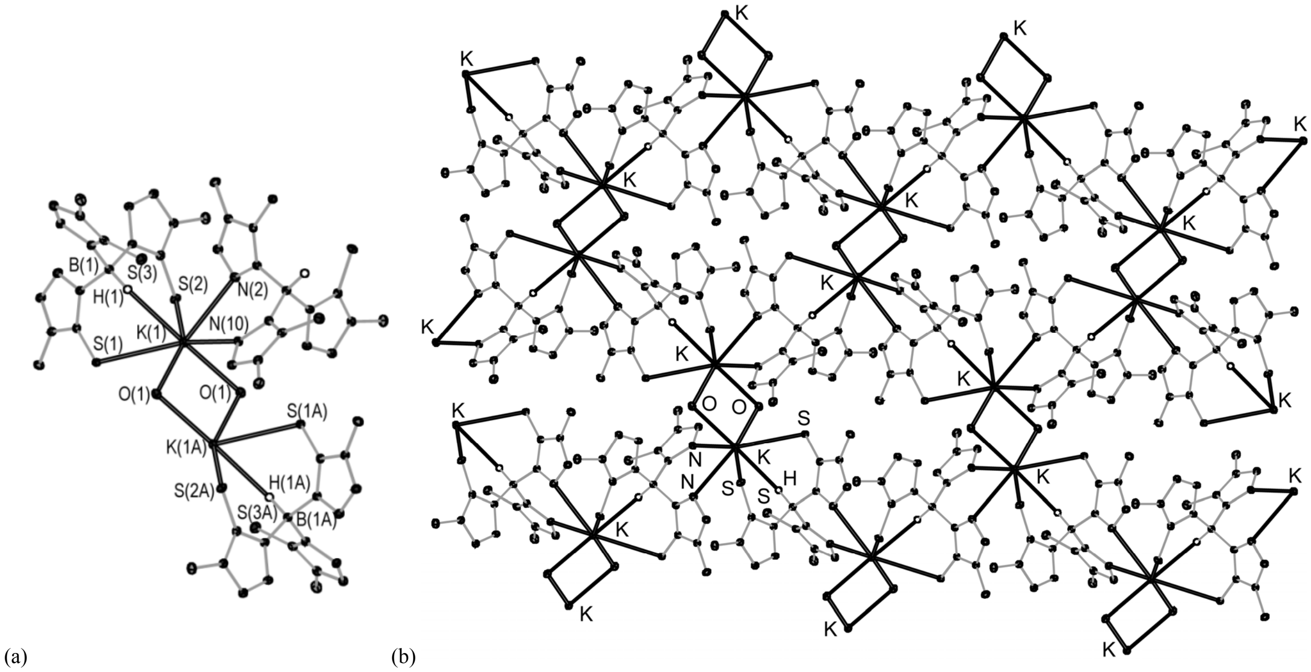


Figure 2. (a) Part of the sheet structure of K(ttt^{Me}) (**2a**) (b) sheet structure of K(ttt^{Me}) (**2a**), displacement ellipsoids drawn at 30 % level.

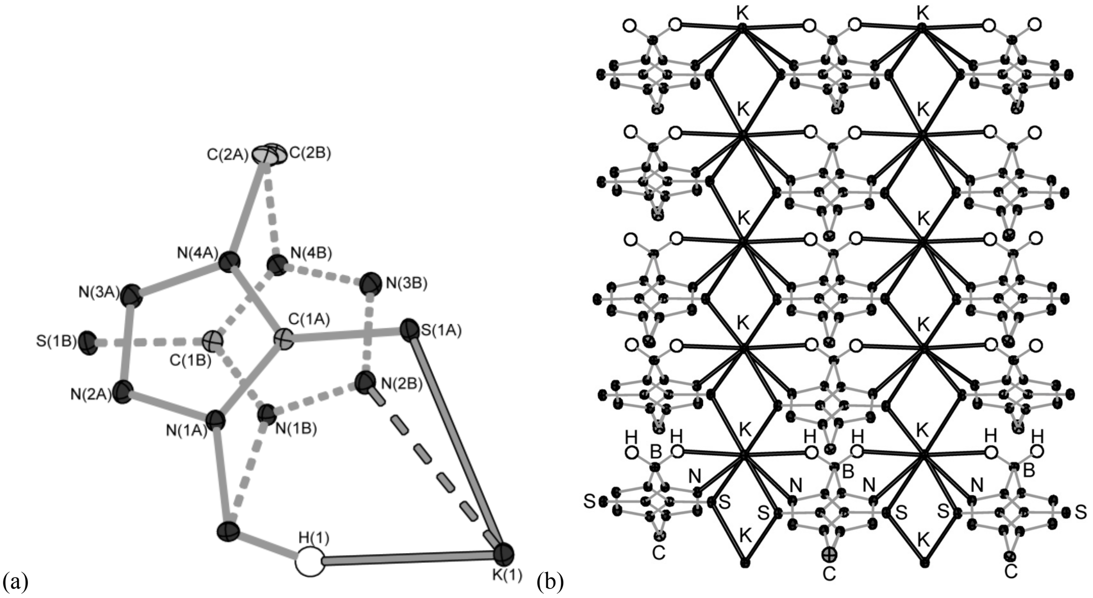


Figure 3. (a) Monomeric part of the K(btt^{Me}) network (**2b**) with the disordered part of the structure shown with dotted lines (see text) (b) part of the sheet like structure of K(btt^{Me}) (**2b**), displacement ellipsoids drawn at 30 % level.

Table 3. Selected bond lengths [Å] and angles [deg] of compound **2b**.

K(1)–S(1A)*	3.297(1), 3.356(1)
K(1)–S(1B)*	3.290(5), 3.377(5)
K(1)–N(2A)	3.021(1)
K(1)–N(2B)	3.033(16)
K(1)–H(1)	2.71(2)
S(1A)–K(1)–S(1A')	98.2(2) – 128.9(2)
S(1B)–K(1)–S(1B')	97.8(2) – 128.7(2)
N(2B)–K(1)–S(1B)	66.8(4) – 164.5(4)
N(2A)–K(1)–S(1B)	66.8(1) – 164.3(1)
K(1)–S(1A)–K(1')	80.6(1)
H(1)–K(1)–H(1')	174.5(7)

*bridging function

Compound **4** crystallizes in monoclinic space group $P2_1/c$. It represents a polymeric chain aggregate running along the *a* axis (Figure 4). The sodium ions adopt the coordination number 8 and are part of $NaH_2S_2N_2O_2$ units. Each (btt^{Ph})$^-$ ligand coordinates to two sodium ions, to each with coordination mode κ^3-H,N,S. Moreover, two water ligands are terminally bound to each sodium ion and makes links to the next chain via H···S contacts (H(2B)–S(2) 2.35(6) Å, H(1D)–S(1) 2.48(2) Å). The bond lengths Na(1)–N(6) 2.634(3) Å and Na(1)–N(2) 2.637(3) Å are equal within experimental error. The Na–S bonds have different lengths, 2.941(2) Å to S(2) and 3.081(2) Å to S(1) (Table 4). The Na–O bonds between 2.302(3) and 2.465(3) Å in length are similar to the corresponding values of $[Na(H_2O)_6][Na(tt)_2]$ (tt = hydrotris-(thioxotriazolyl)borate), where water ligands are terminally bound. The structure has also similarity regarding the parameter values of our recent report on Na(bt^{Me}).[20] Na(bt^{Me})[20] and **4**, both exhibit polymeric structures, however, the Na–S bond lengths and B–H···Na distances of **4** are comparatively longer than those of Na(bt^{Me})[20] but are within the range reported by Silva et al. for related distances.[3]

Table 4. Selected bond lengths [Å] and angles [deg] of compound **4**.

Na(1)–S(1)	3.081(2)
Na(1)–S(2)	2.941(2)
Na(1)–N(6)	2.634(3)
Na(1)–N(2)	2.637(3)
Na(1)–H(1A)	2.83(1)
Na(1)–H(1B)	2.97(1)
Na(1)–O(1)	2.465(3)
Na(1)–O(2)	2.302(3)
O(2)–Na(1)–O(1)	83.6(2)
O(2)–Na(1)–N(6)	90.3(2)
O(1)–Na(1)–N(6)	123.7(2)
O(2)–Na(1)–S(1)	138.3(2)
O(1)–Na(1)–S(1)	71.4(2)
N(6)–Na(1)–S(1)	77.5(2)

The molecular structure of bismuth complex **5** established from X-ray crystallography is shown in Figure 5 and its important bond lengths and angles are tabulated in Table 5. The complex is monomeric with coordination number 7 at the bismuth ion. Its coordination environment comprises five sulphur atoms from two Janus scorpionate ligands (ttt^{Me})$^-$ and two oxygen atoms from a bidentate acetate group forming a core of BiS_5O_2. Both (ttt^{Me})$^-$ ligands coordinate in different modes. One is linked to the bismuth atom in an usual tridentate fashion via three sulphur atoms (κ^3-*S,S,S*) while the second is bound in (κ^2-*S,S*) mode. The κ^3-*S,S,S*-bound ligand makes different Bi–S bond lengths 2.924(2), 2.797(2) and 2.996(2) Å from the atoms S(1), S(2) and S(3), respectively. Similarly the Bi–S bond lengths involving S(4) and S(5) of the (κ^2-*S,S*)-bound ligand are also different at 2.844(2) and 2.789(1) Å, respectively. The structural parameters can be compared with our recent report on $Bi(tr^{Me})(Cl)(\mu\text{-}Cl)_2]_2$ (tr^{Me} = Janus scorpionate based on triazole unit).[19] The latter is a dimeric complex and with both ligands adopting κ^3-*S,S,S* binding modes. The Bi–S bonds in **5** are longer than those in $Bi(tr^{Me})(Cl)(\mu\text{-}Cl)_2]_2$,[19] but can be compared with other scorpionate-based monomeric bismuth complexes.[5,17,21-23] Bi(1)–O(1) and Bi(1)–O(2) bond lengths are 2.495(3) and 2.361(3) Å, respectively, and the O–Bi–O angle is 53.6(2)°, this is comparable to the metrics of other bismuth-bound bidentate acetate ligands in $[Bi(CH_3COO)_3\{SC(NH_2)_2\}_3]$.[24] It is important to mention that the S–Bi–S angles involving the ligand with κ^3 mode deviate from 90° (range: 83.4(2) – 89.9(2)°) while the S(4)–Bi(1)–S(5) angle involving the κ^2-mode ligand is 90.0(1)°. The inter-ligand S–Bi–S angles span over a range from 74.2(2) to 169.7(2)°. In contrast to the above described potassium complexes, there is no evidence for a B–H···Bi interaction, as the B─H bonds are more than 4 Å away from the bismuth ion.

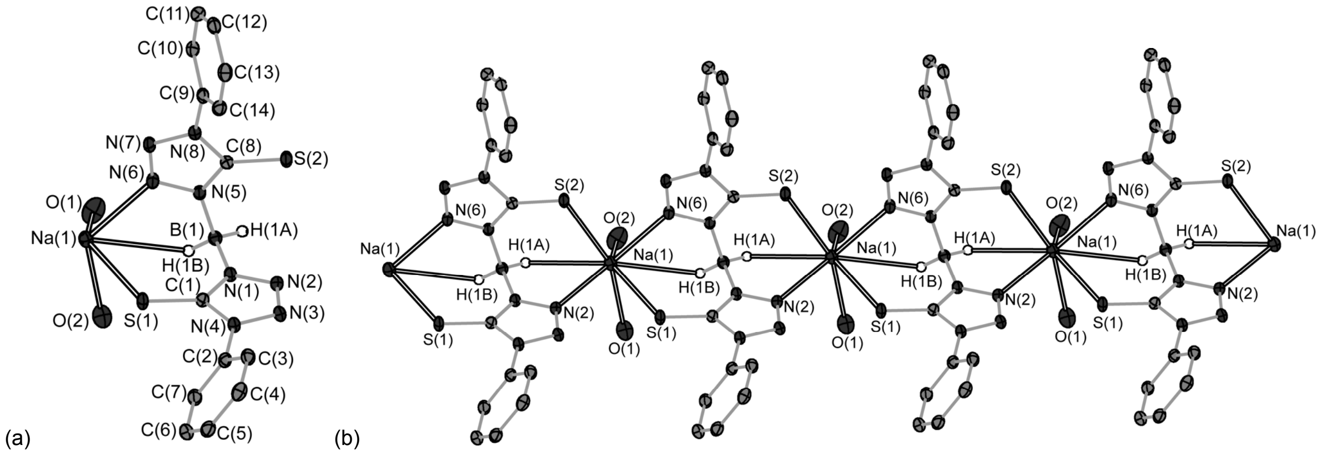


Figure 4. (a) Monomeric part of Na(btt^{Ph}) (**4**) (b) part of the polymeric chain aggregate of Na(btt^{Ph}) (**4**), displacement ellipsoids are drawn at 30 % level.

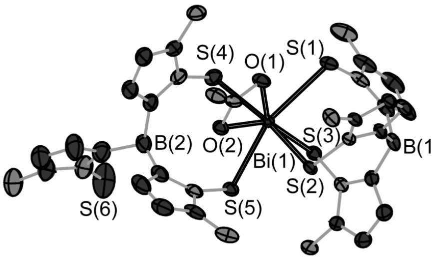


Figure 5. Structure of the bismuth complex [Bi(ttt^{Me})$_2$CH$_3$COO] (**5**). Displacement ellipsoids are drawn at 50 % level.

Table 5. Selected bond lengths [Å] and angles [deg] of compound **5**.

Bi(1)–S(1)	2.924(2)	S(1)–Bi(1)–S(3)	83.4(1)
Bi(1)–S(2)	2.797(2)	S(2)–Bi(1)–S(1)	89.9(2)
Bi(1)–S(3)	2.996(1)	S(2)–Bi(1)–S(3)	89.0(2)
Bi(1)–S(4)	2.844(2)	S(2)–Bi(1)–S(4)	169.7(1)
Bi(1)–S(5)	2.789(1)	S(4)–Bi(1)–S(1)	97.3(1)
Bi(1)–O(1)	2.495(3)	S(4)–Bi(1)–S(3)	99.1(1)
Bi(1)–O(2)	2.361(3)	S(5)–Bi(1)–S(1)	157.2(1)
		S(5)–Bi(1)–S(2)	86.0(1)
		S(5)–Bi(1)–S(3)	74.2(1)
		S(5)–Bi(1)–S(4)	90.0(1)
		O(2)–Bi(1)–O(1)	53.6(1)

Single crystals of compound **6** were obtained from THF and acetonitrile solutions in the form of THF (**6a**) or acetonitrile solvates (**6b**). In both crystals the Bi_2L_4 units are located at a crystallographic centre of symmetry, but the structures are not iso-structural. **6a** crystallizes in the space group *C*2/*c*, **6b** in $P\bar{1}$.

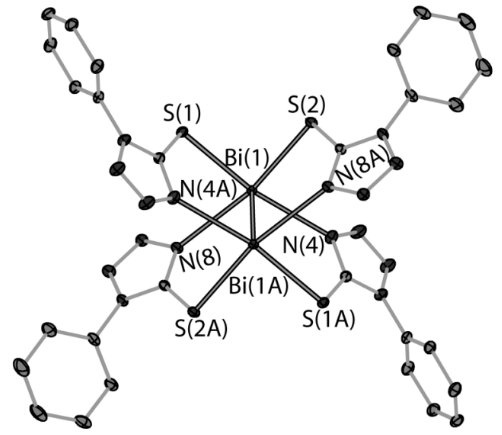


Figure 6. Structure of the bismuth complex $[Bi(L^2)_2]_2$ (**6a**). Displacement ellipsoids are drawn at 30 % level. Hydrogen atoms and solvent molecules have been removed for clarity. Molecular structure representation of **6b** is same as that of **6a**.

Figure 6 shows the molecular structure of compound **6a**. Each ligand behaves in a bidentate chelating manner and coordinates to one bismuth centre through its nitrogen and to the second with its sulphur donor atom resulting in a distorted square pyramidal environment around each bismuth atom defined by the core BiN_2S_2. The Bi–Bi distances in **6a** and **6b** are 3.037(1) Å and 3.045(1) Å, respectively. They may be compared with that in the related dinuclear Bi(II) compound $Bi_2(O_2CCF_3)_4$ with bridging trifluoroacetato ligands (Bi–Bi 2.947 (1) Å.[25] It can also be compared with the slightly shorter and unsupported Bi–Bi bond of 2.990(2) Å in Bi_2Ph_4.[26] All these Bi–Bi bonds are shorter than the Bi–Bi distances in elemental bismuth at 3.071(1) Å.[26,27] The Bi–S bond lengths are in the ranges 2.668(2) – 2.723(2) Å for **6a** and 2.684(2) – 2.700(2) Å for **6b** and are comparable with those in $[BiL^1{}_4Cl_2][BiL^1{}_2Cl_4]$ (L^1 = 2-mercapto-benzimidazole).[20] The

Bi(1)–N(4) and Bi(1)–N(8) bonds for **6a** and **6b** vary within the ranges 2.596(3) – 2.657(3) Å and 2.635(4) – 2.689(3) Å, respectively, and are otherwise normal lengths. The angles around the bismuth atom in **6b** (Table 6) reveal a more distorted square pyramidal geometry compared to **6a**.

The molecular structure of complex **7** is shown in Figure 7. It crystallizes in the trigonal space group $P3c1$ with $Z = 6$. Each of the three different bismuth atoms resides on the special position of a crystallographic three-fold axis making the molecules adopting exact three-fold symmetry; they are stacked like bowls along the polar *c* axis. The complexes are monomeric, the intermolecular Bi···S distances are in the range of 3.132(1) to 3.159(1) Å, the intermolecular Bi···Bi distance along c is 3.908(1) Å. Each bismuth atom is surrounded by hemisphere arrangement of three mono-anionic bidentate ligands (L^2H) via their N and S donor atoms (Figure 7b). Bi–S and Bi–N cover the range 2.672(2) – 2.692(2) Å and 2.823(4) –2.866(4) Å, respectively (Table 7). The sum of covalent and van der Waals radii for nitrogen and bismuth are 2.27 Å and 3.94 Å, respectively.[28] S–Bi–S bond angles are between 87.3(1) °and 88.1(1)°. N–Bi–N angles are 120.0(1)° resulting in an almost perfect trigonal planar coordination by nitrogen; the maximum deviation out of this plane is 0.051(3) Å for Bi(3).

Table 6. Selected bond lengths [Å] and angles [deg] of compounds **6a** and **6b**

6a		**6b**	
Bi(1)–Bi(1A)	3.037(1)	Bi(1)–Bi(1A)	3.045(1)
Bi(1)–S(1)	2.668(2)	Bi(1)–S(1)	2.700(2)
Bi(1)–S(2)	2.723(2)	Bi(1)–S(2)	2.684(2)
Bi(1)–N(4)	2.657(3)	Bi(1)–N(4)	2.635(4)
Bi(1)–N(8)	2.596(3)	Bi(1)–N(8)	2.689(3)
S(1)–Bi(1)–Bi(1A)	96.7(2)	S(1) Bi(1)–Bi(1A)	93.9(1)
S(2)–Bi(1)–Bi(1A)	94.3(2)	S(2)–Bi(1)–Bi(1A)	95.6(1)
S(2)–Bi(1)–S(1)	89.4(2)	S(2)–Bi(1)–S(1)	86.6(1)
S(2)–Bi(1)–N(8)	172.3(2)	S(2)–Bi(1)–N(8)	162.9(2)
S(1)–Bi(1)–N(8)	87.6(2)	S(1)–Bi(1)–N(8)	79.1(1)
S(1)–Bi(1)–N(4)	173.6(2)	S(1)–Bi(1)–N(4)	163.9(1)
N(4)–Bi(1)–N(8)	90.9(2)	N(4)–Bi(1)–N(8)	111.7(2)

Table 7. Selected bond lengths [Å] and angles [deg] of compound **7**.

Bi(1)–S(1)	2.692(2)
Bi(2)–S(2)	2.673(2)
Bi(3)–S(3)	2.672(2)
Bi(1)–N(1)	2.823(4)
Bi(2)–N(2)	2.866(4)
Bi(3)–N(3)	2.848(4)
S–Bi(1)–S	88.1(3)
S–Bi(2)–S	87.8(2)
S–Bi(3)–S	87.3(2)
N–Bi(1-3)–N	120.0(1)

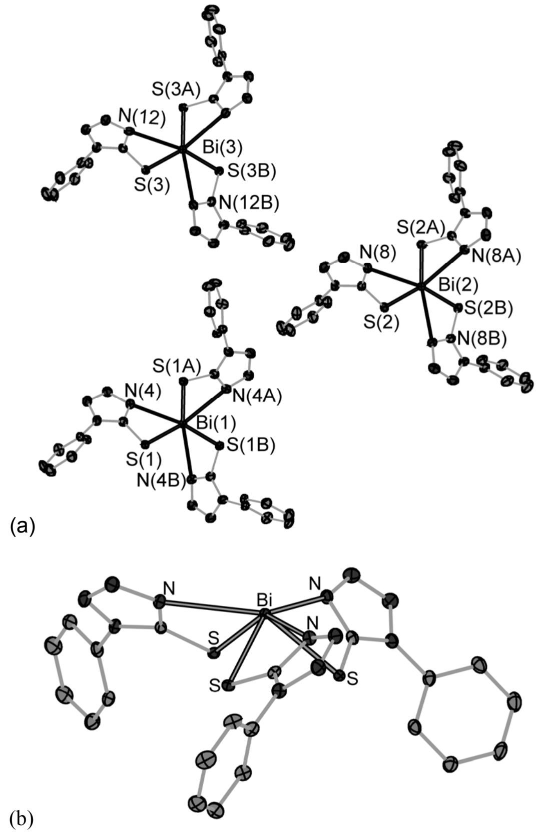


Figure 7. (a) Structures of the three molecules in the asymmetric unit of crystals of bismuth complex $[Bi(L^2)_3]$ (**7**). Displacement ellipsoids are drawn at the 30 % level (b) hemisphere arrangement of ligands around bismuth atom

NMR spectroscopy and mass spectrometry

Compounds **1** – **3** were further characterized in solution by NMR studies using dimethylsulfoxide-*d6* (dmso-*d6*) and dimethyformamide-*d7* (dmf-*d7*) as solvents. The ^{1}H NMR spectrum of **1** in dmso-*d6* exhibits a singlet at 3.78 ppm that can be assigned to the hydrogen atoms of the methyl group. In its ^{13}C NMR spectrum two resonances at 33.8 and 167.6 ppm can be attributed to the methyl and thione units, respectively. The other two compounds, **2a** and **3**, show very similar chemical shifts in their respective ^{1}H and ^{13}C NMR spectra (for details see experimental section). This observation leads to the conclusion that these compounds are dissociated in dmf and dmso solutions and the ions are solvated. This dissociation behaviour of **1**, **2b** and **3** was investigated by ^{1}H-diffusion experiments. The diffusion co-effecients were compared to that of Na(tr^{Me})[19], which was used as reference compound and is predominantly dissociated in dmso solution. The data are given in Table 8. Compounds **1**, **3** and Na(tr^{Me}), (all are tri-substituted species) have almost similar diffusion coefficients indicating that the ligand ions are well separated from the alkali metal ions. Compared to these data of tri-substituted species **1**, **3** and Na(tr^{Me}), the diffusion co-efficient of compound **2b** ($3.09 \cdot 10^{-10}$) is higher, because **2b** is a di-substituted species having smaller size. Negative mode ESI–MS spectra contain a molecular ion peak at $m/z = 356$, indicating the existence as monomers instead of chain/sheet aggregates.

The ^{1}H NMR spectrum of **4** in dmso-*d6* shows two sets of signals. A doublet at 7.89 ppm is assigned to the protons at C2 and C6. A multiplet at 7.60 – 7.48 ppm can be attributed to the other ring protons at C3, C4, and C5. ^{13}C NMR spectra of **1** – **4** were also recorded and the chemical shift values of different carbon atoms are given in experimental section. Common to these spectra is the characteristic resonance of the thione unit in the range between 166.8 and 168.0 ppm.

Table 8. Diffusion coefficients of complexes **1**, **3**, **2b**, Natr^{Me} and **5**

Compound	solvent	Diffusion coefficient (m^{2}s^{-1})
1	dmso-*d6*	$2.19\cdot10^{-10}$ (CH$_3$)
3	dmso-*d6*	$2.16\cdot10^{-10}$ (CH$_3$)
2b	dmso-*d6*	$3.09\cdot10^{-10}$ (CH$_3$)
Natr^{Me} (reference)	dmso-*d6*	$1.77\cdot10^{-10}$ (CH$_3$)
1	dmf-*d7*	$1.235\cdot10^{-9}$ (CH$_3$)
5	dmf-*d7*	$5.15\cdot10^{-10}$ (CH$_3$), $4.90\cdot10^{-10}$ (CH$_3$)

^{1}H NMR and ^{13}C NMR data of complex **5** were recorded in CDCl$_3$ solution. The methyl resonance **5** is shifted to 3.88 ppm compared to 3.92 ppm for the free ligand. Similarly the C═S resonance appears at 162.6 ppm, i.e. downfield compared to that of the free ligand (165.0 ppm), indicating coordination of the thione units. The ^{1}H NMR spectrum of **5** in dmf-d7 exhibits two methyl resonances at 4.00 and 4.10 ppm. The diffusion coefficient determined using the resonance at 4.00 is with $5.15\cdot10^{-10}$ slightly higher than the value of $4.90\cdot10^{-10}$, determined at the resonance at 4.10. This indicates the existence of two species exhibiting slightly different hydrodynamic radii. From these data it can be concluded that complex **5** dissociates in dmf according to following equation.

$$[\mathrm{Bi(ttt^{Me})_2CH_3COO}] \underset{-\mathrm{dmf}}{\overset{+\mathrm{dmf}}{\rightleftarrows}} [\mathrm{Bi(ttt^{Me})}]^+ + [\mathrm{ttt^{Me}}]^- + \mathrm{CH_3COO}^-$$

ESI-MS spectrum of **5**, exhibits molecular ion peaks at m/z = 922.9, which can be attributed to a [(ttt^{Me})$_2$Bi]$^+$ fragment similar to that observed for the related compounds [Bi(tr^{Et,Me})$_2$]$^+$ and [Bi(tt)$_2$]$^+$.[21] NMR and other analytical data of complexes **6** and **7** have also been recorded and are given in experimental section.

Conclusion

We describe here two novel boron-centred soft ligands (ttt^{Me})$^-$ and (btt^{Ph})$^-$ and their coordination modes towards Na, K and Bi(III) ions. The anion (ttt^{Me})$^-$ is a typical Janus scorpionate ligand and exhibits versatile coordination modes κ^3-*H,S,S,* κ^3-*S,S,S;* κ^2- *S,S,* κ^1- *S* and κ^2- *N, N* in sodium, potassium and bismuth complexes. In contrast to other related alkali metal Janus scorpionates,[3,4,19] Na(ttt^{Me}) (**1**) and K(ttt^{Me}) (**2**) exhibit sheet-like structures and have better solubility in common protic solvents. The reaction of Na(btt^{Ph}) (**4**) with Bi(III) ions yielded a complex (**6**) of Bi(II) with a short Bi–Bi bond. The proposed reduction ability of Na(btt^{Ph}) with a BH$_2$ unit contrast the behaviour of Na(ttt^{Me}) (**1**) with BH unit and opens a new dimension to investigate further bismuth-hydride activation or possible Bi→B dative bond formation.

<<A part on photo-physical measurement has to be included here>>

Acknowledgement

We are thankful to Gerd Lipinski, Klaus-Peter Mester for recording NMR spectra and to Brigitte Michel for elemental analyses. M. I. acknowledges with special thanks the Deutscher Akademischer Austausch Dienst (DAAD) for providing a PhD stipend.

Experimental work

All solvents used during this work were dried and distilled before use. KBH$_4$, NaBH$_4$, 1-methyl-5-thiotetrazole (L^{1}H), 1-phenyl-5-thiotetrazole (L^{2}H) and Bi(CH$_3$COO)$_3$ were procured from Alfa Aesar, Acros Organic and used without further purification. NMR spectra were recorded on Bruker Avance 300, Bruker DRX 500 or Bruker Avance 500 spectrometers and the chemical shifts were referenced to the residual proton (^{1}H) or the carbon signals of the deuterated solvents and are reported in ppm. Diffusion NMR measurements have been performed by using the LED sequence with bipolar gradients (ledbpgp2s) delivered by the manufacturer. For these experiments the probe was disconnected from the gas supply and the sample was allowed to thermally equilibrate for four hours within the probe/magnet prior to recording data. The duration of the gradients was incremented linearly in 16 steps. The diffusion coefficients have been calculated by using the relaxation module of the Bruker software TOPSPIN®. Elemental analyses were performed using a EuroEA Elemental Analyser. ESI-MS spectrum was measured using Esquire 3000 (Bruker Daltonik 2000) spectrometer. Melting points were determined using a Büchi B 545 melting point apparatus and are uncorrected. All operations were carried out in an inert atmosphere of nitrogen using Schlenk and glove box techniques unless otherwise stated. Described methods with certain modifications were followed for the synthesis of alkali metal scorpionates.[3,19]

Na(ttt^{Me}) (**1**): NaBH$_4$ (0.192 g, 5.45 mmol) and 1-methyl-5-thiotetrazole (2.09 g, 18.0 mmol) were ground separately and then mixed with a magnetic stirrer bar in a Schlenk flask connected to a gas bubbler. The resulting mixture was heated to 160 °C in an oil bath for 2 h. In the course of the reaction gas evolution was observed at 118 °C, which enhanced vigorously at 130 °C and finally ceased at 160 °C. This mixture was further heated to 160 °C for 1 h and then cooled to room temperature. The solid obtained was washed with toluene (3 × 25 mL), CHCl$_3$ (3 × 25 mL), diethyl ether (3 × 20 mL) and then dried under vacuum. Yield: 1.40 g, 67 %; colourless powder; m.p. 236–238 °C (with decomposition). NMR studies were performed with the product obtained before recrystallization and represent data of this water-free material. ^{1}H NMR (dmso-*d6*) δ = 3.78 (s, 9H, H$_3$C); ^{13}C NMR (dmso-*d6*) δ = 167.6 (C═S), 33.8 (H$_3$C); ^{11}B NMR (dmso-*d6*) δ = –6.51 (br); ^{1}H NMR (dmf-*d7*) δ = 4.0 (s, 9H, H$_3$C); ^{13}C NMR (dmf-*d7*) δ = 167.9 (C═S), 33.2 (H$_3$C); ^{11}B NMR (dmf-*d7*) δ = –6.3 (br); ^{1}H NMR (CDCl$_3$) δ = 3.93 (s, 9H, H$_3$C); ^{13}C NMR (dmso-*d6*) δ = 165.0 (C═S), 33.9 (H$_3$C); ESI-MS (negative mode) *m/z* = 356.8 [(ttt^{Me})]$^-$. Single crystals of **1**·6H$_2$O (for X-ray diffraction) were obtained by slow evaporation of a mixture of water/thf/toluene (ratio 1:5:4) of **1**. Anal. of these crystals calcd for $C_{12}H_{20}B_2Na_2N_{24}S_6\cdot6H_2O$ (found): C 16.59 (16.54), H 3.71 (3.54), N 38.71 (38.15).

K(ttt^{Me}) (**2a**): Method A: This compound was prepared by reacting KBH$_4$ (0.277 g, 5.14 mmol) and 1-methyl-5-thiotetrazole (2.09 g, 18.0 mmol) according to same procedure as described above for **1**. Gas evolution was observed when the oil bath reached 120 °C and ceased at 160 °C. The resulting mixture was further heated to 160 °C for 1 h and then cooled to room temperature. Yield 0.62 g, 32 %, colourless powder, m.p: above 300 °C with decomposition. NMR studies were performed with the product obtained before crystallization and represent the water-free material. ^{1}H NMR (dmso-*d6*) δ = 3.78 (s, 9H, H$_3$C); ^{13}C NMR (dmso-*d6*) δ = 167.4 (C=S), 33.9 (H$_3$C); ^{1}H NMR (dmf-*d7*) δ = 3.85 (s, 9H, H$_3$C); ^{13}C NMR (dmf-*d7*) δ = 168.2 (C=S), 33.2 (H$_3$C); ESI-MS (negative mode) *m*/*z* = 356.9 [(ttt^{Me})$^{-}$]. Single crystals of **2a**·2H$_2$O were obtained by slow evaporation of a mixture of water/thf/toluene (ratio 1:5:4) of **2a**.Anal. of these crystals calcd for $C_6H_{10}BKN_{12}S_3\cdot 2H_2O$ (found): C 15.89 (16.37), H 2.67 (3.32), N 37.07 (37.28).

Method B: KBH$_4$ (0.304 g, 5.75 mmol) and 1-methyl-5-thiotetrazole (2.09 g, 18.0 mmol) were mixed together and 50 mL of toluene were added. The reaction mixture was heated to reflux at 130 °C for 12 h. Hydrogen evolution was observed. The reaction mixture was allowed to cool to room temperature. The resulting solid was washed with small amounts of toluene and ether and then dried. Yield 1.47 g, 63 %, colourless powder, no m.p. determined due to decomposition above 300 °C. Anal. calcd for $C_4H_8N_8S_2BK.H_2O$ (found): C 16.00 (16.19), H 3.36 (3.76), N 37.33 (36.98); ^{1}H NMR (dmso-*d6*) δ = 3.72 (s, 9H, H$_3$C); ^{13}C NMR (dmso-*d6*) δ = 167.0 (C=S), 33.8 (H$_3$C); ^{11}B NMR (dmso-*d6*) δ = −11.4 (br); Crystals suitable for X-ray diffraction were obtained by slow evaporating the thf solution of **2b** from a sample vial with holes in its plastic lid at around 4 °C in a refrigerator.

KNa(ttt^{Me})$_2$ (**3**). (0.038 g, 0.1 mmol) of Na(ttt^{Me}) (**1**) and (0.040 g, 0.1 mmol) K(ttt^{Me}) (**2a**) were dissolved in a 30 mL of thf. The mixture was stirred with heating at 95 °C for 4 h. The resulting solution was filtered hot and first slowly cooled to room temperature, followed by keeping in refrigerator resulting in the precipitation of colourless solid. The solid obtained was isolated by filtration and then washed with diethyl ether (3 × 10 mL), *n*-pentane (2 × 10 mL), and finally dried under vacuum. Yield 0.037 g, 94 %; colourless powder; m.p. 320 – 324 °C; ^{1}H NMR (dmso-*d6*) δ = 3.78 (s, 9H, H$_3$C); ^{13}C NMR (dmso-*d6*) δ = 167.6 (C=S), 33.8 (H$_3$C); ^{11}B NMR (dmso-*d6*) δ = –6.8 (br); ^{1}H NMR (dmf-*d7*) δ = 3.83 (s, 9H, H$_3$C); ^{13}C NMR (dmso-*d6*) δ = 168.2 (C=S), 32.9 (H$_3$C); ESI-MS (negative mode) *m*/*z* = 356.9 [(ttt^{Me})$^{-}$].

Na(btt^{Ph}) (**4**). 1-Phenyl-5-thiotetrazole (20.0 mmol, 3.56 g) and NaBH$_4$ (10.0 mmol, 0.375 g) were ground, mixed and then dissolved in 20 mL of freshly distilled thf. The resulting solution was heated to 55 °C for 8 h. Evolution of hydrogen gas was observed through gas bubbler. The clear solution obtained was filtered, concentrated under vacuum and then cooled in a refrigerator overnight. A colourless precipitate formed which was filtered, washed with small amounts of toluene, diethyl ether and finally dried under vacuum. The solid was further re-crystallized from hot toluene. Yield 2.52 g, 66 %; m.p. 224 – 226 °C (with decomposition); Anal. calcd. for $C_{14}H_{12}BN_8NaS_2\cdot H_2O$ (found): C 41.19 (41.91), H 3.46 (3.20), N 27.45 (27.70); ^{1}H NMR (dmso-*d6*) δ = 7.89 – 7.92 (dd, 2H, C2H, C6H), 7.48 – 7.60 (m, 3H, C3H–C5H); ^{13}C NMR (dmso-*d6*) δ = 166.8 (C=S), 135.6 (C1), 129.4(C2, C6) 129.1 (C3, C5) 124.7(C4); ^{11}B NMR (dmso-*d6*) δ =−12.1 (br);); ^{1}H NMR (dmso-*d6*) δ = 8.02 – 8.06 (dd, 2H, C2H, C6H), 7.49 – 7.63 (m, 3H, C3H–C5H); ^{13}C NMR (dmso-*d6*) δ = 166.9 (C=S), 136.1 (C1), 129.0 (C2, C6) 128.6 (C3, C5) 124.2 (C4); ESI-MS (negative mode) *m*/*z* = 367.0 [(btt^{Ph})$^{-}$]. Crystals suitable for diffraction were obtained by slow evaporation of **4** from a mixture of THF in refrigerator.

[Bi(ttt^{Me})$_2$CH$_3$COO] (**5**). Na(ttt^{Me}) (**2a**) (0.288 g, 0.760 mmol) was dissolved in 20 mL of acetonitrile. Bi(CH$_3$COO)$_3$ (0.146 g, 0.380 mmol) was also dissolved in 20 mL of acetonitrile along with addition of 2mL of dmf. Then the solution of **2a** was slowly added to that of Bi(CH$_3$COO)$_3$ solution under N$_2$ atmosphere. The resulting orange yellow solution was stirred at room temperature for 4 h and then filtered. The solvent was removed under vacuum resulting in the precipitation of an orange solid. This solid was re-dissolved in 10 mL of chloroform and filtered. To the resulting filtrate was added 30 mL of *n*-hexane. An orange solid precipitated, was filtered, washed with *n*-hexane and dried in vacuum. This extraction procedure was repeated two times. Yield 0.248 g, 68%; m.p. 250 – 254 °C (with decomposition); ^{1}H NMR (CDCl$_3$) δ = 3.88 (s, 9H, H$_3$C-ttt^{Me}), 2.08 (s, CH$_3$-acetate); ^{13}C NMR (CDCl$_3$) δ = 162.6 (C=S), 33.5 (CH$_3$-ttt^{Me}), 31.5 (CH$_3$-acetate); ^{1}H NMR (dmf-*d7*) δ = 4.10 (s, H$_3$C-complex **5**) 4.00 (s, H$_3$C-ttt^{Me} (free ligand); ^{13}C NMR (dmf-*d7*) δ = 167.9 (C=S), 33.2 (H$_3$C), not observed (CH$_3$-acetate); ESI-MS *m*/*z* = 922.9 [Bi(ttt^{Me})$_2$$^{+}$]. HRMS calcd for $C_{12}H_{20}N_{24}S_6B_2Bi^{+}$ (found): 923.06101 (923.06115) (dev. 0.15 ppm). Crystals suitable for X-ray diffraction were obtained by slow diffusion of *n*-pentane into a chloroform solution of **5**.

Bi(btt^{Ph})$_n$ (**6**). In two experiments, using two different solvents thf and CH$_3$CN, this complex was prepared according to the same procedure as described above by reacting Na(btt^{Ph}) (0.253 g, 0.650 mmol) and Bi(CH$_3$COO)$_3$ (0.125 g, 0.325 mmol); the resulting compounds are [Bi(L^2)$_2$]$_2$·0.5THF **6a** and [Bi(L^2)$_2$]$_2$·2CH$_3$CN **6b**, respectively. Single crystals of compound **6a** and **6b** were obtained from thf (**6a**) and acetonitrile solutions (**6b**) by keeping their respective solutions for several weeks refrigerated in a Schlenk flask. Both crystals are red. Analysis was carried out on **6a**. Complex **6b** was characterized solely by single crystal X-ray diffraction. Yield 0.227 g, 61 %; m.p. 115 – 117 °C (with decomposition); Anal. calcd. for $C_{28}H_{20}Bi_2N_{16}S_4\cdot 2C_4H_8O$ (found): C 34.02 (33.89), H 2.85 (3.13), N, 17.63 (18.18), S 10.06 (10.46), ^{1}H NMR(CDCl$_3$) δ = 7.52 – 7.76 (m, 5H, C2H–C6H); ^{13}C NMR (dmso-*d6*) δ = 155.1 (C=S), 140.6 (C1), 133.0 (C2),130.3 (C6), 129.5 (C3), 124.0 (C5) 121.1(C4); ESI-MS(+) *m*/*z* = 943 [BiL$_4$]$^{+}$.

6a was dissolved in small amount of acetonitrile and placed for slow evaporation at room temperature. After few days yellow crystals appeared that were analysed by XRD as [Bi(L^2)$_3$] (**7**). Yield 0.115 g, 50 %; m.p. 278 – 280 °C (with decomposition); Anal. calcd. for $C_{21}H_{15}BiN_{12}S_3$ (found) : C 34.06 (33.52), H 2.04 (2.06), N, 22.70 (22.25), ^{1}H NMR (CDCl$_3$) δ = 7.86 – 7.89 (dd, 2H, C2H, C6H), 7.52 – 7.61 (m, 3H, C3H–C5H);^{13}C NMR (dmso-*d6*) δ = 161.9 (C═S), 133.2 (C1), 130.4(C2, C6) 129.5 (C3, C5) 124.0(C4).

Luminescence activity

For luminescence activity, these compounds are under investigation in co-operation with Dr. Uwe Monkowius, Linz, Austria. Outcome of these investigations will be included in this manuscript accordingly.

X-ray Crystallographic Analysis. X-ray diffraction data were collected for **1**, **2a**, **2b**, **4**, **5**, **6a**, **6b** and **7**. Single-crystals suitable for X-ray diffraction were picked under inert paratone oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer. Data sets for **1** and **2a** were collected on a Bruker Nonius Kappa CCD diffractometer using Mo-K$_\alpha$ radiation, while data sets for compounds **4** and **7** were collected using a Bruker AXS Kappa (APEX II) with Cu-K$_\alpha$ radiation. Data sets for **2b**, **5** and **6** were collected on a Super Nova using Mo-K$_\alpha$ radiation. A summary of data collection and structure refinement is reported in Table 9. The structures were solved by Direct Methods and refined by full-matrix least squares cycles (programs SHELXS-97 or SHELXL-97).[29] CCDC 981804 – 981811 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 9. X-ray crystallographic data for compounds **1**, **2a**, **2b**, **4**, **5**, **6a**, **6b** and **7**

Compound	**1**	**2a**	**2b**	**4**	**5**	**6a**	**6b**	**7**
empirical formula	$C_{12}H_{32}B_2N_{24}Na_2O_6S_6$	$C_6H_{14}BKN_{12}O_2S_3$	$C_4H_8BKN_8S_2$	$C_{14}H_{16}BN_8NaO_2S_2$	$C_{14}H_{23}B_2BiN_{24}O_2S_6$	$C_{30}H_{24}Bi_2N_{16}S_4O_{0.5}$	$C_{32}H_{26}Bi_2N_{18}S_4$	$C_{21}H_{15}BiN_{12}S_3$
M_r	868.58	432.38	282.21	426.27	982.52	1162.85	1208.91	740.61
T (K)	100(2)	100(2)	100.0(1)	100(2)	100.0(1)	100.0(1)	100.0(1)	100.0(1)
crystal system	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic	trigonal
space group	$P\bar{1}$	$P2_1/n$	$Pccn$	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P3c1$
a (Å)	9.3355(2)	8.8211(1)	7.23114(12)	7.1466(2)	16.5137(3)	23.6264(3)	7.07185(17)	24.0122(6)
b (Å)	12.8329(3)	16.1067(1)	17.5695(3)	6.1686(2)	11.80455(11)	6.72789(5)	11.5039(4)	24.0122(6)
c (Å)	15.7966(3)	12.8346(1)	8.60830(15)	43.2407(11)	19.3087(2)	24.3264(2)	13.7591(5)	7.8167(2)
α (°)	83.0920(13)	90	90	90	90	90	67.741(3)	90
β(°)	89.0734(15)	103.1234(6)	90	92.392(1)	104.4135(14)	95.9510(8)	89.501(2)	90
γ(°)	85.1892(11)	90	90	90	90	90	78.825(2)	120
Z	2	4	4	4	4	4	1	6
V (Å^3)	1872.06(7)	1775.90(3)	1093.67(3)	1904.58(9)	3645.50(9)	3845.97(6)	1013.72(6)	3903.17(17)
F(000)	896	888	576	880	1920	2200	574	2136
crystal size (mm)	0.30 x 0.11 x 0.04	0.30 x 0.28 x 0.16	0.13 × 0.05 × 0.05	0.24 x 0.15 x 0.09	0.34 × 0.22 × 0.04	0.36 × 0.11 × 0.08	0.53 × 0.10 × 0.05	0.26 x 0.09 x 0.04
refl measured	16165	71800	59018	12737	240962	241494	59206	52485
unique refl	8547	5164	1592	3598	10616	5650	5928	5043
R_{int}	0.037	0.037	0.038	0.023	0.057	0.057	0.053	0.029
no of param	525	282	102	265	457	226	283	395
R_1 ($I > 2\sigma(I)$)	0.0399	0.0248	0.0264	0.0507	0.0311	0.0232	0.0260	0.0176
wR_2 (all refl)	0.1057	0.0659	0.0588	0.1155	0.0829	0.0604	0.0656	0.0484
Goodness-of-fit	1.030	1.036	1.208	1.286	1.053	1.191	1.158	1.215
$\rho_{\text{max/min}}$ (e Å^{-3})	0.37/–0.36	0.32/–0.29	0.39/–0.20	0.55/–0.41	1.44/–2.35	2.76/–1.68	3.63/–1.46	1.11/–0.63
CCDC-No.	981804	981805	981806	981807	981808	981809	981810	981811

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Manuscript-6

Crystallographic report on a dihydrobis(2-mercapto-4-methylthiazolyl)borate) mixed-ligand bismuth complex [Bi(bt^{Me})(phen)Cl$_2$]

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[Bi(bt^{Me})(phen)Cl$_2$] (bt^{Me} = dihydrobis(2-mercapto-4-methylthiazolyl)borate) is a mixed-ligand bismuth complex possessing a $BiS_2N_2Cl_2$ core with distorted octahedral environment constituted by two sulphur atoms from the dipodal boron-centred soft ligand (bt^{Me})$^-$, two nitrogen atoms of phenanthroline and two chloro ligands.

Key words: bismuth, mixed-ligand complex, soft ligand

Comment:

Heterocycle-disubstituted boron centred soft ligands such as dihydrobis(methimazolyl)-borate (bm),[1] dihydrobis(2-thiopyridone)borate (bmp)$^-$,[2] dihydrobis(thioxotriazolyl)-borate(bt)$^-$,[3–4] and dihydrobis(1-methyl-5-thiotetrazolyl)borate (btt^{Me})$^-$[5] etc. have been used to complex different metal ions in order to find new substances for applications in radiopharmaceutical and bio-inorganic chemistry.[5–8] The ligand (bt^{Me})$^-$ is also a di-substituted boron-centred soft ligand and exhibits (κ^2-*S,S*) coordination mode in our recently reported complex [Bi(bt^{Me})$_3$], a compound emissive in solid state at λ_{max} = 674 nm.[9] The title complex [Bi(bt^{Me})(phen)Cl$_2$] is a mixed-ligand complex based on (bt^{Me})$^-$ as primary ligand with phenanthroline and chloro co-ligands.

Experimental:

The title complex was prepared by reacting together $BiCl_3$ (0.157 g, 0.5 mmol) and phenanthroline (0.09 g, 0.5 mmol) followed by the slow addition of [Na(bt^{Me})] (0.147 g, 0.5 mmol, [Na(bt^{Me})] was prepared as described in our recent report.[9] The resulting mixture was stirred at room temperature for 3 h and then filtered. The solvent was removed in a rotary evaporator and the resulting solid was washed with small amount of methanol and *n*-pentane. Crystals suitable for X-ray diffraction were grown by slow evaporation of a chloroform solution of complex. Yield 0.230 g, 62 %, colour: dark red, m.p. 137 °C, ^{1}H NMR ($CDCl_3$) δ = 9.21 (4H, dd, H(2,9)), 8.26 (4H, dd, H(4,7)), 7.81 (4H, s, H(5,6)), 7.64 (4H, dd, H(3,8)), 6.17 (s, 2H, CH), 2.20 (s, 6H, H_3C); ^{13}C NMR ($CDCl_3$) δ = 187.1 ($C{=}S$), 150.4 (C2, C9), 146.2 (C1a, C10a), 139.8 (CH-bt^{Me}), 136.0 (C4, C7), 128.7 (C4a, C6a), 127.0 (C5, C6), 123.1 (C3, C8), 108.9 ($C\text{-}CH_3$), 17.4 (H_3C).

X-Ray diffraction data were recorded at 100(2) K using a Nonius Kappa CCD diffractometer. Empirical formula $C_{22}H_{20}BBiCl_8N_4S_4$; M_r 972.05, crystal system triclinic, space group $P\bar{1}$, *a* 10.1151(2) (Å), *b* 10.3285(2) (Å), *c* 17.4505(3)(Å), α 99.166(2)°, β 102.910(2)°, γ 110.150(2)°, *Z* 2, *V* 1611.70(5) Å^3, *F*(000) 936, crystal size (mm) 0.24 x 0.10 x 0.04, reflections measured 38133, unique reflections (R_{int}) 7371(0.070), $R_1(I>2\sigma(I))$ 0.0290, wR_2 (all data) 0.0646, $\rho_{\text{max/min}}$ (e Å^{-3}) 1.44/–1.37, Programs used.[11,12]

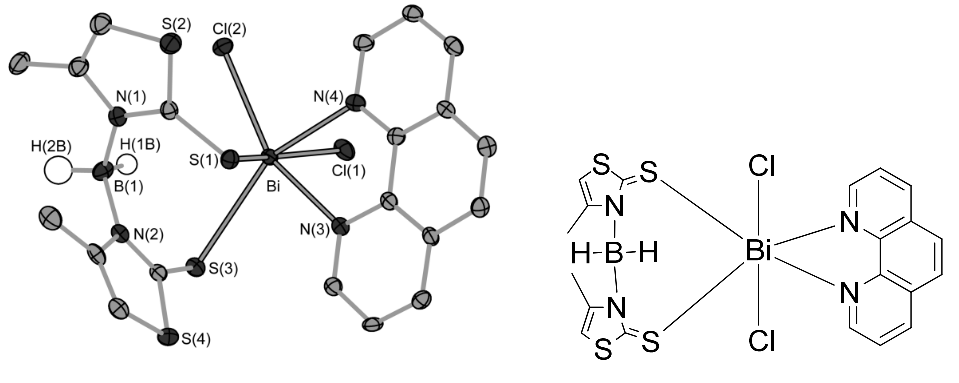

Figure 1. Molecular structure of [Bi(bt^{Me})(phen)Cl_2]; hydrogen atoms except (B–H) have been omitted for clarity; displacement ellipsoids are drawn at 50 % level. Selected important structural parameter values: Bi–S(1) 2.740(1), Bi–S(3) 2.993(1), Bi–N(3) 2.483(3), Bi–N(4) 2.480(3), Bi–Cl(1) 2.708(1), Bi–Cl(2) 2.667(1), S(1)–Bi–S(3) 89.9(1)°, N(3)–Bi–N(4) 67.4(1)°, Cl(1)–Bi–Cl(2) 93.7(1)°, Cl(2)–Bi–S(1) 92.0(2)°, Cl(2)–Bi–S(3) 119.9(1)°, Cl(1)–Bi–S(1) 161.0(1)°, Cl(1)–Bi–N(3) 91.3(1)°, Cl(1)–Bi–N(4) 80.9(1)°, N(3)–Bi–S(1) 75.3(1)°, N(3)–Bi–S(3) 86.3(1)°, N(4)–Bi–S(1) 81.5(1)°, N(4)–Bi–S(3) 153.6(1)°.

Acknowledgement:

M. I. acknowledges with special thanks the Deutscher Akademischer Austausch Dienst (DAAD) for providing a PhD stipend.

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Manuscript-7

Monomeric bismuth complex with 2-mercapto-4-phenylthiazole $[Bi(C_9H_6NS_2)_3]$

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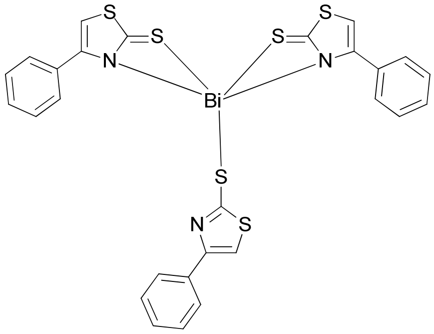
The title compound was prepared by reacting $BiCl_3$ and 2-mercapto-4-phenylthiazole (LH) at room temperature in a stochiometric ratio 1:4 respectively. The molecular structure reveals a distorted square pyramidal geometry around bismuth atom. Two of three monoanionic ligands behave as bidentate while one shows monodentate mode of coordination revealing coordination umber 5 of bismuth atom. Bi–S bond lengths are 2.608(1), 2.594(1), 2.555(1) to the atoms S(1), S(3) and S(5), respectively. Bi–N bond lengths are 2.797(2) and 2.734(2) to N(1) and N(2), respectively.



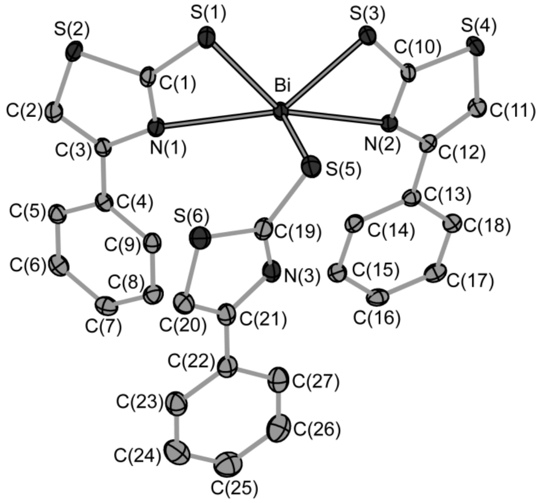


Figure 1. Molecular structure of the title compound

Literature:

For general background on this type of bismuth chemistry with S or N,S donor ligands: see Battaglia et al. (1981, 1983, 1992), Diemer et al. (1995), Stavila et al. (2006), Briand et al. (2000). For further structural parameter comparison, see related bismuth complexes with heterocyclic (N,S) ligands reported by Mitzel et al. (2013, 2014).

Experimental

Crystal data

$[Bi(C_9H_6NS_2)_3]$

M_r = 785.78

crystal system = triclinic, $P\bar{1}$

a (Å) =9.19758(16)

b (Å) = 10.8904(2)

c (Å)= 14.6041(2)

α(°) = 82.0966(15)

β(°) = 78.5197(14)

γ(°) = 70.9346(17)

Z = 2

V (Å^3) = 1350.77(4)

crystal size (mm) = 0.12 × 0.06 × 0.03

Data collection:

Super Nova diffractometer with Atlas detector

reflections measured = 25693,

unique reflections (R_{int}) = 5325 (0.021)

Refinement:

$R_1(I>2\sigma(I))$ = 0.0143,

wR_2 (all reflections) = 0.0356

$\rho_{\mathrm{max/min}}$ (e Å^{-3}) = 0.49/-0.62

Programs used:

SHELXL (2008), OLEX2: (2009).

Acknowledgement:

M. I. acknowledges with special thanks the Deutscher Akademischer Austausch Dienst (DAAD) for providing a PhD stipend.

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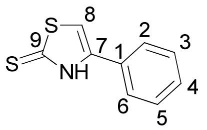
Supplementary data

Synthesis:

The title compound was prepared by reacting $BiCl_3$ (1 mmol, 0.315 g) and 2-mercapto-4-phenyl thiazole (LH) (4 mmol, 0.773 g) in THF at room temperature. After stirring for four hours, the resulting yellow solution was concentrated, a yellow solid was obtained. The resulting solid was seperated by decantation and then washed with small amount of THF followed by diethyl ether. The solid was dried and again re-crystallized from a mixture of THF/pentane (ratio 1:3). Crystals suitable for difraction were obtained by slow evaporation of the THF solution of complex. Yield 76 %; m.p, 234 °C; color yellow. ^1H NMR ($CDCl_3$) δ = 7.58 – 7.60 (dd, 2H, C2H, C6H), 7.42 – 7.49 (m, 3H, C3H–C5H), 6.78 (CH–thiazole ring); ^{13}CNMR ($CDCl_3$) δ = 188.5 (C9), 142.5 (C8), 129.9 (C2,6), 129.4 (C3,5), 128.1(C4), 125.9(C1), 108.9(C7). For numbering, see structure below



Comment

Coordination chemistry of bismuth has been studied in detail with thiourea and thio-semi carbazide ligands by Battaglia et al., (1981, 1983, 1992).Thio-urea were found to be only S donor while thio-semi carbazide showed N,S coordination mode. Recently we have reported the coordination modes of three heterocyclic ligands (3-mercapto-4-methyl-1,2,4-triazole (L^1H), 2-mercapto-benzimidazole (L^1H) and 2-mercapto-4-methylthiazole (L^3H) in their respective three bismuth complexes $[Bi(L^1H)_4(Cl)_2]Cl)$, $[Bi(L^2H)_4Cl_2][Bi(L^2H)_2Cl_4]$ and $[Bi(L^3H)_2Cl_2(\mu\text{-}Cl)]_2$ (Mitzel et al., 2013, 2014). These ligands have coordinated via their sulphur donor atoms inspite of N,S possibility. In the title compound, the ligand LH (2-mercapto-4-phenyl thiazole)exhibits both S and N,S coordination modes contrast to our recent studies (Mitzel et al., 2013, 2014). Two among the three ligands coordinate in bidentate fashion (via N,S) while the third one exhibit monodentae mode via S donor atom (after deprotonation) resulting a distorted square pyramidal geometry.