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An unusual [4 + 4 + 4] bishelical complex, $Cu_3(H_2L)(L)\cdot 2H_2O$ [H_4L' = *N*,*N*′-bis(3-hydroxysalicylidene)-1,4-diaminobutane]: synthesis and crystal structure

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An electrochemical cell [$Cu_{(+)}|MeCN + H_4L|Pt_{(-)}$] ($H_4L$ = title ligand), yielded powdery [$Cu_2(L)(H_2O)]_n$ and crystalline $Cu_3(H_2L)(L)\cdot 2H_2O$; the crystal structure of the latter shows an unusual helicate with an isosceles triangle core assembled by two μ-phenoxo bridges [Cu···Cu 3.413(3) and 3.858(3) Å], in which tetracoordinated Cu ions are in tetrahedrally distorted square planar environments.

The coordinating ability of compartmental ligands has been the subject of research owing to the interesting optical, magnetic and structural properties of polynuclear complexes.[1,2] Furthermore, there is much interest in the development of new polydentate ligands that can organise supermolecules upon complexation to two or more metal ions.[3]

We have recently reported some mono- and bi-nuclear Cu(II) complexes with asymmetrical Schiff bases.[4] This work has been extended to the direct electrochemical synthesis of polynuclear Cu(II) complexes with the title ligand, H_4L (prepared by condensation of 2,3-dihydroxybenzaldehyde and 1,4-diaminobutane in a 2:1 molar ratio) as a simple and efficient procedure to obtain them.

The electrochemical method [in this case summarised as: $Cu_{(+)}|MeCN + H_4L|Pt_{(-)}$] has been widely used by us.[5,6] An MeCN solution of H_4L (0.20 g) was electrolysed (V = 6.8 V) for a given time (3.25 h) according to the reaction $Cu_{(s)} + H_4L \rightarrow Cu(H_2L) + H_{2(g)}$. Anodic copper dissolved in the reaction mixture (0.066 g), whilst hydrogen evolved at the Pt cathode. An insoluble product was isolated which was analytically and spectroscopically identified† as $Cu_2(L)(H_2O)$ **1** (yield: 58%). The resulting solution was slowly evaporated and small crystals, suitable for X-ray diffraction studies,‡ were identified as $Cu_3(H_2L)(L)\cdot 2H_2O$, **2**·$2H_2O$ (yield 25%).

A single-crystal diffraction analysis of **2**·$2H_2O$ revealed an asymmetric unit containing half a molecule, with the central Cu(2) ion lying on a twofold axis. The neutral trinuclear complex is formed by two molecules of the coordinated ligand, one tetraanionic, L^{4-}, the other dianionic, H_2L^{2-}, and two water molecules linked by hydrogen bonds to the outer phenolic atoms of H_2L^{2-}, O(11) and O(11A). The molecular structure along with the atomic numbering scheme for the asymmetric unit is shown in Fig. 1. All atoms generated by the symmetry operation related to the twofold axis ($-x, y, 0.5 - z$) have been labelled with an A.

The three Cu(II) ions are held together by two μ-phenoxo bridges, through O(20) and O(20A) of L^{4-}. The Cu(2)···Cu(1) distances, 3.413(3) Å, are similar to those found for other trinuclear copper complex which also contain alkoxo bridges between the central and terminal Cu(II) ions, but here they show a more planar geometry.[7] The longer Cu(1)···Cu(1A) distance, 3.858(3) Å, seems to be imposed by the spatial arrangement of both ligands and the three metal centres form an isosceles triangle arrangement.

These Cu···Cu separations are similar to those found for some copper(II) proteins such as oxyhaemocyanin from *Plimulus polyphemus*[8] (3.6 Å) which contain N-donor atoms and oxo-bridges. Furthermore, the trinuclear site of oxidised ascorbate oxidase from green zucchini[9,10] is also approximately isosceles triangular; two such sites are present with intermetallic distances in the range 3.66–3.90 Å.

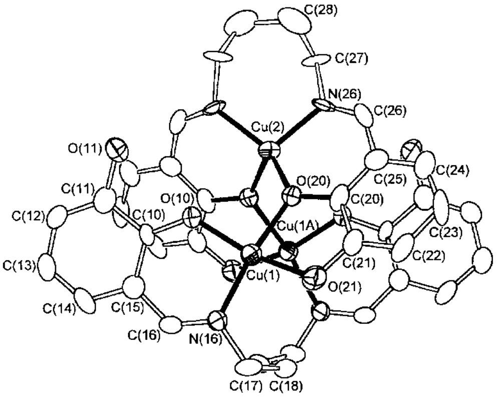

Fig. 1 ORTEP plot for **2**, showing the numbering scheme of the asymmetric unit. H-atoms and disordered atoms have been omitted for clarity. Significant distances (Å): Cu(1)–O(10) 1.872(8), Cu(1)–O(21) 1.900(8), Cu(1)–N(16) 1.950(10), Cu(1)–O(20) 1.976(8), Cu(2)–O(20) 1.905(9). Angles (°) around Cu(1) 84.0(4)–161.2(4), around Cu(2) 94.4(5)–139.0(4).

The central Cu(2) ion lies within the N_2O_2 inner compartment of L^{4-}. This donor set is usually quasi-planar in homo- and hetero-binuclear complexes containing very related ligands, but with a $(CH_2)_2$ or $(CH_2)_3$ chain. [11,12] However, in the present case with a $(CH_2)_4$ chain it is very severe tetrahedrally distorted. The longer $(CH_2)_4$ is more flexible and allows the ligand to twist and so achieve additional coordination to Cu(1) and Cu(1A) by means of both outer O_2 donor sets [O(20) and O(20A), acting as μ-phenoxo bridges], instead of a more typical binucleating fashion ($N_2O_2 + O_4$) for this type of ligand. Thus, L^{4-} is clearly behaving as a helicand with three metal-binding domains ($O_2 + N_2O_2 + O_2$). The helical arrangement is shown schematically in Fig. 2.

The absence of spacers other than the $(CH_2)_4$ between these donor sets, and the pronounced twist observed probably causes uncertainty in the atomic positions of the methylene chain. This may result in the observed disorder of its atoms, which are found in two different positions [C(27) and C(27′); C(28) and C(28′); with *ca.* 60 and 40% occupation factors, respectively]. In spite of this unusual ligand behaviour, the inner N_2O_2 compartment of L^{4-} still retains a suitable environment to effectively coordinate a copper(II) ion with usual bond lengths, but not in an ideally planar arrangement.

As Cu(1) and Cu(1A) do not satisfy their co-ordination numbers with co-ordination only to L^{4-}, the other ligand unit H_2L^{2-} must complete these. This ligand is bisbidentate and binucleating, by use of the double NO donor set of its inner

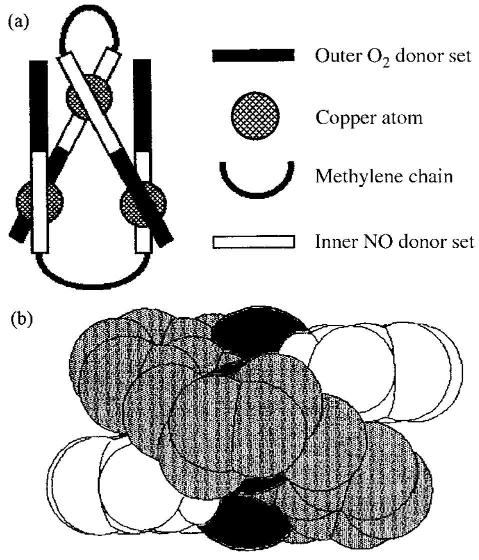

Fig. 2 (a) A scheme showing the helical arrangement for **2** and (b) a space-filling model of **2**, showing the helicand behaviour of L^{4-} (grey) and H_2L^{2-} (white) surrounding the three metal centes (black).

compartment. Thus, the NO_3 environment of Cu(1) and Cu(1A) is achieved through the O-atoms of L^{4-} [O(20) and O(21)], and the inner O(10) and N(16) atoms of H_2L^{2-} complete the coordination sphere leading to a slightly distorted square-planar coordination environment. The distortion appears to be caused by the steric hindrance between both ligand units and the twist of L^{4-} (Fig. 2). The other two potential donor oxygen atoms, O(11) and O(11A), remain protonated and are uncoordinated, but are linked by hydrogen interactions to solvated water molecules.

The bisbidentate bonding fashion observed for H_2L^{2-} (ON + NO), has been previously reported for other acyclic imines with similar[13] (but not helicand) and different donor atom sets (N_2 + N_2 but helicand).[3] However, H_2L^{2-} is not as twisted as L^{4-}, and adopts a nearly 'stepped-like' conformation, so that the two aromatic ring planes are almost parallel and fairly well separated. Overall, an unusual [4 + 4 + 4] bishelical arrangement is formed by three metal centres and two ligand units (Fig. 2).

This complex differs from usual bishelical structures, in which both helixes are similar or virtually so and the metal environments are seldom planar but more usually tetra- or octahedral.[3] Probably, the reasons for such an unusual arrangement can be found in the type of ligand used. It was previously reported that related ligands containing $(CH_2)_2$ and $(CH_2)_3$ chains could coordinate in both compartments (N_2O_2 + O_4) to Cu(II) ions.[11] The behaviour in the present system can be regarded as potentially compartmental, binucleating and leading to essentially square-planar coordination. L^{4-} acts as a trinucleating (O_2 + N_2O_2 + O_2) ligand while H_2L^{2-} is binucleating (ON + NO). Thus, the more flexible $(CH_2)_4$ chain ligand can coordinate two (NO + NO) and even three (O_2 + N_2O_2 + O_2) metal centres. Each moiety of L^{4-} is binucleating (O_2 + ON) but the flexible $(CH_2)_4$ chain allows the ligand to fold and so contain a metal centre in its inner compartment, in what can even be considered as O_2 + ON + NO + O_2 ligating behaviour.

Thus, both ligand units with their repeated metal-binding domains and a very flexible $(CH_2)_4$ chain spacer, lead to a bishelical arrangement. Perhaps, since there is no spacer between the inner NO and the outer O_2 donor sets of each moiety, both units cannot behave in the same way, as there would be a high steric hindrance between them (Fig. 2).

The assembling behaviour of this potentially N_2O_4 donor Schiff base is also unusual, as the majority of molecular threads giving rise to helicates incorporate at least one pyridine-type nitrogen donor.[3] The L^4 unit is unusual in that O-atoms predominantly coordinate and despite the presence of a long spacer it is bound to three close metal centres.

Although both ligand units show diverse behaviour, all the Cu–N and Cu–O distances are very similar in both cases, *ca.* 1.95 and 1.90 Å, respectively, which are within the usual range for copper ions coordinated to Schiff bases. Only the Cu(1)–O(20) distance [1.976(8) Å] is slightly longer than those usually found in the literature.[14] This is probably because O(20) is acting as a μ-bridge between Cu(2) and Cu(1).

Further studies are in progress; for example, magnetic data show a significant dependence with structure. EPR data for **2**·$2H_2O$ indicate a strucural change at *ca.* 100 K, probably related to the $(CH_2)_4$ moiety and its disorder.

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Notes and references

† Elemental analysis. Found (calc.): for **1**: C, 45.4(46.0); H, 3.4(3.8); N, 6.5(6.0), O, 17.5(17.1%); for **2**·$2H_2O$: C, 49.8(49.3); H, 3.9(4.4); N, 6.3(6.4); O, 17.9(18.2%).

‡ *Crystal data* for **2**·$2H_2O$: $C_{36}H_{38}Cu_3N_4O_{10}$, M_r = 877.32, monoclinic, space group $C2/c$ (no. 15), a = 17.098(7), b = 13.871(6), c = 15.366(7) Å, β = 110.0630(6)°, Z = 4, U = 3423(3) Å^3, T = 293 K, μ(Mo-Kα) = 1.914 mm^{-1}; 3146 reflections measured, 3021 reflections unique (R_{int} = 0.1634), $R1$ = 0.0611, $wR2$ = 0.1386; for all data $R1$ = 0.2972, $wR2$ = 0.2269. The structure was solved by standard direct methods and refined against F^2 by least squares.[15] All non-hydrogen atoms of the complex were readily located and refined anisotropically, except disordered atoms C(27′) and C(28′), which were treated isotropically. For H-atoms a riding model was employed, except for those bound to O-atoms, which were directly identified on Fourier maps, and given isotropic displacement parameters of 0.1 Å^2. Data were corrected for Lorentz and polarisation effects, and at a later stage in the refinement, an analytical absorption correction was applied. CCDC 182/1359. See http://www.rsc.org/suppdata/cc/1999/1953/ for crystallographic files in .cif format.

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