

A mixed valent heterometallic Cu^{II}/Na^I coordination polymer with sodium–phenyl bonds†Cite this: *Dalton Trans.*, 2014, **43**, 5558Amitabha Datta,^{*a} Kuheli Das,^b Chiara Massera,^c Jack K. Clegg,^{*d} Chittaranjan Sinha,^b Jui-Hsien Huang^{*a} and Eugenio Garribba^eReceived 20th January 2014,
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A mixed valent heterometallic Cu^{II}/Na^I coordination polymer (**1**) is generated by the reaction of a Schiff base ligand, (6,6'-(1*E*,1'*E*)-(2-hydroxypropane-1,3-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)-bis(2-methoxyphenol)) with copper(II) acetate and sodium perchlorate. In addition to the presence of alcohol oxygen–sodium coordination bonds, the single crystal X-ray structure reveals that the 1D coordination polymer is stabilised by the formation of phenyl–sodium η²-bonds, face-to-face π–π contacts and Cu–π interactions.

Introduction

Recent developments in the field of supramolecular chemistry have shown that the self-assembly of small building blocks can lead to the production of large well defined structures, which are held together by non-covalent interactions.¹ The combination of multidentate ligands with transition metals has resulted in the preparation of a diverse range of complicated metallo-supramolecular architectures with a high degree of predictability, which in turn display a range of interesting functionalities including catalysis and host–guest chemistry.² These systems typically employ one metal ion, and the synthesis of hetero-nuclear coordination compounds continues to be an intensive and challenging area of investigation.³ Mixed donor Schiff base ligands are ideal for the formation of multi-nuclear complexes as they can be readily prepared from inexpensive starting materials and their coordination chemistry has been extensively studied.^{4,5}

Many of these complexes, particularly those containing tetradentate Schiff base ligands with N₂O₂ donor sets, often

occupy four coordination sites of a metal ion in a planar quasi-macrocyclic fashion leaving the metal ion coordinatively unsaturated,^{6,7} which allows for the controlled formation of multi-nuclear systems or coordination polymers by reaction with suitable bridging ligands.^{8–10}

The versatility of Schiff base ligands allows for the ready incorporation of additional donor atoms into the ligand backbone, which combined with the well established tendency of phenoxy ligands to bridge metal ions can provide a binding site for the coordination of a second metal ion, in a compartmental approach.^{5,11} Following this approach, the Schiff base ligand formed from the condensation of two equivalents of *o*-vanillin and propylenediamine (H₂vanpn) has been employed to prepare heterometallic 3d/4f^{10,12,13} and 3d/alkali metal complexes.^{13,14}

With the aim of preparing new multinuclear heterometallic coordination polymers^{8,15} we have modified the H₂vanpn Schiff base ligand to incorporate an additional alcoholic donor group, through the substitution of 1,3-diamino-2-propanol for propylenediamine.^{16,17} Upon reaction with Cu(II) and sodium perchlorate a new 1D coordination polymer (**1**) was formed. Its crystal structure, visible fluorescence, infra-red, UV-vis and EPR spectra are presented.

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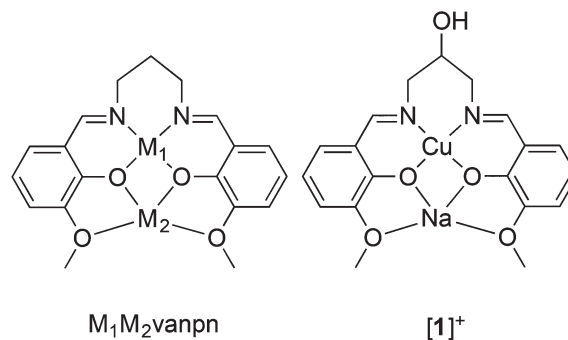
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Experimental

Synthesis of 1, $\{[\text{CuNaL}]\cdot\text{ClO}_4\cdot 0.5\text{H}_2\text{O}\}_n$

The ligand was prepared by adaptation of a literature procedure.¹⁶ *o*-Vanillin (0.304 g, 2 mmol) was combined with 1,3-diamino-2-propanol (0.090 g, 1 mmol) in methanol (25 mL) and brought to reflux. After 2 h the pale yellow solution was cooled to room temperature. The solvent was removed under reduced pressure, and the Schiff-base ligand was obtained as a light-yellow oil which was directly added to a 20 mL methanolic solution of $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ (0.199 g, 1 mmol), which immediately produced an intensely yellowish-green solution. A solution of NaClO_4 (0.122 g, 1 mmol) in methanol (10 mL) was added dropwise to the mixture and it was stirred for 1/2 h with warming. The green solution was placed in a refrigerator. Dark green block-shaped single crystals appeared after several days. Yield: 73%. Elemental analysis. Found: C, 40.87; H, 3.51; N, 5.33%. Calcd for $\text{C}_{38}\text{H}_{42}\text{Cl}_2\text{Cu}_2\text{N}_4\text{Na}_2\text{O}_{19}$ (1102.72): C, 41.39; H, 3.84; N, 5.08%.

Crystallography

Data were collected with an Oxford Gemini Ultra employing graphite monochromated $\text{Mo-K}\alpha$ radiation generated from a sealed tube (0.71073 Å) with ω and ψ scans at 120(2) K.¹⁸ Data integration and reduction were undertaken with CrysAlisPro¹⁸ and subsequent computations were carried out using the WinGX-32 graphical user interface.¹⁹ Gaussian absorption corrections were applied using CryAlisPro.¹⁸ The structure was solved by direct methods using SHELXS-97,²⁰ then refined and extended with SHELXL-97.²⁰ Non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Oxygen-bound hydrogen atoms were first located in the difference Fourier map before refinement with bond length and angle restraints. The Flack²¹ parameter refined to 0.000(11). Formula $\text{C}_{38}\text{H}_{42}\text{Cl}_2\text{Cu}_2\text{N}_4\text{Na}_2\text{O}_{19}$, M 1102.72, monoclinic, space group $P2_1(\#4)$, a 9.7605(2), b 17.0778(3), c 12.4657(3) Å, β 94.379(2), V 2071.81(7) Å³, D_c 1.768 g cm⁻³, Z 2, crystal size 0.47 by 0.23 by 0.21 mm, colour brown, habit block, temperature 120(2) Kelvin, $\lambda(\text{MoK}\alpha)$ 0.71073 Å, $\mu(\text{MoK}\alpha)$ 1.265 mm⁻¹, $T(\text{Analytical})_{\text{min,max}}$ 0.719, 0.819, $2\theta_{\text{max}}$ 61.12, hkl range -13 5, -23 12, -16 17, N 11390, N_{ind} 7842 (R_{merge} 0.0278), N_{obs} 6969 ($I > 2\sigma(I)$), N_{var} 614, residuals $*R_1(F)$ 0.0373, $wR_2(F^2)$ 0.0880, $\text{GoF}(\text{all})$ 1.024, $\Delta\rho_{\text{min,max}}$ -0.534 , 0.498 e⁻ Å⁻³.

$*R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o > 2\sigma(F_o)$; $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum (w(F_c^2)^2))^{1/2}$ all reflections $w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$. CCDC 865240.

Results and discussion

The Schiff base condensation of *o*-vanillin with 1,3-diamino-2-propanol in methanol^{16,17} followed directly by the addition of copper(II) acetate and sodium perchlorate yielded dark green crystals of $\{[\text{CuNaL}]\cdot\text{ClO}_4\cdot 0.5\text{H}_2\text{O}\}_n$, **1**, in 73% yield after several days of refrigeration. Structural analysis shows that **1**

crystallises with two $[\text{CuNaL}]$ complexes in the asymmetric unit in a dimeric arrangement with the sodium atoms coordinated to both the alcohol and a phenyl ring in adjacent complexes (Fig. 1) resulting in an infinite one-dimensional coordination polymer (Fig. 2). The copper(II) centres are formally square-planar with typical bond lengths and angles, while the sodium(I) centres are bound to five oxygen donors (two phenol and two methoxy oxygens from the vanillin groups and the alcohol group from an adjacent complex) as well as a phenyl ring from an adjacent ligand in an η^2 fashion. The five oxygens encircle the sodium ion in an almost planar array with bond lengths ranging from 2.32 to 2.47 Å. O–Na–O angles (between adjacent oxygens) range from 64.4 to 81.0° resulting in a pseudo macrocyclic arrangement reminiscent of sodium bound by 15-crown-5.²² The alcohol group deviates slightly (0.75 Å and 1.2 Å for each of the two independent complexes) from the mean plane of the other oxygen donors. Combined with the apical η^2 -phenyl donor the coordination geometry of the sodium is best described as a slightly distorted pentagonal pyramid. The sodium–carbon bond lengths are between 2.874(4) and 3.088(4) Å with a Na(1)–centre of the C–C bond distance of 2.90 Å and the same interaction for Na(2) at 2.96 Å.

The sodium–ring centroid distances are 3.21 Å and 3.14 Å, respectively, placing these bond lengths in the range of similar interactions previously observed.²³ While these distances are longer than those typically observed in Na–Cp bonds (often as short as 2.5 Å),²⁴ the present separations are significantly shorter than the sum of the van der Waals radii of sodium and carbon (3.97 Å) confirming the presence of a sodium–phenyl bond. Indeed, sodium–benzene interactions of this type and in similar orientations have been predicted to have interaction energies of approximately -20 kcal mol⁻¹,²⁵ which in this case

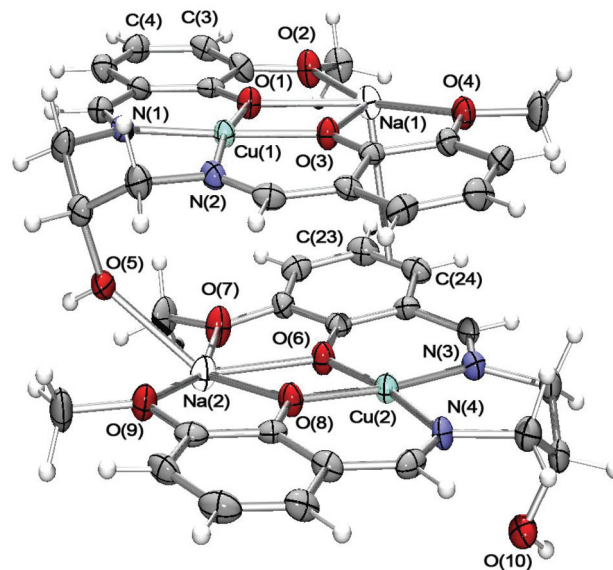


Fig. 1 ORTEP representation of the asymmetric unit of the crystal structure of $\{[\text{CuNaL}]\cdot\text{ClO}_4\cdot 0.5\text{H}_2\text{O}\}_n$ shown with 70% probability ellipsoids. Only metal ions and donor atoms are labelled for clarity. Solvent and anions are not shown.

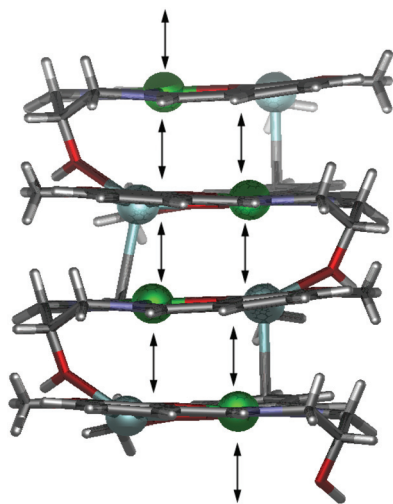


Fig. 2 Two schematic representations of part of the one-dimensional coordination polymer formed through Na–O and Na–C bonds. Double headed arrows indicate the presence of π – π and Cu– π interactions. Cu shown as green balls and Na as pale blue.

contribute to the stabilisation of the polymeric structure in the solid state.

While sodium–phenylene bonds have previously been observed,²³ they are uncommon in transition metal complexes. Indeed, of the 3374 single crystal structures (with *R*-factors of less than 10%) containing both phenyl rings and sodium in the Cambridge Structural Database (v1.15, 2013) only 13% contain carbon–sodium ‘contacts’ of less than 3.97 Å. When the search criteria are restricted to only include structures where the sodium ion is located above the face of the phenyl ring in a suitable position for η -type bonding to occur²⁵ (*i.e.* with the Na–ring centroid–phenylene plane angle of between 60 and 120 degrees); there are only 138 examples, of which 61 are sodium salts of organic compounds. Of those remaining, only 11 have Na–C separations of less than 3.1 Å and only four show η^2 rather than η^4 or η^6 bonding.

The close stacking of the complexes in the present complex is further stabilised by a series of offset face-to-face π – π contacts and Cu– π interactions (Fig. 2). The copper– π distances of between 3.1 and 3.5 Å are similar to those observed in a series of related complexes.²⁶ Adjacent polymeric chains interact with their neighbours through a series of hydrogen bonds (Fig. 3, Table S1†). Each of the coordinated alcohol groups acts as a hydrogen bond donor to either a perchlorate anion or a solvent water molecule. The water molecule further acts as a hydrogen bond donor interacting with two perchlorate anions. Cumulatively, this results in the formation of hydrogen bonded two-dimensional sheets that propagate parallel to the crystallographic *ac*-plane (Fig. 3).

Each of these two-dimensional sheets participates in further intermolecular interactions with its adjacent neighbours, undergoing edge-to-face π – π stacking indicated by $C_{\text{phenyl}}\text{H}\cdots\text{phenyl-centroid}$ separations of 3.0 Å that extend

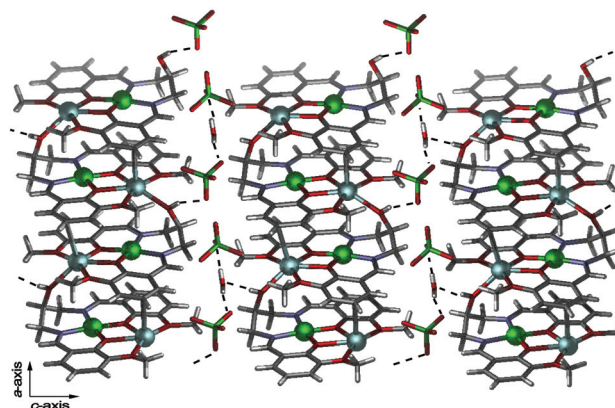


Fig. 3 Schematic representations of part of the two-dimensional sheet formed through hydrogen-bonding interactions between the ligands, solvent and anions. Dashed lines indicate hydrogen bonding. Cu is shown as green balls and Na as pale blue.

infinitely along the crystallographic *b*-axis in a herringbone-like motif (Fig. 4). The net effect of the coordinate, hydrogen bonding and π -interactions is an infinite three-dimensional array.

The IR spectrum of **1** shows a shift in $\nu(\text{C–O})$ to 1093 cm^{-1} from 1648 cm^{-1} in the free ligand, which is due to deprotonation of the ligand. The band at 1576 cm^{-1} ($\nu(\text{C=N})$) is also shifted compared to the free ligand (1677 cm^{-1}).²⁷ The $\nu(\text{M–N})$ and $\nu(\text{M–O})$ stretching frequencies appeared at 434 and 327 cm^{-1} , respectively. In the UV-vis spectrum, the free ligand shows intense bands at 220, 260, 293, 332 and 419 nm. The absorption bands at 220, 260 and 293 nm are attributed to $\pi \rightarrow \pi^*$ transition whereas the bands that appeared at 332 and

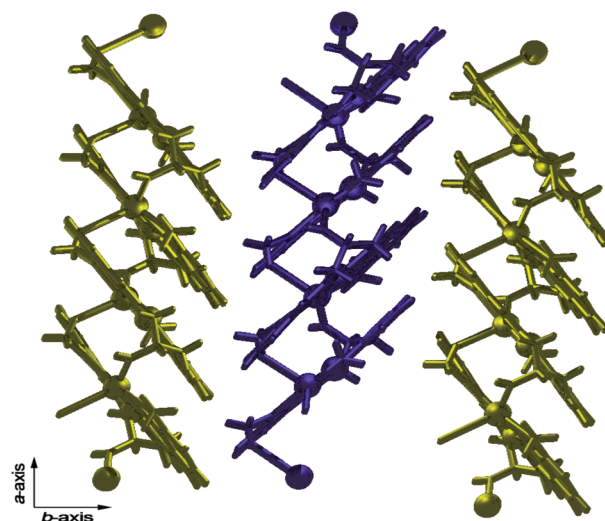


Fig. 4 View of the packing down the crystallographic *c*-axis. Adjacent two-dimensional hydrogen bonded sheets interact through edge-to-face π – π stacking resulting in a three-dimensional array. Two-dimensional sheets are coloured alternately.

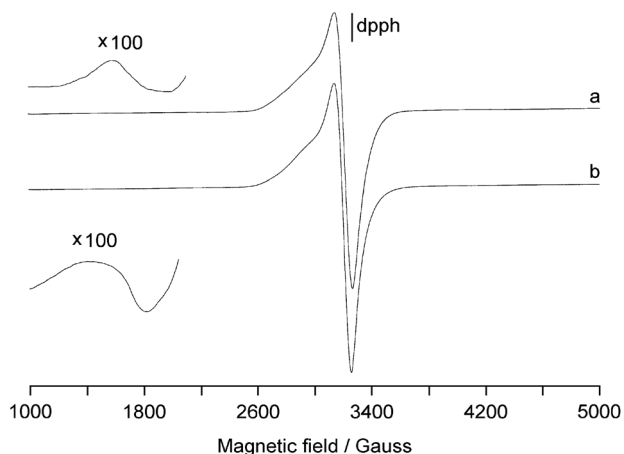


Fig. 5 X-band EPR spectra of the polycrystalline complex **1** at (a) RT and (b) 77 K. Diphenylpicrylhydrazyl (dpph) is the standard field marker ($g = 2.0036$). The half-field region of the spectra was amplified 100-fold.

419 nm, represents $n \rightarrow \pi^*$ transition.²⁸ On complexation, the $n \rightarrow \pi^*$ transition band in both are shifted from 332 to 363 nm. A broad d-d absorption band at 673 nm and an intense band at 516 nm are consistent with the square planar geometry of the copper ion.²⁹ As expected, the fluorescence of the ligand upon complexation is significantly quenched (Fig. S1 in the ESI†).

The EPR spectra of polycrystalline powder of **1**, recorded at 77 K and room temperature, are tetragonal with $g_z > g_x = g_y > g_e$ (Table S2 in the ESI† and Fig. 5). This situation is characteristic of a $d_{x^2-y^2}$ ground state,³⁰ and is consistent with the square planar geometry of the Cu(II) ion; the spectra do not change appreciably with the temperature. The half field signal at $g \sim 4$ can be assigned to the $\Delta M_s = \pm 2$ forbidden transition and is typical of dinuclear copper(II) species;³¹ this denotes a weak magnetic interaction between adjacent copper(II) ions in the polymeric chain. In particular, such a resonance is observed in the EPR spectrum of other Cu(II) dimers with metal-metal distances between 5.0 and 6.0 Å,³² even when isolated from biological matrices such as *Agaricus bispora* tyrosinase and *Cancer magister* hemocyanin.³³

When complex **1** is dissolved in an organic solvent, dissociation of the polymeric structure occurs and EPR signals attributable to mononuclear Cu(II) centres with a well-resolved hyperfine structure appear (Fig. 6).³⁴

The spectra measured in DMSO, DMF and CH₃CN were simulated with WinEPR³⁵ and show a very slight rhombicity. They are characterised by similar g and A values, consistent with a $d_{x^2-y^2}$ ground state and a geometry close to the limit of square planar (Table S3 in the ESI†). The ^{63,65}Cu A_z values are characteristic of Cu(II) species with a (O_{phenolic}, N_{imine}, N_{imine}, and O_{phenolic}) donor set, for example the four-coordinate complexes of salpn derivatives.⁷ Therefore, EPR results indicate that in all the three solvents an identical species is formed with the four donors of a ligand molecule bound to copper in the equatorial positions.

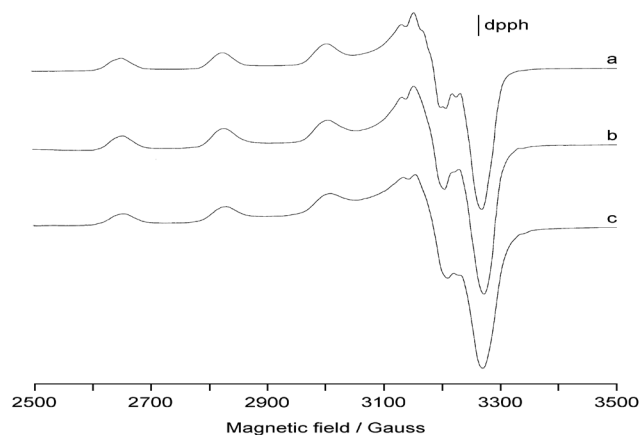


Fig. 6 Anisotropic X-band EPR spectra of **1**: (a) in DMSO, (b) in DMF and (c) in CH₃CN. Diphenylpicrylhydrazyl (dpph) is the standard field marker ($g = 2.0036$).

Conclusions

The Schiff-base ligand 6,6'-(1*E*,1'*E*)-(2-hydroxypropane-1,3-diyl)-bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2-methoxyphenol) forms a heterometallic mixed-valence complex upon reaction with copper(II) and sodium perchlorate. In the solid state, the complex exists as an infinite one-dimensional polymer stabilised by an uncommon phenyl-sodium bond, while in solution the coordination polymer dissociates into discrete complexes. Future work will explore mechanistic pathways and synthetic modifications to rationally design mixed-valence metal complexes of new organic precursors. Further studies will investigate the structural effects systematically varying the metal ions employed.

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