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Heavier alkali metal complexes of 2-phenylamidopyridine: An X-ray crystallographic and theoretical study of a structurally diverse series of crown ether adducts**

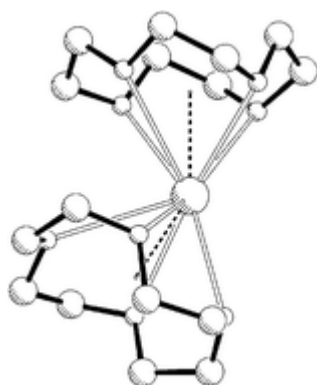Stephen T. Liddle,[1] William Clegg[1],* and Carole A. Morrison[2]

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Graphical abstract:

Abstract

Complexes of the anion of the secondary amine 2-phenylaminopyridine (LH) with the heavier alkali metals Na–Cs have been prepared in the presence of various macrocyclic polyether crowns [12-crown-4 (12C4), 15-crown-5 (15C5), and 18-crown-6 (18C6)], which coordinate to the metal ions in all cases. Depending on the combination of alkali metal and crown, the products include separated ion pairs [(crown)$_2$M]$^+$L$^-$ (12C4/Na, 15C5/K, 15C5/Rb, 15C5/Cs) and contact-ion-pair neutral molecules [(crown)ML] (15C5/Na, 18C6/Na, 18C6/K, 18C6/Rb) in which L$^-$ acts as a bidentate ligand. [{(12C4)KL}$_2$] is a dimer in which the amido and pyridine N atoms of two ligands bridge the metal ions, while [{(18C6)KL$_2$K}$_\infty$] is a chain polymer with crown O and pyridyl N atoms acting as bridges in corner-sharing KOKN four-membered rings. [{(18C6)Cs$_2$L$_2$}$_\infty$] is also polymeric, with a basic arrangement like that of [{(12C4)KL}$_2$], but with each 18C6 ligand μ-κ^6:κ^6 to two metal centres, generating the polymer. Although most of the [(crown)$_2$M]$^+$ sandwich cations have essentially parallel crown ligands, [(12C4)$_2$Rb]$^+$ is markedly bent, both in the complex incorporating THF as an additional ligand and in the THF-free complex, where two of these cations form a centrosymmetric dimer through two bridging oxygen atoms; DFT calculations indicate that the bending is inherent, thus enabling the coordination by an extra oxygen atom rather than being a consequence of this coordination. Attempts to isolate the caesium 12C4 derivative were unsuccessful. The compounds have been characterized by NMR spectroscopy, CHN microanalysis and, in most cases, X-ray crystallography.

Introduction

The structure and reactivity of alkali metal derivatives of alkyls, enolates, imides, and amides has received considerable attention over the past two decades.[1] The widespread synthetic utility of these compounds as ligand transfer reagents, and their widespread applications in organic synthesis,[2] have led to structural investigations revealing a rich and diverse collection of structural motifs ranging from monomeric to polymeric species.[3] However, while a search of the Cambridge Structural Database (November 2003 release)[4] reveals a plethora of structural data available on lithium amides, the number of structural reports of heavier alkali metal complexes diminishes rapidly as the group is descended, though reports are now becoming more prevalent. Since the metal-amide bonding is essentially ionic in nature, and more so for the heavier congeners, the structures adopted are highly dependent upon the alkali metal (charge-to-radius ratio, polarisation), the electronic and steric properties of the substituents at the anionic donor centre, and the presence, or absence, of neutral Lewis base co-ligands. Given that the coordination of additional donor ligands to alkali metals generally improves their reactivity by reducing the extent of aggregation, we have become interested in combining alkali metal amides with matched or mismatched crown ethers to investigate the structural consequences for the solid-state structures adopted as a consequence of variation of the crown. We previously reported structural investigations of alkali metal complexes of the secondary amide 2-trimethylsilylamidopyridine with 12-crown-4 (12C4), 15-crown-5 (15C5) and 18-crown-6 (18C6), which revealed a range of structural motifs including monomer, dimer, separated 'ate' ion pairs, heterobimetallic separated ion triplets, and polymers, as well as four instances of N–Si cleavage.[5] In these studies, only the alkali metal or

crown was varied. More recently, we have sought systematically to prepare and characterise alkali metal complexes with other, closely related, amides in order to investigate structural changes brought about by substitution of the trimethylsilyl group, in conjunction with a change in the metal or co-ligand. In a preliminary study of the 12C4 adducts of alkali metal complexes of the closely related secondary amide 2-phenylamidopyridine (L),[6] we found that deprotonation of the parent amine in the presence of 12C4 was not as trivial as initially expected, rendering the fully metallated lithium salts inaccessible. Furthermore, the amide exhibited a pronounced tendency to exist as the uncomplexed anion, in direct contrast to 2-trimethylsilylamidopyridine, demonstrating the steric and electronic differences between the two amides. A number of homometallic alkali metal complexes of 2-phenylamidopyridine have previously been reported,[7] revealing a variety of coordination modes for the anion, and in general aminopyridine complexes have found widespread applications as supporting ligands for main group (*s* and *p* block), lanthanide and transition metals.[8] Here we report the synthesis and characterisation of twelve new heavier alkali metal complexes of 2-phenylamidopyridine with matched and mismatched crown ethers (**1–12**), which exhibit a remarkable degree of structural diversity.

$[Na(12C4)_2]^+(L^-)$ (**1**) $[Na(L)(15C5)]$ (**2**) $[Na(L)(18C6)]$ (**3**)

$[\{K(L)(12C4)\}_2]$ (**4**) $[K(15C5)_2]^+(L^-)$ (**5**) $[\{K(18C6)K(L)_2\}_\infty]$ (**6**)

$[Rb(12C4)_2(THF)]^+(L)^-$ (**7**) $[\{Rb(12C4)_2\}_2]^{2+}(L^-)_2$ (**8**) $[Rb(15C5)_2]^+(L^-)$ (**9**)

$[Rb(L)(18C6)]$ (**10**) $[Cs(15C5)_2]^+(L^-)$ (**11**) $[\{Cs(18C6)Cs(L)_2\}_\infty]$ (**12**)
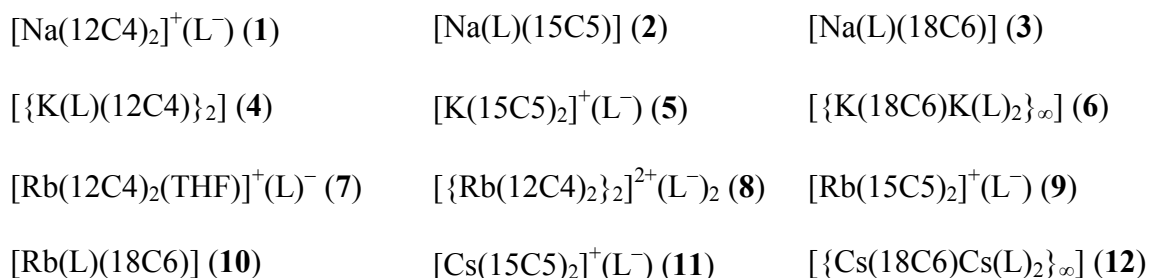
Results and Discussion

Synthesis and Characterisation

We previously reported that, in the presence of 12C4, we could not fully metallate LH by lithiation and, followed by metathesis, achieved instead a consistent formation of the half-deprotonated complex $[\{Na(12C4)_2\}^+\{L^-\cdot L(H)\}]$.[6] The use of sodium hydride also repeatedly resulted in the isolation of the same complex in high yields. In contrast, we find that direct metallation of LH by *in situ* formed methyl-sodium, followed by addition of 12C4, gives $[\{Na(12C4)_2\}^+(L^-)]$ (**1**) in excellent yield as air- and moisture-sensitive yellow crystals after recrystallisation from hot THF. In direct contrast to these observations, we find that a lithiation-metathesis protocol *is* effective when 15C5 and 18C6 are employed instead of 12C4. Thus, metathesis of sodium *tert*-butoxide with a preformed solution of LH, one equivalent of Bu^nLi, and the appropriate crown ether affords, after recrystallisation, the fully metallated complexes [Na(L)(crown)] [crown = 15C5 (**2**); 18C6 (**3**)] as air- and moisture-sensitive yellow crystals in good yields.

Direct metallation of LH by potassium hydride in the presence of 12C4 in refluxing benzene, in contrast to the sodium case, gives the fully metallated potassium complex $[\{K(L)(12C4)\}_2]$ (**4**) in excellent yield as air- and moisture-sensitive yellow blocks. The use of potassium hydride is particularly beneficial, as it allows 'clean' access to the desired potassium amide and avoids the synthesis of methyl-potassium. It is also essential for success, as a metathesis protocol does not generate the desired complex; as in the sodium case, a lithiation-metathesis protocol repeatedly gives

$[\{K(12C4)_2\}^+\{L^-\cdot L(H)\}]$.[6] The synthesis of $[\{K(15C5)_2\}^+(L^-)]$ (**5**) and $[\{K(18C6)\}_\infty K(L)_2]$ (**6**) is readily accomplished by direct metallation with potassium hydride in the presence of either two equivalents of 15C5, or one equivalent of 18C6, in an aromatic solvent; in fact **5** and **6** are always formed and isolated preferentially, irrespective of the amount of crown ether employed. Once formed, **5** is only soluble in refluxing THF and **6** is only soluble in refluxing toluene or THF. However, in contrast to **4**, and analogous to **2** and **3**, **5** and **6** are also readily accessible *via* metathesis of a preformed solution of LH, one equivalent of Bu^{n}Li, and the appropriate crown ether with potassium *tert*-butoxide, in excellent yields as yellow air- and moisture-sensitive crystals.

In contrast to these results for sodium and potassium, on descending the group to rubidium, we find that metathesis of rubidium-2-ethylhexoxide with a preformed solution of LH, one equivalent of Bu^{n}Li, and the appropriate crown ether proceeds smoothly affording the rubidium amides $[\{Rb(12C4)_2(THF)\}^+(L^-)]$ (**7**), $[\{Rb(12C4)_2\}^+(L^-)]$ (**8**), $[\{Rb(15C5)_2\}^+(L^-)]$ (**9**), and $[Rb(L)(18C6)]$ (**10**) in good yields as dark yellow air- and moisture-sensitive crystals. The formation of **7** or **8** is dictated by the solvent(s) employed; thus, **7** is obtained from cold ($-30°$C) THF, whereas **8** is obtained from cold ($-30°$C) toluene/HMPA. The lithium alkoxide by-product is extremely soluble, even in hydrocarbons, and can thus easily be removed by washing with petrol. Complex **7**, containing THF, is soluble in aromatic and ether solvents, whereas **8** (THF-free **7**) requires overnight stirring with HMPA to afford dissolution in aromatic solvents. Complex **9** is, as for **5**, only soluble in refluxing THF, whereas **10** is soluble in hot toluene. The coordinated THF in **7** is weakly bound and is readily removed by prolonged exposure to vacuum, as illustrated by (i)

elemental analysis, which is correct for solvent-free **7** (i.e. the same as **8**), and (ii) the visual degradation of crystalline samples *in vacuo*.

Complexes $[\{Cs(15C5)_2\}^+(L^-)]$ (**11**) and $[\{Cs(18C6)Cs(L)_2\}_\infty]$ (**12**) are readily synthesised by metathesis of caesium-2-ethylhexoxide with a preformed solution of LH, one equivalent of Bu^nLi, and the appropriate crown ether. They show marked differences to the other complexes with respect to solubilities; **11** is soluble in toluene at room temperature, whereas **12** requires an excess of HMPA (~3:1 molar ratio) and refluxing in aromatic solvents or THF. All attempts, to date, to synthesise a caesium complex with 12C4 have resulted in intractable viscous oils, of which satisfactory characterisation and analysis has not been possible; this is indicative of an ill-defined product, and this is perhaps not surprising given the unfavourable host-guest fit, despite our previously successful isolation of the closely related complex $[\{Cs(PyNSiMe_3)(12C4)\}_2].^{[5d]}$

The ^1H and ^{13}C NMR solution spectra of all complexes are in accord with the solid-state structures in terms of integrated ratios of amide:crown, and corroborate the 2:1 ratio of L to 18C6 in **6** and **12** and the unexpected absence of HMPA in **8** and **12**. However, the NMR spectra are, unsurprisingly, uninformative as to the precise structures adopted by complexes **1–12**, consequently X-ray crystallographic studies of the complexes were performed. Unfortunately, although crystals of **11** and **12** were obtainable, they were repeatedly of poor quality and served only to confirm the chemical composition and gross structural features. Satisfactory CHN microanalyses were obtained for all complexes **1–12**.

Solid State Structures

The molecular structure of **1** is shown in Figure 1 and selected bond lengths and angles for this and the other structures can be found in Table 1. The complex crystallises as a separated ion pair. The sodium cation is sandwiched between two 12C4 molecules (one of which is two-fold disordered) in a staggered conformation exhibiting pseudo-D_{4d} symmetry. The Na–O bond lengths span the range 2.404(6)–2.510(6) Å, which compares favourably with previously reported examples such as $[\{Na(12C4)_2\}\{L.L(H)\}]$,[6] the lutetium aqua complex $[\{Na(12C4)_2\}\{Lu(H_2O)_8\}(Cl)_4].H_2O$,[9] and $[\{Na(12C4)_2\}(ClO_4)]$.[10] The sodium cation lies 1.457–1.483 Å from the mean plane of the oxygen atoms of each crown, and the crown-sodium-crown bending angle (measured as the dihedral angle between the two oxygen mean planes) is 2.3 or 3.8° (for the two disorder components). The anion is isolated and shows no significant intermolecular contacts. To the best of our knowledge, this is the first structurally authenticated example of the free 2-phenylamidopyridine anion, and is an indication of the stabilisation of this anion by resonance delocalisation; this is in marked contrast to the 2-trimethylsilylamidopyridine anion, which is yet to be observed as a free anion, and which is coordinated to sodium in the closely related complex $[\{Na(12C4)_2\}\{Na(PyNSiMe_3)_2(THF)\}]$.[5d] The anion is disordered by exchange of the phenyl and pyridyl rings, so that observed bond lengths and angles are averages of those appropriate for the two different orientations. In both, the orientation of the pyridyl ring is such as to avoid close H…H contact between the two *ortho*-H atoms of the rings; this represents a rotation of the pyridyl ring by approximately 180° from the orientation necessary for the anion to act as a chelating ligand. Because of the lack of

unfavourable H…H interactions, it is essentially planar, with a dihedral angle of 3.0°

between the two rings, allowing for extensive orbital overlap across the whole anion.

The bond angle of 125.8(3) at the amido N atom is in good agreement with that

observed previously for the anion hydrogen-bonded to its parent amine.[6]

The structure of **2** is shown in Figure 2. The complex crystallises as a contact ion pair,

with the anion coordinated to sodium; there is also half a molecule of toluene in the

asymmetric unit. The sodium cation is seven-coordinate with five Na–O and two Na–

N bonds; the amide occupies one coordination hemisphere and the 15C5 the other.

The Na–O bond lengths span the range 2.4874(9)–2.5321(9) Å, within the ranges

reported for the β-diketonate complex $[Na\{HC[C(O)CF_3]_2\}(15C5)]$[11] and for the

related complex $[Na(2\text{-}S\text{-}Py)(15C5)]$.[12] The sodium cation thus lies 1.008 Å above

the mean oxygen plane of the crown. This smaller value than in **1** is a consequence of

the better host-guest fit of sodium with 15C5 compared to 12C4. The two Na–N bond

lengths of 2.4503(10) and 2.4819(10) Å are comparable to those observed in

$[\{Na(PyNSiMe_3)_2(THF)\}\{Na(12C4)_2\}]$[5d] and $[\{Na(L)\}_2(HMPA)_3]$,[7f] and are shorter

than observed in $[\{Na(L)(PMDETA)\}_2]$, where the anion is bridging.[7f] The N_{amido}–

$C_{pyridyl}$ bond length of 1.3361(15) Å is shorter than in the parent amine [1.378(3) Å],[13]

consistent with delocalisation of charge into the pyridyl ring. The bite angle of the

ligand, 55.32(3)°, is consistent with previous examples.[5d,7f] In order for the amido

anion to act as a chelating ligand, the pyridyl ring must be rotated about the C–N_{amido}

bond from the orientation found in the uncoordinated anion in **1**; this brings the *ortho*-

H atoms of the two rings into steric conflict, and so the amide is not planar, the

torsion angle between the two rings being 53.8°.

The molecular structure of **3** is illustrated in figure 3. The complex crystallises as a contact ion pair, similar to that of **2**; the amide occupies one coordination hemisphere and the crown occupies the other. The sodium cation, however, is only six-coordinate with four Na–O and two Na–N bonds. Two of the crown oxygen atoms remain uncoordinated in the solid state, illustrating the mismatch between the crown and cation sizes. The Na–O bond lengths span the range 2.516(2)–2.780(2) Å, which is a higher and wider range than that observed for **2**, reflecting the poor host-guest fit due to the larger crown. This range is in good agreement with those reported by Steed and Junk for the series of complexes [Na(18C6)(H$_2$O)(X)] (X = ClO$_4$, NO$_3$ or ReO$_4$).[14] However, despite the longer Na–O bonds, the sodium cation lies 1.185 Å above the mean plane of the coordinated O atoms of the crown, only slightly further than in **2**. The two non-bonding Na…O distances of 3.561 and 3.408 Å are similar to those in the above series of complexes.[14] The two non-bonding oxygen atoms, O(5) and O(6), do not exhibit any special intra- or intermolecular interactions. For the two N–Na bonds, there is a reversal of the expected order of bond lengths: the Na–N(1) (pyridyl) bond length of 2.449(3) Å is significantly shorter than the N–N(2) (amido) bond length of 2.516(2) Å. This may be due to the asymmetric coordination of the crown, which presents a large void in the region of O(1), O(5) and O(6), allowing a closer approach of the pyridyl group to sodium. The Na–N(1) bond length is in the range typically associated with Na–amide bond distances (*cf.* **2**), whereas the Na–N(2) bond distance is within ranges normally associated with tertiary amine donors. For example, bond lengths spanning the range 2.489–2.725 Å are observed for the amine donors in the complexes [{Na[N(H)C$_6$H$_4$-2-OPh](PMDETA)}$_2$][15] and [{Na[N(CH$_2$Ph)$_2$](TMEDA)}$_2$].[16] This reversal of expected bond lengths implies substantial delocalisation of charge into the pyridyl ring and, therefore, a shortening

of the N(2)–C(5) bond would be expected. However, although this bond is relatively short [1.355(4) Å], it is not as short as that in **2**. The bite angle of 54.79(9)° is similar to that in **2**, and once again the phenyl ring is twisted out of the pyridyl plane, by 47.6° in this case.

The molecular structure of **4** is shown in Figure 4. The complex crystallises as a discrete dimer with no significant intermolecular interactions. A molecule of benzene is present in the structure for every molecule of **4**, but merely serves to fill voids; there are no face-to-face or edge-to-face aromatic ring interactions. The dimer is best viewed as constructed around a planar *transoid* $(KN_{amido})_2$ ring with additional bridging coordination by the pyridyl rings. A molecule of 12C4 caps each end of the dimer, completing the coordination sphere of potassium to give eight-coordinate potassium centres; there is minor disorder in one of the crown ligands. The K–O bond lengths span the range 2.738(5)–2.986(5) Å, a larger range than in $[\{K(12C4)_2\}\{L.L(H)\}]$,[6] reflecting the more congested coordination sphere in **4**, and compares well with the range reported for the closely related complex $[\{K(PyNSiMe_3)(12C4)\}_2]$,[5d] for the complex $[\{K(12C4)_2\}\{SnCl_2(CrCO_5)_2\}]$,[17] and for the two alkalide complexes $[\{K(18C6)(12C4\}M]$ (M = Na or K).[18] The potassium cations lie 1.881 and 2.047 Å above the mean oxygen plane of their respective crown ligands. The K–N bond lengths span the ranges 2.798(4)–2.904(5) Å (amido) and 2.906(4)–2.991(5) Å (pyridyl). The $K-N_{amido}$ bond lengths are towards the higher limit of distances reported previously, reflecting the bridging nature of the amido centres and the high coordination number of potassium.[7a,7e,19–21] The $K–N_{py}$ bond lengths are greater, as expected, and are at the higher end of the range of distances previously reported for neutral tertiary amine donors.[22–24] Both types of bonds are considerably

longer than observed in the complex [{K(L)(TMEDA)}$_2$],[7e] in keeping with the higher coordination number of potassium in **4** (eight *vs* six). The two amides are not planar, with torsion angles of 46.1 and 48.7° between the pyridyl and phenyl rings. Also of interest is the fact that the pyridyl rings are not aligned perpendicular to the K(1)...K(2) vector. Each ring tilts from this orientation towards one potassium and away from the other, by angles (15.6 and 13.0°) very similar to those observed in [{K(PyNSiMe$_3$)(12C4)}$_2$][5d] and [{[K(L)]$_2$(THF)$_3$}$_\infty$].[7a] This is a manifestation of the relatively soft nature of potassium, with an increased preference (even if not achieved fully) for multihapto bonding with aromatic π systems, compared with lithium and sodium.

The molecular structure of **5** is shown in Figure 5. The complex crystallises as a separated ion pair with no additional interactions between anion and cation, or among ion pairs. The potassium ion is centrosymmetrically sandwiched between two 15C5 molecules in a staggered conformation exhibiting pseudo-D_{5d} symmetry. The K–O bond lengths span the range 2.827(8)–2.981(2) Å, which compares favourably with those reported in the complexes [{K(15C5)$_2$}{Nb(PMe$_3$)$_2$(CO)$_4$}],[25] [{K(15C5)$_2$}(Sb$_3$I$_{12}$)][26] and [{K(15C5)$_2$}Te$_8$].[27] This results in the potassium cation being displaced 1.588 or 1.724 Å (two disorder components) from the oxygen mean planes of the crowns, reflecting the better host-guest fit of potassium with 15C5 than with 12C4 in **4**. The crown-potassium-crown bending angle is necessarily 180° (ignoring disorder), as a consequence of the inversion centre at the potassium ion. The amide anion is isolated, is disordered in the same way as in **1**, and is essentially planar with a torsion angle of 7.5° between the two rings.

The structural repeat unit of **6** is shown in Figure 6. The complex crystallises as a polymer, which runs along the crystallographic *a* axis (Figure 7). This is a surprising observation, as a monomeric contact ion pair of the form [K(L)(18C6)] was expected, as observed for the complex [K(Py-2-S)(18C6)].[12] The polymer is composed of units consisting of contact ion pair 'ate' dimers. Both independent potassium ions lie in special positions on crystallographic symmetry elements. K(1), on an inversion centre, lies exactly in the mean plane of the 18C6 molecule and is bonded to two bridging pyridyl nitrogen atoms, one in the same unit and one in the next, giving hexagonal-bipyramidal eight-coordinate potassium. K(2), on a twofold rotation axis, is coordinated by two chelating amide anions and two bridging oxygen atoms, one from the crown in the same unit and one from the next, resulting in highly distorted octahedral six-coordinate potassium. The fact that the pyridyl nitrogen atoms bridge, but the amido nitrogen atoms are terminal, is highly surprising, as a reverse arrangement would be expected and has been observed in a number of structures. Indeed, to the best of our knowledge, this is the first time the 2-phenylamidopyridine ligand has been observed with this coordination mode in a homometallic complex, although it is found in the heterobimetallic complex [{Al(L)Me$_2$}$_2$(Li$_2$O)(THF)$_2$].[28] In the K(18C6) fragment, the six K(1)–O bond lengths span the range 2.7844(18)– 2.8409(17) Å, in good agreement with ranges reported in, for example, the complexes [{K(18C6)}{La(Cp')$_2$(C$_6$H$_6$)}{K(18C6)(Cp')}]   (Cp'   =   1,3-SiMe$_3$C$_5$H$_3$),[29] [{K(18C6)}{Rh[P(OEt)$_3$]$_2$}],[30]   [{K(18C6)}{Fe$_4$Au(PEt$_3$)(CO)$_{13}$}],[31]   and [{K(18C6)(THF)$_2$}{Co(Bu^{t}CHCHCHCHBu^t)$_2$}].[32] The K(1)–N(pyridyl) bond lengths are 3.0184(19) Å, which is at the higher end of previously reported tertiary amine-potassium bond lengths.[22–24,33] In the 'ate' fragment, the two K(2)–O bonds, of length of 2.8577(16) Å, are slightly longer than the other six K–O bonds, as would be

expected from their bridging nature. Together with the K(1)–N(1) and K(2)–N(1) bonds a (K$_2$NO) ring is formed. This is quite unusual, but there is precedent of a (K$_2$NO) ring in the complex [K{K(18C6)}$_2${Bi(SCN)$_6$}].[34] The corner sharing of the four-membered rings is in sharp contrast to the edge sharing principle now firmly established for lithium amides.[1d,3] The K(2) coordination environment is completed by four K–N bonds, which are a short pair of 2.748(2) Å (amide), and a long pair of 2.855(2) Å (pyridyl), and these compare well with previously reported examples.[7e,35] This gives a natural bite angle of 48.71(6)° for the chelating ligand, smaller than observed in **2** and **3**, commensurate with the larger ionic radius of potassium compared to sodium. It is noteworthy that, as in **4**, the pyridyl ring is not perpendicular to the K(1)…K(2) vector but tilted. The hinge angles are similar to that observed in **4**. The two phenyl rings are twisted relative to the pyridyl rings, with a dihedral angle of 56.8°.

The molecular structure of **7** is illustrated in Figure 8. The complex crystallises as a separated ion pair involving solvation of cations by THF. There are one and a half ion pairs in the asymmetric unit, one of the cations lying on a crystallographic twofold rotation axis (requiring disorder of THF) and one of the anions being disordered over an inversion centre. Indeed, there is considerable disorder in the structure, affecting all the cations and anions in different ways. However, the main features of the independent cations and of the independent anions are essentially identical so only the pair without crystallographic symmetry (suffering less from disorder) is illustrated and discussed for brevity. The rubidium cation is sandwiched by two 12C4 molecules in a bent configuration, the crown–Rb–crown bending angle being 147.5°. This facilitates coordination by a molecule of THF, which makes rubidium cation nine-

coordinate. The question naturally arises whether the coordination of THF is the cause of the bent sandwich arrangement, or the result of an inherent bending. There are parallels of **7** with bent metallocene complexes of groups 1, 2 and 14, and the lanthanides.[36] Consequently, a theoretical study of the bending was carried out (see below). It is noteworthy that the overall gross architecture of this sandwich is similar to that of the barium complex $[Ba(NCS)_2(12C4)_2]$,[37] the recently reported pyrrolyl complexes $[M(2-5-Bu^t_2C_4H_2N)_2(THF)]$ (M = Sr or Ba)[38] and the ytterbium(II) complex $[Yb(C_5Me_5)_2(THF)]$,[39] and the bending angle is comparable to that observed in the solid-state structure of $[Ca(C_5Me_5)_2]$.[40] The Rb–O_{crown} bond lengths span the range 2.912(6)–2.983(5) Å. This compares well with those reported in the alkalide complexes $[\{Rb(18C6)(12C4)\}M]$ (M = Na or Rb).[18] The Rb–O_{THF} bond length is appreciably longer at 3.199(10) Å, reflecting the weak nature of the bond, as further evidenced by the ease with which the coordinated THF may be removed *in vacuo*. This is at the higher end of previously reported neutral donor O–Rb bond lengths. For example, Rb–O bond lengths of 2.860(4), 2.899(5) and 3.023(8) Å have been reported in the complexes $[Rb(TB24C8)(DIOX)_{1.5}(H_2O)_{0.18}].(Cl).(DIOX).1.82(H_2O)$ (TB24C8 = tetrabenzo24-crown-8 ether, DIOX = dioxane),[41] $[\{Rb[P(SiMe_3)_2](THF)\}_\infty]$,[42] and $[Rb\{(Cy)N(H)Sb(\mu-NCy)_2\}_2Sb].2(THF)$ (Cy = cyclohexane).[43] The rubidium ion is displaced from the mean plane of the crown by a mean value of 2.162 Å, in reasonable agreement with the two alkalide complexes described above.[18] The amide anion is, again, isolated and shows no short intermolecular contacts. It is essentially planar, with a torsion angle between the pyridyl and phenyl rings of 4.9°. These two rings are disordered in the same way as for **1** and **5**, with further disorder over an inversion centre for one-third of the anions in the structure.

The molecular structure of **8** is illustrated in Figure 9. The complex crystallises as a separated ion triple consisting of a loosely bound cation dimer on an inversion centre and two uncoordinated anions, each of which is disordered over an inversion centre as found for some of the anions of **7**. It is surprising that no HMPA is present in this complex. HMPA was used as a strong donor molecule that, with pseudo-C_3 symmetry, might overcome the twinning consistently observed in crystals of **7**. However, the HMPA appears not to coordinate to Rb in this reaction. The fact that it requires overnight stirring for the HMPA to dissolve the complex (and by inference to coordinate) indicates weak bonding at best. This is counter-intuitive, as HMPA is a much stronger Lewis base than THF. It is, however, much bulkier when viewed with space-filling models and it would seem that its bulk prevents strong coordination here. It is pertinent to note that complex **8** is essentially **7** without the THF, the nine-fold coordination of each rubidium ion being completed by a bridging 12C4 oxygen in order to compensate for the absence of coordinated THF. Thus solvation of **8**, to give **7**, reduces the degree of aggregation from two to one. Bridging crowns are rare, but not unknown.[44] The Rb–O bond lengths span the range 2.859(4)–3.061(4) Å, with two additional weak long bridging Rb–O bonds of 3.861(5) Å. The two bridging bond lengths are exceptionally long, longer than the 'long' Rb–O contacts of 3.393 Å in the complex $[\{(Bu^tOLi)_5(Bu^tORb)_4(Li_2O_2)(TMEDA)_2\}_\infty]$,[45] and could be regarded as largely coulombic or electrostatic; they are certainly weak interactions, as evidenced by the fact that addition of THF easily cleaves the dimer to produce monomeric **7**. The bending angle of 142.8° or 144.8° (two disorder components for the non-bridging crown) is similar to that observed in **7**. Given the similar chemistry generally exhibited by rubidium and potassium it is unusual that, in the presence of 12C4, **7** and **8** both adopt separated ion pair/triples with sandwiched cation centres, whereas **4**

adopts a contact ion pair dimer structure, especially since the host-guest fit is worse for the larger rubidium; for the related 2-trimethylsilylamidopyridine complexes essentially isostructural dimers $[\{M(PyNSiMe_3)(12C4)\}_2]$ (M = K or Rb) are formed.[5d] This unexpected trend serves to underline the delicate balance that exists between structural architectures adopted in the solid state of alkali metal complexes. The amide anions are again isolated, and show no short intermolecular interactions. They are essentially planar, with dihedral angles of 2.3° and 4.6° between the (disordered) phenyl and pyridyl rings; the geometry of these anions is of relatively low precision because of the extensive disorder.

Complex **9** crystallises as a separated ion pair that is isostructural with **5**. There are no significant interactions other than coulombic between the cation and anion or among the ion pairs. The rubidium ion, on an inversion centre, is sandwiched between two 15C5 molecules in a staggered conformation exhibiting pseudo-D_{5d} symmetry. The Rb–O bond lengths span the range 2.955(3)–3.051(2) Å, in good agreement with those reported in the complexes $[\{Rb(15C5)_2\}(TlBr_4)]$,[46] $[\{Rb(15C5)_2\}\{TcCl_4(N)(H_2O)\}]$[47] and $[\{Rb(15C5)_2\}Na]$.[48] The rubidium ion lies 1.697 or 1.874 Å (two disorder components for one of the oxygen atoms) from the 15C5 mean plane. This is further than in **5**, reflecting the larger ionic radius of rubidium compared to potassium. The two 15C5 ligands are necessarily parallel (ignoring disorder). The anion is isolated, two-fold disordered, and essentially planar, with a dihedral angle of 4.2° between the two aromatic rings.

The structure of **10** is illustrated in Figure 10. The complex crystallises as a monomeric contact ion pair of the form that was originally expected for **6**. The 18C6

macrocycle occupies one coordination hemisphere, with the amide occupying the other. The rubidium ion is eight-coordinate with six Rb–O bonds and two Rb–N bonds. The only significant chemical difference in the preparation of **6** and **10** is the change from potassium to the larger rubidium, which has markedly altered the structure adopted in the solid state from a polymer to a monomer. Presumably one of the contributory factors is that rubidium is too large to fit in the cavity of 18C6, and must therefore lie above it. Consequently the corner sharing in **6**, *via* potassium centres and bridging crown oxygen atoms, is not viable. The Rb–O bond lengths span the range 2.8689(9)–3.0539(10) Å, longer than in **6** and comparing well with Rb–O bond lengths previously reported.[49] This results in the rubidium ion lying 0.969 Å above the mean plane of the crown, reflecting a more favourable host-guest fit than with 15C5 in **9**. The two Rb–N bond lengths consist of a short Rb–N(2) of 2.9516(11) Å (amide) and a long Rb–N(1) of 3.0230(11) Å (pyridyl), in good agreement with previously reported examples of Rb–N amide[5d,50,51] and amine bonds.[24,52–54] This gives a natural bite angle of 45.28(3)°, slightly smaller than that observed in **4** and **6**, reflecting the larger ionic radius of rubidium compared to potassium.

The molecular structure of **11** is of the same general architecture as **5** and **9**, as shown by a preliminary X-ray study.[55] Despite repeated attempts at recrystallisation, data collection and refinement it was not possible to obtain a good set of data. However, although the data are not sufficiently precise to allow a detailed discussion of bond lengths and angles, they do give an unambiguous confirmation of the chemical composition and molecular connectivity. The complex crystallises as a separated ion pair. The ten-coordinate caesium ion is sandwiched between two 15C5 molecules in a staggered conformation exhibiting pseudo-D_{5d} symmetry, and Cs–O bond lengths are

comparable to those reported in the complex $[\{Cs(15C5)_2\}K]$.[56] The sandwich is slightly more bent than in **9** (by about 7°), reflecting the more polarisible nature of caesium. The amide anion is essentially planar.

Although crystals of **12** were obtained, these gave only poor diffraction data, with a rapid decline in intensity at higher angles, indicative of severe structural disorder. This could not be improved despite repeated recrystallisation.[57] The structure solution was complicated by a high degree of pseudo-translational symmetry, compounded by apparent multiple disorder of the amide. However, it is clear that the complex crystallises as an infinite polymer of Cs_2L_2 dimer units incorporating bridging amide and pyridyl centres, of similar core architecture to that of **4**, linked by bridging μ-κ^6:κ^6-18C6 molecules (Figure 11), which is of generally similar architecture to that of the complex $[\{[Cs(PyNH)]_2(18C6)\}_\infty]$.[5a]

Theoretical Calculations

The bent nature of some group 14 complexes has until recently been explained by the presence of a stereochemically active lone pair with p character. This has, however, been called into question by the sterically demanding parallel plumbocene derivative $[Pb\{C_5(Pr^i)_3H_2\}_2]$[58] and the homologous series $[M\{C_5(SiMe_2Bu^t)Me_4\}_2]$ (M = Ge, Sn or Pb),[59] where the lone pair is ascribed s character due to its apparent stereochemical inertness. The assignment of s character is directly supported by photoelectron spectroscopy studies of germanocenes, stannocenes and plumbocenes.[60] In the case of $[Pb\{C_5(Pr^i)_3H_2\}_2]$ it is argued that interligand repulsion can be ruled out and that the parallel nature is due to crystal packing forces.[58] The delicate balance between bent

and linear lead(II) compounds has also been highlighted recently by two lead(II) tris(1-pyrazoyl)methane complexes.[61] However, ions of groups 1 and 2, and the lanthanides, do not possess a stereochemically active lone pair, or valence electrons, yet they frequently exhibit bent configurations for their complexes. In studies to date, van der Waals forces, long-range intermolecular interactions and f orbital interactions have almost been ruled out and the debate over d orbital interaction continues. It is generally assumed that the ligands polarise the metal centre and induce a dipole. Indeed, it has been calculated that this dipole can interact with a uninegative ligand (such as Cp or Cp*) more effectively.[62] Given that there is evidence that various group 2 and lanthanide metallocene complexes are inherently bent in the solid state and in the gas phase, it seems plausible that **7** is also inherently bent, due to the easily polarisable rubidium cation, and that the coordinated THF is present as a result of, and not as the cause of, the bending.[63] This proposal is corroborated by the structure of **8**, which is solvent-free and also bent. Given that the energy to bend an alkaline earth metallocene by 20° is estimated to be of the order of 2–3.5 kJ/mol,[64,65] a theoretical calculation, at the b3lyp level,[66] was conducted on the model $[Rb(12C4)_2]^+$ (**7a**) cationic component of **7** in order to assess (i) whether the bending is inherent, and (ii) whether the bending energy is comparable to that of metallocene congeners.

The conformational minimum obtained from the b3lyp/(lanl2dz;d95*) geometry optimisation for **7a** is given in Figure 12(a), alongside the idealised parallel geometry (b) (obtained by rotating the lower ligand about the Rb atom to the horizontal position), which was then subjected to a single-point energy calculation to derive some estimation of the energy barrier to complex bending [as all attempts to optimise a parallel geometry resulted in saddle points (D_{4h} and D_{4d} symmetry) or, in the

absence of symmetry constraints, a return to the conformational minimum previously found, i.e. bent]. In general, computed parameters for the optimised **7a** (Table 2) are in reasonable agreement with experimental values obtained by X-ray diffraction for **7** with, for example, the Rb–O_{12C4} distances in the range 2.960–3.242 Å for **7a** [*c.f.* 2.912(6)–2.983(5) Å in **7**]. This comparison is encouraging, bearing in mind that the calculation ignores any crystal packing forces, which can distort the molecular geometry, and that the model **7a** did not include coordinated THF. The X–Rb–X angle (where X denotes the centroid of the four oxygen atoms in each crown ligand) in the optimised model is calculated to be 145.4º, exactly the same as found experimentally in **7** and indicates, in answer to point (i), that the $[Rb(12C4)_2]^+$ cation is, indeed, inherently bent. [This angle is not exactly equal to the bending angle defined as the dihedral angle between crown oxygen mean planes, used in the discussion above.] The conclusion from this is that the THF coordinates as a result of inherent bending and is not the cause of the bending. In consideration of point (ii), although attempts to calculate an optimised structure with parallel crown ligands proved difficult, a single-point energy calculation was successfully performed after rotating one crown ligand from the optimised bent geometry to generate an X–Rb–X angle of 180º. The energy value obtained from this calculation was higher by 7.5 kJ/mol. While this value does not represent the *true* barrier to complex bending, as no allowance has been made for atomic relaxation, it does represent the *maximum* possible value that can be attributed to this conformational change, within the limits of the accuracy of the calculation. This puts the slight preference for a bent structure of **7a** on a par with that for stannocene $[Sn(Cp)_2]$, as reported recently by Smith and Hanusa,[67] and is comparable to values calculated previously for $[M(Cp^*)_2]$ complexes (M = Ca, Sr, Ba, Sm, Eu and Yb) by Bosnich and co-workers.[68] Such low barriers to

bending are to be expected for "floppy" systems, where large, soft, polarisable metals exhibit shallow potential energy curves for bending.

Conclusions

Twelve new heavier alkali metal amide complexes have been synthesised and characterised, ten of them with full crystal structure determinations. The choice of crown ether macrocycle is crucial in determining the solid-state structure adopted. Whereas some structures are the expected contact or separated ion pairs due to relative host-guest fit, a number of surprises have emerged. In particular, the potassium complex **6** is unexpected, given the apparent preference for the highly unusual pyridyl bridging rather than amido bridging; **7** and **8** are surprising, as a bridged dimer was predicted on the basis of previous work[5d] and the unfavourable host-guest fit. In this case the effect of substituting a trimethylsilyl group by a phenyl group becomes apparent in the increased ability of the amido anion to exist as a free resonance-delocalised anion, undoubtedly encouraging the formation of separated ion-pair species. DFT calculations indicate that the $[Rb(12C4)_2]^+$ cation is inherently bent, and that the THF coordinated in **7** is present as a result of, and not the cause of, the bending. The modest increase in stability of the bent configuration with respect to the parallel configuration is in line with 'floppy' soft and polarisable systems and is in agreement with analogous bent metallocene complexes.

Experimental

General Comments

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Light petroleum (bp 40–60ºC), benzene, toluene, ether and THF were distilled from sodium-benzophenone ketyl radical under an atmosphere of dry nitrogen and stored over activated 4A molecular sieves. HMPA was dried over CaH_2 and stored over activated 4A molecular sieves. 12-crown-4 and 15-crown-5 were dried by, and stored over activated 4A molecular sieves. 18-crown-6 was dried over activated 4A molecular sieves and recrystallised from ether. Deuteriated solvents were distilled from a potassium mirror, deoxygenated by three freeze-pump-thaw cycles and stored over activated 4A molecular sieves. Butyllithium and methyllithium were purchased from Acros as a 2.5 M solution in hexanes and a 1.6 M solution in diethyl ether, respectively. The compounds 2-phenylaminopyridine, Bu^tONa, and Bu^tOK were purchased from Aldrich and were used without any further purification. Sodium and potassium hydride were washed repeatedly with petrol, baked and stored under dry nitrogen. Rubidium-2-ethylhexoxide and caesium-2-ethylhexoxide were prepared by a modification of a literature method.[70]

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200 spectrometer, and ^{133}Cs spectra on a Bruker WM300 spectrometer operating at 200.1, 50.3 and 39.4 MHz respectively; ^1H and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane and ^{133}Cs chemical shifts relative to external 0.01 M CsI. Elemental analyses were carried out by Elemental Microanalysis Ltd., Okehampton, UK.

Preparation of [{Na(12C4)$_2$}$^+${N(Py)(Ph)}$^-$] (1).

A 100 mL Schlenk flask was charged with Bu^{t}ONa (0.19 g, 2.00 mmol) dissolved in ether (40 mL). The solution was cooled to 0°C and MeLi (1.4 mL, 2.20 mmol) was added dropwise to give a turbid solution. To this was added 2-anilinopyridine (0.34 g, 2.00 mmol) in ether (40 mL) to give a clear yellow solution. Dropwise addition of 12-crown-4 (0.64 mL, 4.00 mmol) with stirring afforded a yellow precipitate. The precipitate was filtered from the mother liquor, washed with petrol (3 × 5 mL) and dried *in vacuo*. The solid was recrystallised from hot THF to give crystals of **1** suitable for an X-ray crystallographic study (0.99 g, 90.1%). Microanalysis for **1**: C, 59.24; H, 7.60; N, 4.99. C$_{27}$H$_{41}$N$_2$O$_8$Na requires C, 59.54; H, 7.59; N, 5.14. Spectroscopic data for **1**: δ_H (d$_8$-THF) 3.67 (32 H, s, 12C4), 6.12 (1 H, t, β-H-Py), 6.61 (1 H, t, γ-H-Py), 6.80 (1 H, d, β′-H-Py), 7.11 (1 H, t, *para*-H-Ph), 7.13 (2 H, t, *meta*-H-Ph), 7.28 (2 H, d, *ortho*-H-Ph) and 7.94 (1 H, d, α-H-Py). δ_C ([^{2}H]$_8$ THF) 71.33 (12C4), 109.04 (β-C-Py), 118.23 (γ-C-Py), 121.30 (β′-C-Py), 129.37 (*para*-C-Ph), 136.87 (*meta*-C-Ph), 142.35 (*ipso*-C-Ph), 149.60 (*ortho*-C-Ph), 152.11 (α-C-Py) and 163.94 (α′-C-Py).

Preparation of [Na{N(Py)(Ph)}(15C5)]·½(PhMe) (2).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 15-crown-5 (0.40 mL, 2.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.80 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to Bu^{t}ONa (0.19 g, 2.00 mmol) and brief heating gave a deep orange solution. Removal of volatiles *in vacuo* yielded a yellow solid, which was washed with petrol (3 × 5 mL). Recrystallisation from hot toluene over three days gave crystals of **2** suitable for an X-ray crystallographic study (0.65 g, 71.0%). Microanalysis for **2**: C, 60.03; H, 7.12; N,

6.49. $C_{21}H_{29}N_2O_5Na$ requires C, 61.15; H, 7.09; N, 6.79. Spectroscopic data for **2**: δ_H ($[^2H]_8$ THF) 3.66 (20 H, s, 15C5), 6.08 (1 H, t, β-H-Py), 6.61 (1 H, d, β´-H-Py), 6.62 (1 H, t, γ-H-Py), 7.06 (1 H, t, *para*-H-Ph), 7.11 (2 H, t, *meta*-H-Ph), 7.23 (2 H, d, *ortho*-H-Ph) and 7.90 (1 H, d, α-H-Py). δ_C ($[^2H]_8$ THF) 70.90 (15C4), 107.30 (β-C-Py), 111.34 (γ-C-Py), 116.09 (β´-C-Py), 121.42 (*para*-C-Ph), 128.73 (*meta*-C-Ph), 135.96 (*ipso*-C-Ph), 152.11 (*ortho*-C-Ph), 163.94 (α-C-Py) and 164.69 (α´-C-Py).

Preparation of [Na{N(Py)(Ph)}(18C6)] (3).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 18-crown-6 (0.53 g, 2.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.80 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to Bu^{t}ONa (0.19 g, 2.00 mmol) and brief heating gave a deep orange solution. Removal of volatiles *in vacuo* yielded an orange oil. Recrystallisation from toluene at −30ºC over four weeks gave crystals of **3** suitable for X-ray crystallography (0.46 g, 50.4%). Microanalysis for **3**: C, 57.97; H, 7.19; N, 5.52. $C_{23}H_{33}N_2O_6Na$ requires C, 60.51; H, 7.29; N, 6.14. Spectroscopic data for **3**: δ_H ($[^2H]_8$ THF) 3.59 (24 H, s, 18C6), 5.81 (1 H, t, β-H-Py), 6.36 (1 H, t, γ-H-Py), 6.63 (1 H, d, β´-H-Py), 6.84 (2 H, t, *meta*-H-Ph), 6.98 (1 H, t, *para*-H-Ph), 7.06 (2 H, d, *ortho*-H-Ph) and 7.82 (1 H, d, α-H-Py). δ_C ($[^2H]_8$ THF) 72.45 (18C6), 106.11 (β-C-Py), 110.63 (γ-C-Py), 116.23 (β´-C-Py), 123.40 (*meta*-C-Ph), 130.39 (*para*-C-Ph), 136.54 (*ipso*-C-Ph), 151.06 (*ortho*-C-Ph), 159.12 (α-C-Py) and 168.43 (α´-C-Py).

Preparation of [{K(PyNPh)(12C4)}$_2$].(C$_6$H$_6$) (4).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.85 g, 5.00 mmol), 12-crown-4 (0.80 mL, 5.00 mmol) and toluene (40 mL). This solution was added to KH (0.2 g, 5.00 mmol) to give a turbid green solution. Gentle heating afforded a dark orange solution, which on cooling precipitated a yellow crystalline solid. Removal of volatiles *in vacuo* and recrystallisation from hot benzene yielded crystals of **4** suitable for X-ray crystallography (1.6 g, 75.6%). Microanalysis for **4**: C, 61.96; H, 6.68; N, 6.64. C$_{38}$H$_{50}$N$_4$O$_8$K$_2$.C$_6$H$_6$ requires C, 62.38; H, 6.66; N, 6.61. Spectroscopic data for **4**: δ_H ([^{2}H]$_8$ THF) 3.65 (32 H, s, 12C4), 6.27 (2 H, t, β-H-π), 6.67 (2 H, t, γ-H-π), 6.73 (2 H, d, β′-H-π), 7.12 (4 H, t, *meta*-H-Ph), 7.16 (2 H, t, *para*-H-Ph), 7.35 (4 H, d, *ortho*-H-Ph) and 7.99 (2 H, d, α-H-π). δ_C ([^{2}H]$_8$ THF) 72.53 (12C4), 110.99 (β-C-π), 112.66 (γ-C-π), 120.75 (β′-C-π), 122.76 (*meta*-C-Ph), 130.50 (*para*-C-Ph), 148.18 (*ipso*-C-Ph), 150.32 (*ortho*-C-Ph), 162.12 (α-C-π) and 163.46 (α′-C-π).

Preparation of [{K(15C5)$_2$}$^+$(PyNPh)$^-$] (5).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 15-crown-5 (0.40 mL, 2.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.8 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to Bu^{t}OK (0.22 g, 2.00 mmol) gave a dark yellow precipitate. Volatiles were removed *in vacuo* and subsequent addition of 15-crown-5 (0.4 mL, 2.00 mmol) and THF (20 mL) with gentle heating afforded a dark red solution, which on cooling yielded crystals of **5** suitable for X-ray crystallography (1.16 g, 89.3%). Microanalysis for **5**: C, 57.32; H, 7.84; N, 4.23. C$_{31}$H$_{49}$N$_2$O$_{10}$K requires C, 57.39; H, 7.61; N, 4.32. Spectroscopic data

for **5**: δ_H ([^{2}H]$_8$ THF) 3.70 (40 H, s, 15C5), 6.04 (1 H, t, β-H-π), 6.50 (1 H, t, γ-H-π), 6.81 (1 H, d, β′-H-π), 7.03 (1 H, t, *para*-H-Ph), 7.08 (2 H, t, *meta*-H-Ph), 7.57 (2 H, d, *ortho*-H-Ph) and 7.93 (1 H, d, α-H-π). δ_C ([^{2}H]$_8$ THF) 72.05 (15C5), 108.51 (β-C-π), 112.43 (γ-C-π), 117.31 (β′-C-π), 122.55 (*para*-C-Ph), 129.88 (*meta*-C-Ph), 136.68 (*ipso*-C-Ph), 150.21 (*ortho*-C-Ph), 155.13 (α-C-π) and 165.76 (α′-C-π).

Preparation of [K(18C6){K(PyNPh)$_2$}$_\infty$] (6).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 18-crown-6 (0.53 g, 2.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.8 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to Bu^{t}OK (0.22 g, 2.00 mmol) with heating gave a dark orange solution, which precipitated a yellow solid on cooling. The solid was isolated from the mother liquor and washed with petrol (3 × 5 mL) and dried *in vacuo*. Recrystallisation from hot toluene yielded crystals of **6** suitable for X-ray crystallography (0.52 g, 76.4%). Microanalysis for **6**: C, 59.96; H, 6.27; N, 8.03. C$_{34}$H$_{42}$N$_4$O$_6$K$_2$ requires C, 59.97; H, 6.22; N, 8.23. Spectroscopic data for **6**: δ_H ([^{2}H]$_8$ THF) 3.65 (24 H, s, 18C6), 5.44 (2 H, t, β-H-π), 6.55 (2 H, t, γ-H-π), 6.74 (2 H, d, β′-H-π), 6.96 (4 H, t, *meta*-H-Ph), 7.07 (2 H, t, *para*-H-Ph), 7.11 (4 H, d, *ortho*-H-Ph) and 7.91 (2 H, d, α-H-π). δ_C ([^{2}H]$_8$ THF) 71.14 (18C6), 105.40 (β-C-π), 108.48 (γ-C-π), 116.10 (β′-C-π), 122.35 (*meta*-C-Ph), 129.10 (*para*-C-Ph), 135.84 (*ipso*-C-Ph), 150.06 (*ortho*-C-Ph), 157.03 (α-C-π) and 166.79 (α′-C-π).

Preparation of [{Rb(12C4)$_2$(THF)}$^+$(PyNPh)$^-$] (7).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 12-crown-4 (0.64 g, 4.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.8 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to rubidium-2-ethylhexoxide (0.43 g, 2.00 mmol) gave a yellow precipitate. The solid was isolated from the mother liquor and washed with petrol (3 × 5 mL) and dried *in vacuo.* Recrystallisation from THF at −30°C yielded crystals of **7** suitable for X-ray crystallography (0.92 g, 67.9%). Microanalysis for **7**: C, 53.64; H, 6.82; N, 4.65. C$_{27}$H$_{41}$N$_2$O$_8$Rb requires C, 53.42; H, 6.81; N, 4.61. Spectroscopic data for **7**: δ_H ([^{2}H]$_8$ THF) 1.91 (4 H, m, CH$_2$-THF), 3.71 (32 H, s, 12C4), 3.75 (4 H, m, OCH$_2$-THF), 6.04 (1 H, t, β-H-π), 6.57 (1 H, t, γ-H-π), 6.78 (1 H, d, β′-H-π), 7.06 (1 H, t, *para*-H-Ph), 7.15 (2 H, d, *ortho*-H-Ph), 7.18 (2 H, d, *meta*-H-Ph) and 7.94 (1 H, d, α-H-π). δ_C ([^{2}H]$_8$ THF) 25.74 (CH$_2$-THF), 67.81 (OCH$_2$-THF), 71.67 (12C4), 107.18 (β-C-π), 109.13 (γ-C-π), 117.07 (β′-C-π), 121.65 (*para*-C-Ph), 129.46 (*ortho*-C-Ph), 136.44 (*ipso*-C-Ph), 149.99 (*meta*-C-Ph), 155.13 (α-C-π) and 165.50 (α′-C-π).

Preparation of [{Rb(12C4)$_2$}$^+$(PyNPh)$^-$] (8).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 12-crown-4 (0.64 g, 4.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.8 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to rubidium-2-ethylhexoxide (0.43 g, 2.00 mmol) gave a yellow precipitate. Addition of HMPA (0.35 mL, 2.00 mmol) and stirring overnight afforded a dark red solution. Concentration and storage at −30°C yielded crystals of **8** suitable for X-ray

crystallography (0.84 g, 69.3%). Microanalysis for **8**: C, 53.59; H, 6.91; N, 4.59. $C_{54}H_{82}N_4O_{16}Rb_2$ requires C, 53.42; H, 6.81; N, 4.61. Spectroscopic data for **8**: δ_H ([^{2}H]$_8$ THF) 3.69 (64 H, s, 12C4), 5.90 (2 H, t, β-H-π), 6.50 (2 H, t, γ-H-π), 6.76 (2 H, d, β′-H-π), 6.96 (2 H, t, *para*-H-Ph), 7.06 (4 H, d, *ortho*-H-Ph), 7.08 (4 H, d, *meta*-H-Ph) and 7.88 (2 H, d, α-H-π). δ_C ([^{2}H]$_8$ THF) 72.15 (12C4), 106.01 (β-C-π), 110.00 (γ-C-π), 117.02 (β′-C-π), 123.02 (*para*-C-Ph), 130.35 (*ortho*-C-Ph), 137.05 (*ipso*-C-Ph), 151.20 (*meta*-C-Ph), 158.31 (α-C-π) and 167.87 (α′-C-π).

Preparation of [{Rb(15C5)$_2$}$^+$(PyNPh)$^-$] (9).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 15-crown-5 (0.40 mL, 2.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.8 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to rubidium-2-ethylhexoxide (0.42 g, 2.00 mmol) gave a dark yellow precipitate. Volatiles were removed *in vacuo* and subsequent addition of 15-crown-5 (0.4 mL, 2.00 mmol) and THF (20 mL) with gentle heating afforded a dark red solution, which on cooling yielded crystals of **9** suitable for X-ray crystallography (0.98 g, 70.4%). Microanalysis for **9**: C, 53.56; H, 7.35; N, 3.98. $C_{31}H_{49}N_2O_{10}Rb$ requires C, 53.56; H, 7.10; N, 4.03. Spectroscopic data for **9**: δ_H ([^{2}H]$_8$ THF) 3.69 (40 H, s, 15C5), 6.06 (1 H, t, β-H-π), 6.52 (1 H, t, γ-H-π), 6.83 (1 H, d, β′-H-π), 7.02 (1 H, t, *para*-H-Ph), 7.06 (2 H, t, *meta*-H-Ph), 7.56 (2 H, d, *ortho*-H-Ph) and 7.95 (1 H, d, α-H-π). δ_C ([^{2}H]$_8$ THF) 72.05 (15C5), 108.53 (β-C-π), 112.43 (γ-C-π), 117.32 (β′-C-π), 122.55 (*para*-C-Ph), 129.89 (*meta*-C-Ph), 136.68 (*ipso*-C-Ph), 150.21 (*ortho*-C-Ph), 155.12 (α-C-π) and 165.75 (α′-C-π).

Preparation of [Rb(PyNPh)(18C6)] (10).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 18-crown-6 (0.53 g, 2.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.8 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to rubidium-2-ethylhexoxide (0.43 g, 2.00 mmol) gave a yellow precipitate. The solid was isolated from the mother liquor and washed with petrol (3 × 5 mL). Recrystallisation from hot toluene yielded crystals of **10** suitable for X-ray crystallography (0.81 g, 78.1%). Microanalysis for **10**: C, 52.65; H, 6.44; N, 5.25. $C_{23}H_{33}N_2O_6Rb$ requires C, 53.23; H, 6.41; N, 5.39. Spectroscopic data for **10**: δ_H ([^{2}H]$_8$ THF) 3.61 (24 H, s, 18C6), 5.83 (1 H, t, β-H-π), 6.38 (1 H, t, γ-H-π), 6.65 (1 H, d, β′-H-π), 6.86 (2 H, t, *meta*-H-Ph), 7.05 (1 H, t, *para*-H-Ph), 7.09 (2 H, d, *ortho*-H-Ph) and 7.84 (1 H, d, α-H-π). δ_C ([^{2}H]$_8$ THF) 73.16 (18C6), 106.77 (β-C-π), 111.33 (γ-C-π), 116.91 (β′-C-π), 124.10 (*meta*-C-Ph), 130.86 (*para*-C-Ph), 137.22 (*ipso*-C-Ph), 151.74 (*ortho*-C-Ph), 159.83 (α-C-π) and 169.13 (α′-C-π).

Preparation of [{Cs(15C5)$_2$}$^+$(PyNPh)$^-$] (11).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 15-crown-5 (0.80 mL, 4.00 mmol) and toluene (40 mL). Dropwise addition of Bu^{n}Li (0.8 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to caesium-2-ethylhexoxide (0.53 g, 2.00 mmol) gave a dark yellow precipitate. Volatiles were removed *in vacuo* and the solid washed with petrol (3 × 5 mL). Recrystallisation from hot toluene yielded crystals of **11** suitable for X-ray crystallography (1.10 g, 74.1%).

Microanalysis for **11**: C, 50.35; H, 6.67; N, 3.73. $C_{31}H_{49}N_2O_{10}Cs$ requires C, 50.14; H, 6.65; N, 3.77. Spectroscopic data for **11**: δ_H ($[^2H]_8$ THF) 3.61 (40 H, s, 15C5), 6.23 (1 H, t, β-H-π), 6.60 (1 H, t, γ-H-π), 6.82 (1 H, d, β'-H-π), 7.09 (1 H, t, *para*-H-Ph), 7.13 (2 H, t, *meta*-H-Ph), 7.71 (2 H, d, *ortho*-H-Ph) and 8.02 (1 H, d, α-H-π). δ_C ($[^2H]_8$ THF) 70.33 (15C5), 109.42 (β-C-π), 111.97 (γ-C-π), 117.32 (β'-C-π), 120.52 (*para*-C-Ph), 128.59 (*meta*-C-Ph), 135.75 (*ipso*-C-Ph), 148.25 (*ortho*-C-Ph), 150.42 (α-C-π) and 162.03 (α'-C-π). δ_{Cs} ($[^2H]_8$ THF) 10.40.

Preparation of [Cs(18C6){Cs(PyNPh)$_2$}$_\infty$] (12).

A 100 mL Schlenk flask was charged with 2-anilinopyridine (0.34 g, 2.00 mmol), 18-crown-6 (0.53 g, 2.00 mmol) and THF (40 mL). Dropwise addition of Bu^{n}Li (0.8 mL, 2.00 mmol) afforded a yellow solution. Addition of this solution to caesium-2-ethylhexoxide (0.53 g, 2.00 mmol) gave a yellow precipitate. The solid was isolated from the mother liquor and washed with petrol (3 × 5 mL). Recrystallisation from a hot toluene solution containing HMPA yielded crystals of **12** suitable for X-ray crystallography (0.72 g, 82.9%). Microanalysis for **12**: C, 47.02; H, 4.89; N, 6.34. $C_{34}H_{42}N_4O_6Cs_2$ requires C, 47.02; H, 4.87; N, 6.45. Spectroscopic data for **12**: δ_H ($[^2H]_8$ THF) 3.61 (24 H, s, 18C6), 6.38 (2 H, t, β-H-π), 6.72 (2 H, t, γ-H-π), 6.81 (2 H, d, β'-H-π), 7.21 (4 H, d, *ortho*-H-Ph), 7.28 (2 H, t, *para*-H-Ph), 7.51 (4 H, d, *meta*-H-Ph) and 8.08 (2 H, d, α-H-π). δ_C ($[^2H]_8$ THF) 70.81 (18C6), 108.48 (β-C-π), 110.47 (γ-C-π), 118.39 (β'-C-π), 120.46 (*ortho*-C-Ph), 128.88 (*para*-C-Ph), 136.32 (*ipso*-C-Ph), 148.67 (*meta*-C-Ph), 152.72 (α-C-π) and 162.49 (α'-C-π). δ_{Cs} ($[^2H]_8$ THF) 52.22 (s, br).

X-ray Crystallography

Crystal data for complexes **1**–**10** are listed in Table 3. Crystals were examined on a Bruker AXS SMART CCD area detector diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 160 K. Cell parameters were refined from positions of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods or Patterson synthesis and refined on F^2 values for all unique data. Structure **2** contains a severely disordered molecule of toluene which was treated with the PLATON SQUEEZE procedure.[70] Complex **7** was found to be non-merohedrally twinned; several crystals were examined and all were found to exhibit the same twinning effects to varying degrees of severity. In order to deal correctly with overlapping reflections in the diffraction pattern, symmetry-equivalents could not be merged before the refinement. In several of the structures disorder was resolved and refined for crown ether ligands, for THF, and/or for exchange of phenyl and pyridyl rings in uncoordinated anions; in some cases the anions were additionally disordered over an inversion centre. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were constrained with a riding model; U(H) was set at 1.2 times U_{eq} for the parent atom. Programs were Bruker AXS SMART (control) and SAINT integration,[71] and SHELXTL for structure solution, refinement, and molecular graphics.[72] CCDC reference numbers XXX/XXXX–XXX/XXXX.

Theoretical Calculations

DFT calculations for the $[Rb(12C4)_2]^+$ complex ion **7a** were undertaken using the Gaussian98 program.[66] Geometry optimisations were performed using standard gradient techniques with the b3lyp functional[73] and double-zeta quality basis set (lanl2dz for Rb; d95* for C, O and H).[74] One conformational minimum was located on the potential energy surface (verified by all-positive analytic vibrational frequencies). All attempts to obtain an optimised geometry with parallel crown ligands (D_{4h} or D_{4d} symmetry) resulted in either saddle points on the potential energy surface (*i.e.* imaginary vibrational frequencies) or, in the absence of symmetry constraints, a return to the bent conformational minimum found previously. Therefore, in order to obtain an approximate value for the energy of complex bending, a single-point energy calculation was performed on the optimised structure with one ligand rotated about the Rb atom-centre to produce the parallel conformation.

Acknowledgements

References

(1) (a) J. D. Smith, *Adv. Organomet. Chem.,* 1999, **43**, 267; (b) M. A. Beswick and D. S. Wright, *Comprehensive Organometallic Chemistry II*, Eds: E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon Press, Oxford. 1995, **1**, 1; (c) E. Weiss, *Angew. Chem. Int. Ed. Engl.,* 1993, **32**, 1501; (d) R. E. Mulvey, *Chem. Soc. Rev.,* 1991, **20**, 167; (e) K. Gregory, P. von R. Schleyer and R. Snaith, *Adv. Inorg. Chem.,* 1991, **37**, 47; (f) C. Schade and P. von R. Schleyer, *Adv. Organomet. Chem.,* 1987, **27**, 169; (g) W. N. Setzer and P. von R. Schleyer, *Adv. Organomet. Chem.,* 1985, **24**, 353.

(2) (a) L. Brandsma and H. Verkruijsse, *Preparative Polar Organometallic Chemistry 1.,* Springer, Berlin, 1987; (b) B. J. Wakefield, *Comprehensive Organometallic Chemistry II*, Eds: E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon Press, Oxford, 1982, **7**, 1; (c) M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides,* Horwood-Wiley, Chichester, 1980; (d) J. C. Stowell, *Carbanions in Organic Synthesis,* Wiley, New York, 1979; (e) B. J. Wakefield, *Organolithium Compounds*, Pergamon Press, Oxford, 1974.

(3) A. M. Sapse and P. von R. Schleyer, Eds, *Lithium Chemistry. A Theoretical and Experimental Overview*, Wiley Interscience, New York, 1995.

(4) F. H. Allen, *Acta Crystallogr. Sect. B*, 2002, **58**, 380.

(5) (a) S. T. Liddle and W. Clegg, *Acta Crystallogr., Sect. E.,* 2003, **59**, m1062; (b) S. T.Liddle and W. Clegg, *Polyhedron*, 2002, **21**, 2451; (c) S. T.Liddle and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 2001, 3549; (d) S. T.Liddle and W. Clegg, *J. Chem. Soc., Dalton Trans.,* 2001, 402.

(6) S. T. Liddle and W. Clegg, *Polyhedron*, 2003, **22**, 3507.

(7) (a) F. Antolini, P. B. Hitchcock, A. V. Khvostov and M. F. Lappert, *Eur. J. Inorg. Chem.,* 2003, 3391; (b) D. A. Armstrong, R. P. Davies, W. Clegg, S. T. Liddle, D. Linton, P. Schooler, R. Snaith and A. E. H. Wheatley, *Phosphorus, Sulfur and Silicon and The Related Elements*, 2001, **168**, 93; (c) D. R. Armstrong, W. Clegg, R. P. Davies, S. T. Liddle, D. J. Linton, P. R. Raithby, R. Snaith and A. E. H. Wheatley, *Angew. Chem. Int. Ed. Engl.,* 1999, **38**, 3367; (d) M. Polamo and M. Leskelä, *J. Chem. Soc. Dalton Trans.,* 1996, 4345; (e) P. C.Andrews, D. R. Baker, R. E. Mulvey, W. Clegg and P. A. O'Neil, *Polyhedron,* 1991**, 10**, 1839; (f) P. C. Andrews, W.Clegg and R. E. Mulvey, *Angew. Chem. Int. Ed. Engl.,* 1990, **29**, 1440; (g) D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.,* 1984, 1984; (h) D. Barr, W.Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.,* 1984, 469.

(8) R. Kempe, *Eur. J. Inorg. Chem.*, 2003, 791.

(9) R. D. Rogers, E. J. Voss, *Inorg. Chim. Acta,* 1987, **133**, 181.

(10) H. A. Eick and E. Mason, *Acta Cryst.,* Sect. B, 1982, **38**, 1821.

(11) L. J. Farrugia, I. M. Watson, *Acta Cryst.,* Sect. C, 1999, **55**, 326.

(12) S. Chadwick, K. R. Senge, *Chem. Eur. J.,* 1998, **4**, 1768.

(13) M. Polamo, T. Repo and M. Leskelä, *Acta Chemica Scandinavica*, 1997, *51*, 325.

(14) J. W. Steed, P. C. Junk, *J. Chem. Soc. Dalton Trans.,* 1999, 2141.

(15) I. Cragg-Hine, M. G. Davidson, A. J. Edwards, P. R. Raithby, R. Snaith*, J. Chem. Soc. Dalton Trans.,* 1994, 2901.

(16) P. C. Andrews, D. R. Armstrong, D. R. Baker, R. E. Mulvey, W. Clegg, L. Horsburgh, P. A. O'Neil and D. Reed, *Organometallics,* 1995, **14**, 427.

(17) B. Schiemenz, B. Antelmann, G. Huttner and L. Z. Zsolnai, *Z. Anorg. Allg. Chem.,* 1994, **620**, 1760.

(18) R. H. Huang, J. L. Eglin, S. Z. Huang, L. E. H. McMills and J. L. Dye, *J. Am. Chem. Soc.,* 1993, **115**, 9542.

(19) R. W. Alder, M. E. Blake, C. Bortolotti, S. Bufali, C. P. Butts, E. Linehan, J. M. Oliva, A. G. Orpen and M. J. Quayle, *J. Chem. Soc., Chem. Commun.,* 1999, 241.

(20) P. B. Hitchcock, M. F. Lappert and M. Layh, *J. Chem. Soc., Dalton Trans.,* 1998, 3113.

(21) A. R. Kennedy, R. E. Mulvey, C. L. Raston, B. A. Roberts and R. B. Rowlings, *J. Chem. Soc., Chem. Commun.,* 1999, 353.

(22) G. Bombieri, G. Bruno, M. D. Grillone and G. Polizzotti, *Acta Cryst.,* Sect. C., 1984, **40**, 2011.

(23) F. M. MacKenzie, R. E. Mulvey, W. Clegg and L. Horsburgh, *Polyhedron,* 1998, **17**, 993.

(24) D. Hoffmann, W. Bauer, F. Hampel, F.; N. J. R. van E. Hommes, P. von R. Schleyer, P. Otto, U. Pieper, D. Stalke, D. S. Wright and R. Snaith, *J. Am. Chem. Soc.,* 1994, **116**, 528.

(25) T. E. Waldman, B. Waltermire, A. L. Rheingold and R. D. Ernst, *Organometallics,* 1993, **12**, 4161.

(26) B. Borgsen, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.,* 1991, **596**, 55.

(27) B. Schreiner, K. Dehnicke, K. Maczek and D. Fenske, *Z. Anorg. Allg. Chem.,* 1993, **619**, 1414.

(28) D. R. Armstrong, R. P. Davies, D. J. Linton, R. Snaith, P. Schooler and A. E. H. Wheatley, *J. Chem. Soc., Dalton Trans.*, 2001, 2838.

(29) M. C. Cassani, Y. K. Gun'ko, P. B. Hitchcock, M. F. Lappert and F. Laschi, *Organometallics,* 1999, **18**, 5539.

(30) A. S. C. Chan, H. S. Shieh and J. R. Hill, *J. Organomet. Chem.,* 1985, **279**, 171.

(31) C. P. Horwitz, E. M. Holt, C. K. Brock and D. F. Shriver, *J. Am. Chem. Soc.,* 1985, **107**, 8136.

(32) F. G. N. Cloke, P. B. Hitchcock and A. McCamley, *J. Chem. Soc., Chem., Commun.* 1993, 248.

(33) G. Rabe, H. W. Roesky, D. Stalke, F. Pauer and G. M. Sheldrick, *J. Organomet. Chem.,* 1991, **403**, 11.

(34) A. Crispini, R. J. Errington, G. A. Fisher, F. J. Funke, N. C. Norman, A. G. Orpen, S. E. Stratford and O. Struve, *J. Chem. Soc., Dalton Trans.,* 1994, 1327.

(35) P. G. Willard, *Acta Cryst.,* Sect. C., 1988, **44**, 270.

(36) For recent reviews see: (a) P. Jutzi and G. Reumann, *J. Chem. Soc., Dalton Trans.,* 2000, 2237, and references therein; (b) D. Stalke, *Angew. Chem. Int. Ed. Engl.,* 1994, **33**, 2168, and references therein; (c) T. P. Hanusa, *Chem. Rev.,* 1993, **93**, 1023, and references therein; (d) T. J. Marks and R. D. Ernst, *Comprehensive Organometallic Chemistry,* Eds: E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon Press, Oxford, 1982, **3**, 173, and references therein; (e) J. W. Connolly and C. Hoff, *Adv. Organomet. Chem.,* 1981, **19**, 123, and references therein.

(37) Y. Y. Wei, B. Tinant, J. P. Declercq, M. V. Meerssche and J. Dale, *Acta Cryst.,* Sect. C., 1988, **44**, 68.

(38) H. Schumann, J. Gottfriedsen and J. Demtschuk, *J. Chem. Soc., Chem. Commun.,* 1999, 2091.

(39) T. D. Tilley, R. A. Anderson, B. Spencer, H. Ruben, A. Zalkin and D. H. Templeton, *Inorg. Chem.,* 1980, **19**, 2999.

(40) R. A. Williams, T. P. Hanusa and J. C. Huffman, *Organometallics,* 1990, **9**, 1128.

(41) J. C. Bryan, R. A. Sachleben, J. M. Lavis, M. C. Davis, J. H. Burns and B. P. Hay, *Inorg. Chem.,* 1998, **37**, 2749.

(42) U. Englich, K. Hassler, K. Ruhlandt-Senge and F. Uhlig, *Inorg. Chem.,* 1998, **37**, 3532.

(43) A. Bashall, M. A. Beswick, C. N. Harmer, A. D. Hopkins, M. McPartlin, M. A. Paver, P. R. Raithby and D. S. Wright, *J. Chem. Soc., Dalton Trans.,* 1998, 1389.

(44) For examples see: (a) A. Dietrich, B. Neumuller and K. Dehnicke, *Z. Anorg. Allg. Chem.,* 1999, **625**, 619; (b) T. A. Budzichowski, M. H. Chisholm, K. Folting, J. C. Huffman and W. E. Streib, *J. Am. Chem. Soc.,* 1995, **117**, 7428.

(45) W. Clegg, A. M. Drummond, R. E. Mulvey and S. T. Liddle, *J. Chem. Soc., Chem. Commun.,* 1998, 2391.

(46) N. S. Fender, S. S. Finegan, D. Miller, M. Mitchell, I. A. Kahwa and F. R. Fronczek, *Inorg. Chem.,* 1994, **33**, 4002.

(47) J. Baldas, J. F. Boas, S. F. Colmanet, A. D. Rae and G. A. Williams, *Proc. R. Soc., London,* Ser A., 1993, **442**, 437.

(48) S. B. Dawes, D. L. Ward, O. Fussa-Rydel, R. H. Huang and J. L. Dye, *Inorg. Chem.,* 1989, **28**, 2132.

(49) For examples see: (a) J. Hašek and K. Huml, *Acta Cryst.,* Sect. B., 1978, **34**, 1812; (b) M. Dobler and R. P. Phizackerley, *Acta Cryst.,* Sect. B., 1974, **30**, 2746.

(50) S. Neander and U. Behrens, *Z. Anorg. Allg. Chem.*, 1999, **625,** 1429.

(51) F. T. Edelmann, F. Pauer, M. Wedler and D. Stalke, *Inorg. Chem.*, 1992, **31**, 4143.

(52) P. B. Hitchcock, M. F. Lappert, L. Wing-Por, L. Diansheng and T. J. Shun, *J. Chem. Soc., Chem. Commun.*, 1993, 1386.

(53) D. Hoffmann, F. Hampel and P. von R. Schleyer, *J. Organomet. Chem.,* 1993, **456**, 13.

(54) D. Hoffmann, W. Bauer, P. von R. Schleyer, U. Pieper and D. Stalke, *Organometallics*, 1993, **12**, 1193.

(55) Crystals of **11** were triclinic, space group $P\bar{1}$, $a = 8.637(2)$ Å, $b = 9.803(2)$ Å, $c = 11.480(2)$ Å, $\alpha = 67.337(3)°$, $\beta = 89.975(3)°$, $\gamma = 73.630(3)°$, $Z = 1$. They were thin needles giving marginal diffraction data (despite repeated recrystallisation and data collection), and the structure could not be satisfactorily refined to a stable convergence, giving a high R above 0.12, badly shaped displacement ellipsoids, and high residual electron density, indicating probable serious disorder problems that could not be resolved due to the poor quality of the data.

(56) D. L. Ward, R. H. Wang and J. L. Dye, *Acta Cryst., Sect. C.*, 1990, **46**, 1838.

(57) Crystals of **12** were monoclinic, apparent space group $I2/m$, $a = 8.176(4)$Å, $b = 16.881(8)$Å, $c = 13.367(7)$Å, $\beta = 105.265(7)°$, $Z = 2$. Serious disorder of the amides (over four orientations each) was not resolvable, giving $R = 0.078$, and the unit cell and space group remain uncertain from the poor-quality data.

(58) D. J. Burkey, T. P. Hanusa and J. C. Huffman, *Inorg. Chem.,* 2000, **39**, 153.

(59) S. P. Constantine, H. Cox, P. B. Hitchcock and G. A. Lawless, *Organometallics,* 2000, **19**, 317.

(60) (a) G. Bruno, E. Ciliberto, I. L. Fragala and P. Jutzi, *J. Organomet. Chem.,* 1985, **289**, 263; (b) S. G. Baxter, A. H. Cowley, J. G. Lasch, M. Lattman, W. P. Sharum and C. A. Stewart, *J. Am. Chem. Soc.,* 1982, **104**, 4064; (c) S. Cradock and W. Duncan, *J. Chem. Soc. Faraday Trans.,* 1978, **74**, 194.

(61) D. L. Reger, T. D. Wright, C. A. Little, J. J. S. Lamba and M. A. Smith, *Inorg. Chem.,* 2001, **40**, 3810.

(62) M. Guido and G. Gigli, *J. Chem. Phys.,* 1976, **65**, 1397.

(63) (a) M. Kaupp, P. von R. Schleyer, M. Dolg and H. Stoll, *J. Am. Chem. Soc.,* 1992, **114**, 8202; (b) R. A. Andersen, J. M. Boncella, C. J. Burns, R. Blom, A. Haaland and H. V. Volden, *J. Organomet. Chem.,* 1986, **312**, C49.

(64) R. A. Anderson, R. Blom, C. J. Burns and H. V. Volden, *J. Chem. Soc., Chem. Commun.,* 1987**,** 768**.**

(65) R. Blom, K. Faegri Jr. and H. V. Volden, *Organometallics,* 1990, **9**, 373.

(66) *Gaussian 98, Revision A.7,* M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratman, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennnucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Qui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian Inc., Pittsburgh PA, 1998.

(67) J. D. Smith and T. P. Hanusa, *Organometallics,* 2001, **20**, 3056.

(68) T. K. Hollis, J. K.; Burdett and B. Bosnich, *Organometallics,* 1993, **12**, 3385.

(69) M. H. Chisholm, S. R. Drake, A. A. Naiini and W. E. Streib, *Polyhedron*, 1991, **10**, 337.

(70) A. L. Spek, PLATON, University of Utrecht, The Netherlands, 2000.

(71) SMART and SAINT software for CCD diffractometers, Bruker AXS Inc., Madison, WI, USA, 1997.

(72) G. M. Sheldrick, SHELXTL user manual, version 5.1, Bruker AXS Inc., Madison, WI, USA, 1997.

(73) (a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Physical Review B,* 1988, **37**, 785; (c) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.,* 1989, **157**, 200.

(74) (a) T. H. Dunning Jr. and P. J. Hay, *Modern Theoretical Chemistry,* Ed. H. F. Schaefer III, Plenum, New York, 1976, **3**, 1; (b) W. R. Wadt and P. J. Hay, *J. Chem. Phys.,* 1985, **82**, 284.

Tables

Table 1. Selected bond lengths (Å) and angles (°) for compounds **1**–**10**.

Compound 1

Na–O(1)	2.464(2)	Na–O(2)	2.494(2)
Na–O(3)	2.467(2)	Na–O(4)	2.492(3)
Na–O(5A)	2.453(6)	Na–O(6A)	2.461(10)
Na–O(7A)	2.510(6)	Na–O(8A)	2.496(5)
Na–O(5B)	2.510(6)	Na–O(6B)	2.483(10)
Na–O(7B)	2.404(6)	Na–O(8B)	2.444(5)

Compound 2

Na–N(1)	2.4819(10)	Na–N(2)	2.4503(10)
Na–O(1)	2.5078(10)	Na–O(2)	2.4874(9)
Na–O(3)	2.5117(9)	Na–O(4)	2.5321(9)
Na–O(5)	2.5078(10)		
N(1)–Na–N(2)	55.32(3)		

Compound 3

Na–N(1)	2.449(3)	Na–O(2)	2.516(2)
Na–N(2)	2.517(3)	Na–O(3)	2.573(2)
Na–O(4)	2.625(3)	Na–O(1)	2.780(2)
N(1)–Na–N(2)	54.79(9)		

Compound 4

K(1)–N(1)	2.911(5)	K(1)–N(2)	2.798(4)
K(1)–N(3)	2.929(5)	K(1)–N(4)	2.894(5)
K(1)–O(1)	2.981(5)	K(1)–O(2)	2.767(5)
K(1)–O(3)	2.745(5)	K(1)–O(4)	2.752(4)
K(2)–N(1)	2.991(5)	K(2)–N(2)	2.904(5)
K(2)–N(3)	2.906(4)	K(2)–N(4)	2.811(4)
K(2)–O(5)	2.986(6)	K(2)–O(5A)	2.738(14)
K(2)–O(6)	2.765(5)	K(2)–O(7)	2.774(4)
K(2)–O(8)	2.791(4)		
N(1)–K(1)–N(2)	46.94(13)	N(3)–K(1)–N(4)	46.08(13)
N(1)–K(2)–N(2)	45.39(13)	N(3)–K(2)–N(4)	46.95(12)
K(1)–N(1)–K(2)	70.03(10)	K(1)–N(2)–K(2)	72.88(12)
K(1)–N(3)–K(2)	70.98(10)	K(1)–N(4)–K(2)	72.85(11)

Compound 5

K–O(1)	2.915(2)	K–O(2)	2.850(2)
K–O(3A)	2.909(4)	K–O(3B)	2.827(8)
K–O(4)	2.934(2)	K–O(5)	2.981(2)

Compound 6

K(1)–N(1)	3.0184(19)	K(1)–O(1)	2.7844(18)
K(1)–O(2)	2.8187(17)	K(1)–O(3)	2.8409(17)
K(2)–N(1)	2.855(2)	K(2)–N(2)	2.748(2)
K(2)–O(2A)	2.8577(16)		
N(1)–K(2)–N(2)	48.71(6)	K(1)–N(1)–K(2)	85.46(5)
K(1)–O(2)–K(2A)	89.23(4)		

Symmetry operation: A   1–x, 1–y, 1–z

Compound 7

Rb(1)–O(1)	2.983(5)	Rb(1)–O(2)	2.912(6)
Rb(1)–O(3)	2.944(5)	Rb(1)–O(4)	2.974(6)
Rb(1)–O(5)	2.977(5)	Rb(1)–O(6)	2.949(6)
Rb(1)–O(7)	2.929(6)	Rb(1)–O(8)	2.935(7)
Rb(1)–O(9)	3.199(10)		

Compound 8

Rb–O(1)	2.859(4)	Rb–O(2)	2.881(4)
Rb–O(3)	2.931(4)	Rb–O(4)	3.061(4)
Rb–O(5A)	2.910(11)	Rb–O(6A)	2.963(10)
Rb–O(7A)	2.953(9)	Rb–O(8A)	2.915(9)
Rb–O(5B)	3.020(8)	Rb–O(6B)	2.962(9)
Rb–O(7B)	2.957(9)	Rb–O(8B)	2.951(9)

Compound 9

Rb–O(1)	2.999(2)	Rb–O(2)	2.958(2)
Rb–O(2A)	2.958(2)	Rb–O(3A)	2.955(3)
Rb–O(3B)	3.021(6)	Rb–O(4)	2.981(2)
Rb–O(5)	3.051(2)		

Compound 10

Rb–N(1)	3.0230(11)	Rb–N(2)	2.9516(11)
Rb–O(1)	2.9788(9)	Rb–O(2)	2.9903(9)
Rb–O(3)	2.8689(9)	Rb–O(4)	3.0539(10)
Rb–O(5)	2.9757(10)	Rb–O(6)	2.9978(9)
N(1)–Rb–N(2)	45.28(3)		

Table 2

Comparison of geometrical parameters for the experimental crystal structure of 7 and the theoretical structure of 7a

X is the centroid of the O atoms of each crown ligand; the dihedral angle is between the mean planes of the O atoms of the two crown ligands; ΔRb is the displacement of Rb from each of these mean planes.

	7 (experimental)	**7a** (theoretical)
Rb–O(crown)	2.912–2.983	2.960–3.242
Rb–O(THF)	3.199	
Rb–X	2.159, 2.164	2.253, 2.267
X–Rb–X	145.4	145.4
dihedral angle	147.5	154.6
ΔRb	2.159, 2.164	2.247, 2.244

Table 3

Crystallographic data

Compounds 1–5

Compound	1	2	3	4	5
Formula	$C_{16}H_{32}O_8Na^+$ $C_{11}H_9N_2^-$	$C_{21}H_{29}N_2NaO_5$ $\cdot 0.5C_7H_8$	$C_{23}H_{33}N_2NaO_6$	$C_{38}H_{50}K_2N_4O_8$ $\cdot C_6H_6$	$C_{20}H_{40}KO_{10}^+$ $C_{11}H_9N_2^-$
M	544.6	458.5	456.5	847.1	648.8
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$Pca2_1$	$P2_1/n$	$C2/c$	$P2_1/c$	$P\bar{1}$
a /Å	17.860(3)	7.7685(5)	25.053(4)	11.1195(13)	8.8527(9)
b /Å	11.6780(19)	21.5359(13)	13.698(2)	24.947(3)	9.7870(10)
c /Å	13.525(2)	14.8774(9)	17.424(3)	16.4669(18)	11.3106(12)
α /°					66.018(3)
β /°		103.254(2)	126.807(3)	100.675(3)	72.371(2)
γ /°					73.225(2)
V /Å^3	2821.0(8)	2422.7(3)	4787.4(14)	4488.8(9)	837.76(15)
Z	4	4	8	4	1
Data collected	22364	22522	12396	10764	7565
Unique data	6690	6048	4205	6554	3958
R_{int}	0.053	0.026	0.088	0.067	0.032
Refined parameters	454	263	290	533	298
R (on F, $F^2 > 2\sigma$)	0.059	0.037	0.055	0.070	0.066
R_w (on F^2, all data)	0.167	0.096	0.147	0.199	0.180
min, max electron density /e Å^{-3}	0.64, −0.25	0.19, −0.20	0.34, −0.32	0.61, −0.46	0.71, −0.43

Compounds 6–10

Compound	6	7	8	9	10
Formula	$C_{34}H_{42}K_2N_4O_6$	$C_{20}H_{40}O_9Rb^+$ $C_{11}H_9N_2^-$	$C_{16}H_{32}O_8Rb^+$ $C_{11}H_9N_2^-$	$C_{20}H_{40}O_{10}Rb^+$ $C_{11}H_9N_2^-$	$C_{23}H_{33}N_2O_6Rb^+$
M	680.9	679.2	607.1	695.2	519.0
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$I2/a$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a /Å	15.3953(12)	36.589(4)	10.5728(10)	8.8231(8)	10.5347(6)
b /Å	11.1701(8)	11.3191(12)	11.8518(11)	9.7887(9)	14.4623(8)
c /Å	20.056(2)	26.225(3)	13.3647(13)	11.4293(10)	16.3958(10)
α /°			64.205(2)	65.640(2)	
β /°	90.974(2)	110.718(2)	82.099(2)	73.435(2)	96.175(2)
γ /°			75.043(2)	73.737(2)	
V /Å^3	3448.5(5)	10158.8(19)	1456.1(2)	846.86(13)	2483.5(2)
Z	4	12	2	1	4
Data collected	11560	8835	12670	7288	17660
Unique data	4236		6640	3811	5867
R_{int}	0.068		0.016	0.031	0.018
Refined parameters	210	878	569	298	290
R (on F, $F^2 > 2\sigma$)	0.053	0.057	0.049	0.042	0.021
R_w (on F^2, all data)	0.124	0.175	0.142	0.092	0.052
min, max electron density /e Å^{-3}	0.83, −0.58	1.52, −0.55	1.02, −0.52	0.63, −0.67	0.35, −0.28

Figure Captions

Figure 1. The structure of the ion-pair $[\{Na(12C4)_2\}^+(L^-)]$ (**1**). In this and other Figures, selected atom labels are shown, and hydrogen atoms are omitted for clarity. The suffix A denotes an inversion-related atom.

Figure 2. The molecular structure of $[Na(L)(15C6)]$ (**2**).

Figure 3. The molecular structure of $[Na(L)(18C6)]$ (**3**).

Figure 4. The molecular structure of $[\{K(L)(12C4)\}_2]$ (**4**).

Figure 5. The structure of the ion-pair $[\{K(15C5)_2\}^+(L^-)]$ (**5**). The structures of **9** and **11** are essentially identical in appearance. The minor disorder component (including atom O3B) is omitted here and in other representations of disordered structures.

Figure 6. The structural repeat unit of $[\{K(18C6)K(L)_2\}_\infty]$ (**6**).

Figure 7. Polymeric structure of **6**, highlighting the (K_2NO) rings.

Figure 8. One ion-pair (two-thirds of the asymmetric unit) in the structure of $[\{Rb(12C4)_2(THF)\}^+(L)^-]$ (**7**). Only one disorder component of each ion is shown.

Figure 9. A loosely-bound centrosymmetric pair of cations and the two independent anions of $[\{Rb(12C4)_2\}^+(L^-)]$ (**8**). The letter A is used here for major disorder components.

Figure 10. The molecular structure of $[Rb(L)(18C6)]$ (**10**).

Figure 11. The polymeric structure of $[\{Cs(18C6)Cs(L)_2\}_\infty]$ (**12**) as indicated quantitatively by X-ray crystallography.

Figure 12. (a) The optimised geometry of $[Rb(12C4)_2]^+$ (**7a**) obtained at the b3lyp/(lanl2dz,d95*) level; (b) the model used in the single-point energy calculation, derived from the optimised, bent geometry; the lower crown ligand has been rotated about the Rb atom to make the two ligands parallel. Hydrogen atoms are omitted for

clarity; the dotted lines denote the vectors Rb-X (where X is the centroid of the four
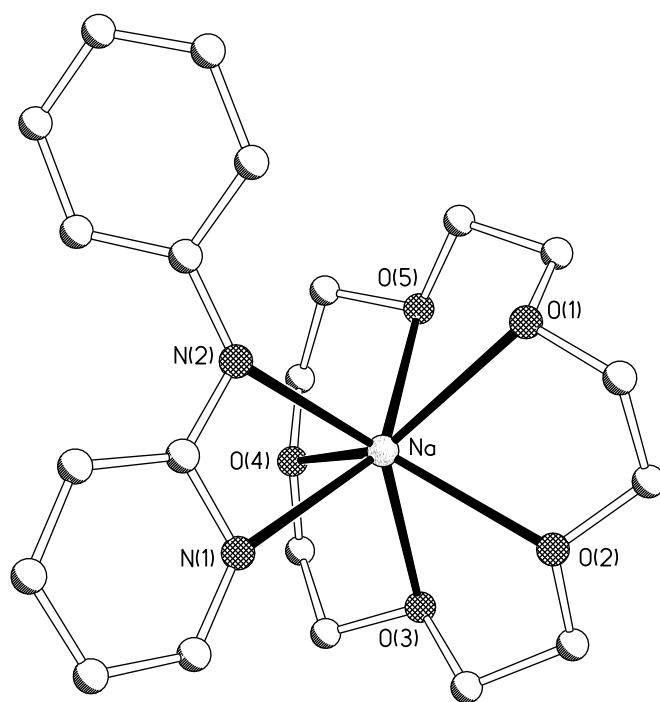
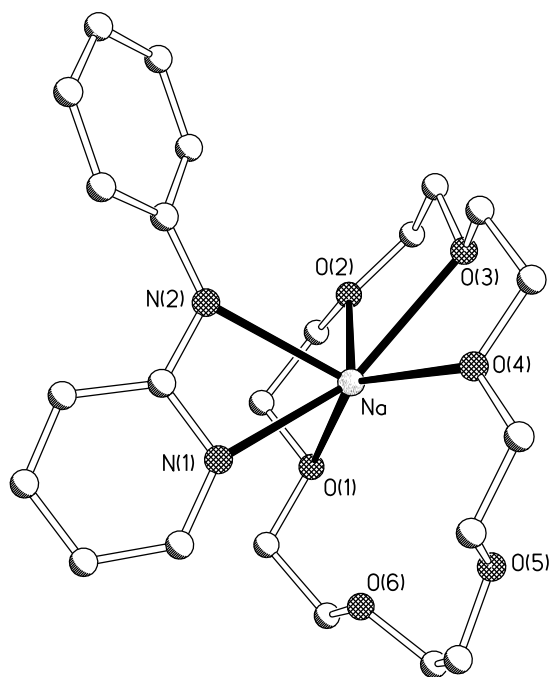oxygen atoms in each crown ligand).

Figures
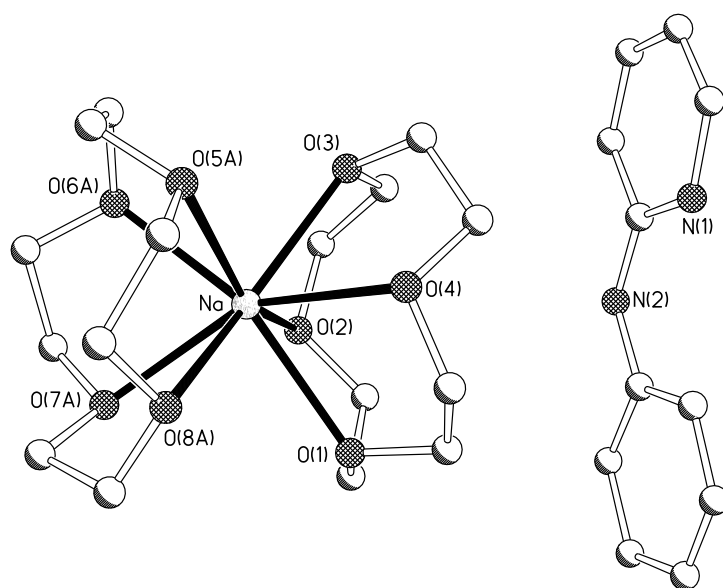
Fig. 1

Fig. 2

Fig. 3
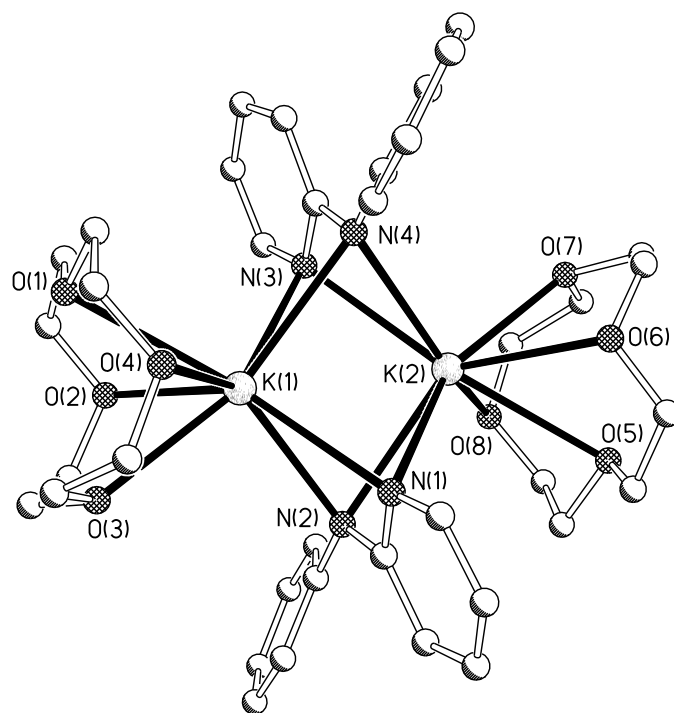
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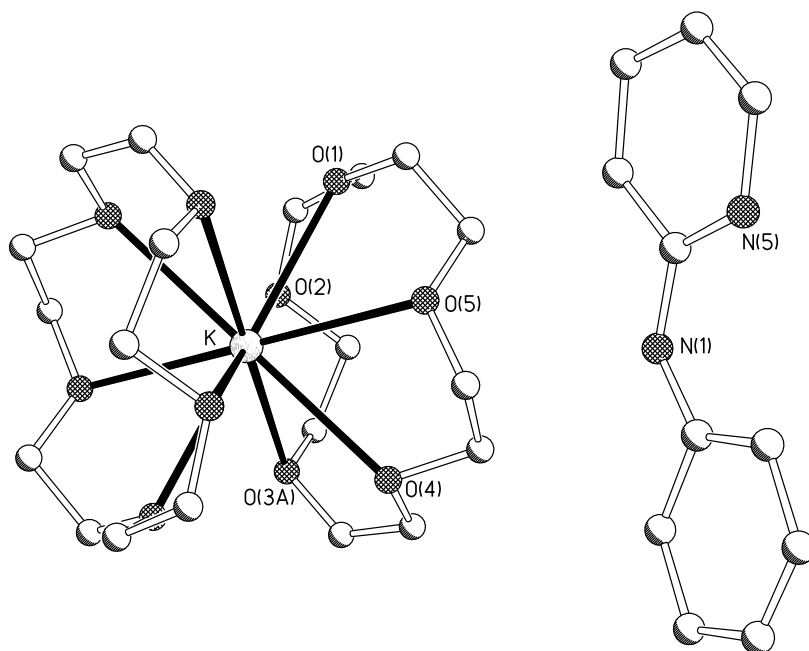
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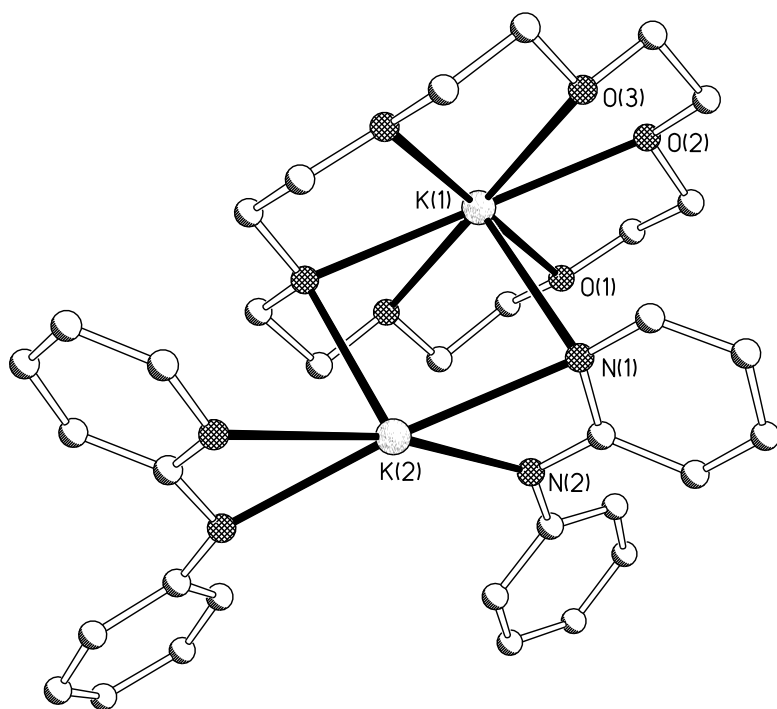
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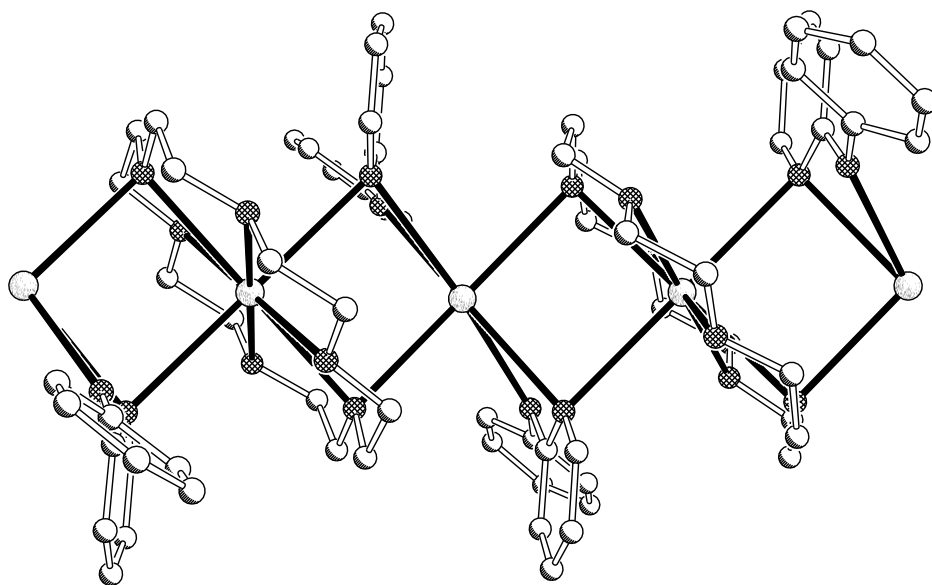
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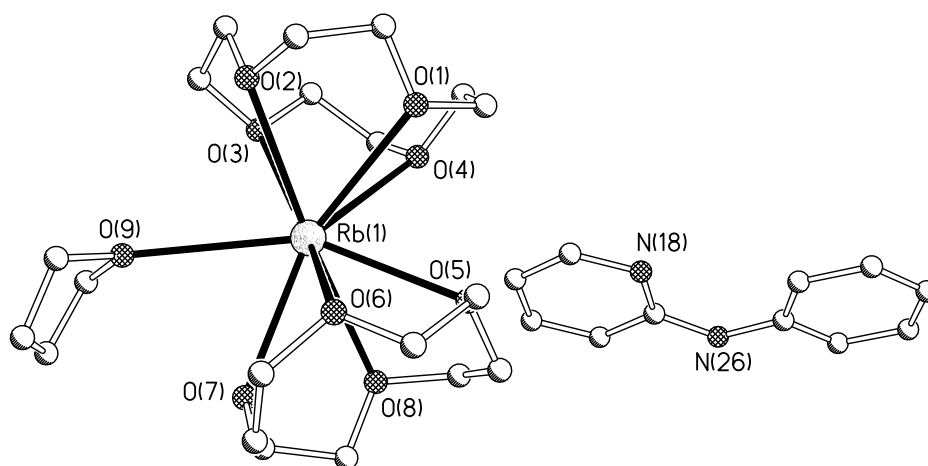
Fig. 8
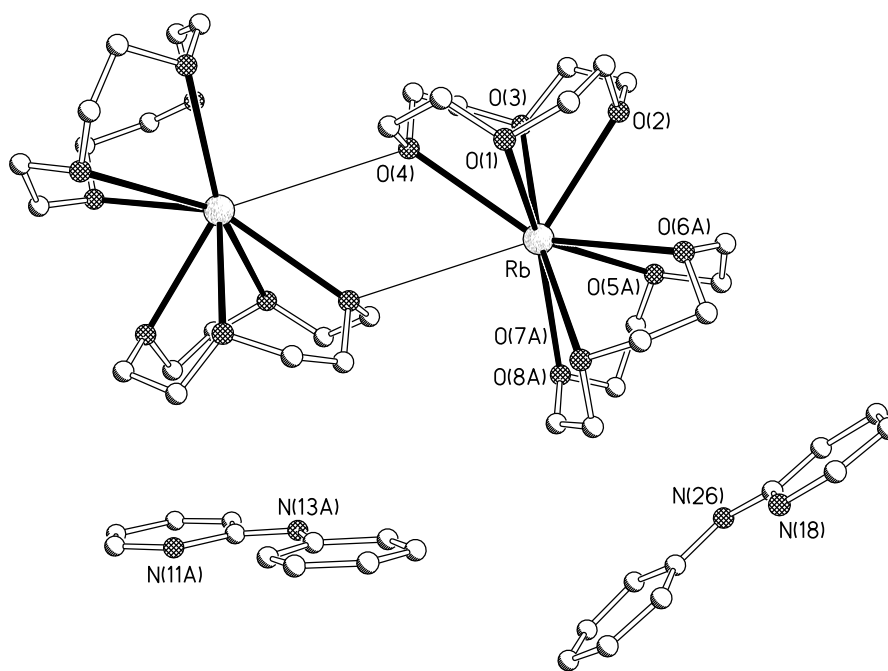
Fig. 9
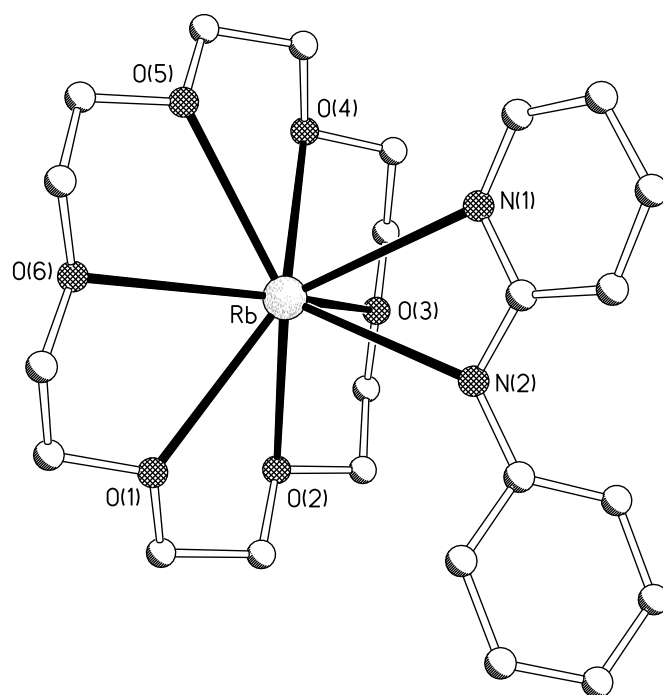
Fig. 10

Fig. 11

Fig. 12(a)   **Fig. 12(b)**