

A short intramolecular hydrogen bond is a key factor in the self-assembly of a dimeric complex with a 22-membered metallamacrocyclic cavity

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The reaction of copper(II) perchlorate with the new open chain oxime–amide ligand, *N,N'*-bis(2-hydroxyiminopropionyl)butane-1,4-diamine (H_2pab) in aqueous solution produced the dimeric complex $[Cu(Hpab)]_2[ClO_4]_2 \cdot 4H_2O$ containing a 22-membered macrocyclic cavity incorporating two copper(II) ions as a part of the ring framework.

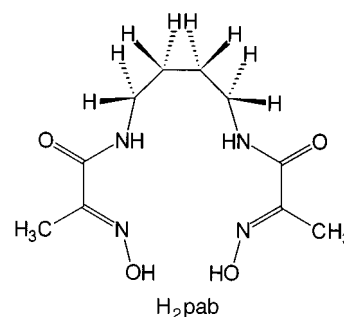
Synthesis of metallamacrocyclic molecules is one of the challenging areas in the field of co-ordination chemistry.¹ Most of the reported compounds of this type were obtained *via* self-assembly determined by a variety of factors such as the types and geometries of the connecting ligands,^{1c} preference of certain metal ions for different donor atoms^{1a} as well as the competing specific intra- and inter-molecular interactions² e.g. H-bonds.

Short intramolecular H-bonds ($=N-O-H \cdots O-N=$) are an important factor in the chemistry of oximes, regulating the co-ordination mode and the subtle structural features of metal oxime complexes. The formation of H-bonds determines the *cis*-arrangement of the co-ordination sphere in bis-oximate complexes,^{3,4} and removal of the bridging proton can lead to the complete isomerisation of the complex.⁵ However, H-bonds play no significant role in open-chain tetradentate oxime ligands,⁶ and are absent in metal chelate complexes with ligands containing strong electron-withdrawing groups attached to the oxime carbon atom (e.g., cyanoximes⁶) which results in a *trans*-arrangement of the ligands. At the same time, the $=N-O-H \cdots O-N=$ H-bond has been recently observed even in cyanoximes (HL)⁷ where the formation of the centrosymmetric anion $[L \cdots H-L]^-$ is dictated by the symmetry requirements, namely its bridging co-ordination to the centrosymmetric cation $[M(18\text{-crown-6})]^+$ ($M = Rb$ or Tl). In this paper we report a new important feature of the short H-bond in oximate complexes: the critical impact of its formation on the spontaneous self-assembly of a metallamacrocyclic molecule based on the novel tetradentate ligand *N,N'*-bis(2-hydroxyiminopropionyl)butane-1,4-diamine (H_2pab) (see below).

Complex $[Cu(Hpab)]_2[ClO_4]_2 \cdot 4H_2O$ **1** was synthesised by the addition of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) to H_2pab ‡ (0.129 g, 0.5 mmol) in aqueous solution. The clear green solution

obtained (pH = 4.1) was heated for 10 min on a water bath and then set aside. The dark green crystalline product which formed over 24 h was separated by filtration, washed with water and air-dried. Yield 0.164 g (72%).§

The view of the dimeric complex cation and the numbering scheme is represented in Fig. 1.¶ The structure is ionic and consists of complex cations $[Cu(Hpab)]_2^{2+}$, perchlorate anions and water molecules. The ligand is co-ordinated in a bis(bidentate) fashion *via* the hydroxyimino nitrogen and amide oxygen atoms forming a five-membered chelate ring. Since two such chelates within one ligand molecule are separated by the tetramethylene chain, the two copper atoms take part in separate chelate formation, and the resulting complex cation is a centrosymmetric dimer with a $Cu \cdots Cu$ ($-x, 1-y, -z$) separation of 7.231(2) Å and a 22-membered metallamacrocyclic cavity. The copper(II) ion is in a distorted tetragonal-pyramidal environment surrounded by two oxime nitrogen and two amide oxygen atoms; the copper atom is raised 0.201 Å out of the basal plane towards the axial O(5) atom. The co-ordination



§ Found: C, 26.05; H, 4.83; Cl, 8.09; Cu, 13.72; N, 11.98. Calc. for $C_{10}H_{21}ClCuN_4O_{10}$ (456.30): C, 26.32; H, 4.64; Cl, 7.77; Cu, 13.93; N, 12.28%.

¶ Crystal data: $C_{10}H_{21}ClCuN_4O_{10}$, $M = 456.30$, triclinic, space group $P\bar{1}$, $a = 8.734(2)$, $b = 9.497(2)$, $c = 11.988(2)$ Å, $\alpha = 103.20(3)$, $\beta = 90.87(3)$, $\gamma = 107.56(3)^\circ$, $U = 919.2(3)$ Å³, $Z = 2$, $\mu(Mo-K\alpha) = 13.90$ cm⁻¹, 4200 measured reflections, 3162 independent reflections, $R1$ ($wR2$) value of 0.0436 (0.1294). Intensities were collected using a KUMA KM4 diffractometer in the ω - 2θ scan mode at 293(2) K. The structure was solved by direct methods using SHELXS 86⁸ and refined by full-matrix, least squares on all F_o^2 using SHELXL 93.⁹ The non-hydrogen atoms were refined anisotropically. The O–H and N–H hydrogen atoms were found on the Fourier-difference map but their positional and thermal displacement parameters were not included in the refinement, the location of the C–H atoms of the methyl and methylene groups was set at calculated positions and allowed to ride on the atoms to which they were linked. CCDC reference number 186/972. See <http://www.rsc.org/suppdata/dt/1998/1535/> for crystallographic files in .cif format.

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‡ The ligand was obtained analogously to *N,N'*-bis(2-hydroxyiminopropionyl)propane-1,3-diamine³ [Found: C, 46.27; H, 6.99; N, 21.95. Calc. for $C_{10}H_{18}N_4O_4$ (258.32): C, 46.49; H, 7.04; N, 21.69%]. ¹H NMR [(CD₃)₂SO, 270 MHz]: δ 1.402 (m, 4 H, ³J = 2.8, β -CH₂), 1.857 (s, 6 H, CH₃), 3.115 (q, 4 H, ³J = 6.1, α -CH₂), 7.857 (t, 2 H, ³J = 5.8 Hz, NH), 11.563 (br s, 2 H, OH). ¹³C NMR [(CD₃)₂SO]: δ 9.40 (CH₃), 26.50 (β -CH₂), 38.25 (α -CH₂), 150.35 (C=N), 163.47 (C=O).

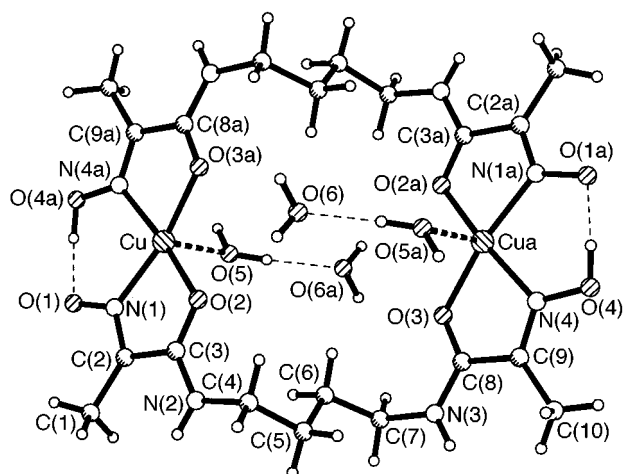


Fig. 1 Structure of the complex cation $[\text{Cu}(\text{Hpab})]_2^{2+}$ in complex **1**. Selected bond lengths (Å) and angles ($^\circ$): Cu–N(1), 1.934(2), Cu–N(4a) 1.957(2), Cu–O(2) 1.968(2), Cu–O(3a) 1.977(2), Cu–O(5) 2.189(3), O(1)–N(1) 1.327(3), O(2)–C(3) 1.249(4), O(3)–C(8) 1.257(4), O(4)–N(4) 1.343(3), N(1)–C(2) 1.285(4), N(4)–C(9) 1.272(4), N(2)–C(3) 1.307(3), N(3)–C(8) 1.300(4); N(1)–Cu–N(4a) 95.98(10), N(1)–Cu–O(2) 81.35(9), N(4a)–Cu–O(2) 169.19(10), N(1)–Cu–O(3a) 166.88(10), N(4a)–Cu–O(3a) 80.30(10), O(2)–Cu–O(3a) 99.94(9), N(1)–Cu–O(5) 98.52(13), N(4a)–Cu–O(5) 94.88(11), O(2)–Cu–O(5) 95.87(11), O(3a)–Cu–O(5) 94.35(13), C(2)–N(1)–O(1) 121.1(2), C(9)–N(4)–O(4) 118.4(2), N(1)–C(2)–C(3) 110.1(2), O(2)–C(3)–N(2) 122.5(3), O(2)–C(3)–C(2) 119.3(2), O(3)–C(8)–N(3) 122.0(3), O(3)–C(8)–C(9) 118.9(3), N(4)–C(9)–C(8) 109.7(2)

sphere is stabilised by the formation of a short intramolecular H-bond between the *cis*-situated hydroxyimino groups [O(4a)–H 0.930; H \cdots O(1) 1.554; O(1) \cdots O(4a) 2.483(3) Å, O(1)–H \cdots O(4) 175.5 $^\circ$].

The co-ordinated ligand indicates a folded geometry with two planar moieties involving oxime and amide groups. The 22-membered macrocyclic fragment formed as a result of dimeric co-ordination of two ligands exhibits a chair conformation (Fig. 2). There are two relatively planar fragments in the dimer parallel to each other linked by the folded fragment of the tetramethylene groups. The dihedral angle between the mean planes of the co-ordination spheres and of the C(5)C(6)–C(5a)C(6a) fragment is 75.2 $^\circ$. The complex cations are packed in a 'stairway' mode so that the square pyramids of the copper atoms belonging to the different dimers find themselves stacked base-to-base with Cu \cdots Cu separations of 4.111(2) Å and a long axial contact Cu \cdots O(3) ($x, -1 + y, z$) = 3.535(2) Å (Fig. 2).

The ionisation of the oxime group in the derivatives of 2(hydroxyimino)propanamide upon complex formation with copper(II) ions starts at much higher pH than dissociation of the amide protons.^{3,10} However, complex **1** contains ligands with a protonated amide and partly deprotonated oxime groups. Such an inversion of the order of ionisation in solution and in the crystal phase is understandable in terms of the important stabilising role of the short H-bond in *cis*-oximate complexes. Further deprotonation of similar tetradentate ligands by increasing the pH is accompanied by the formation

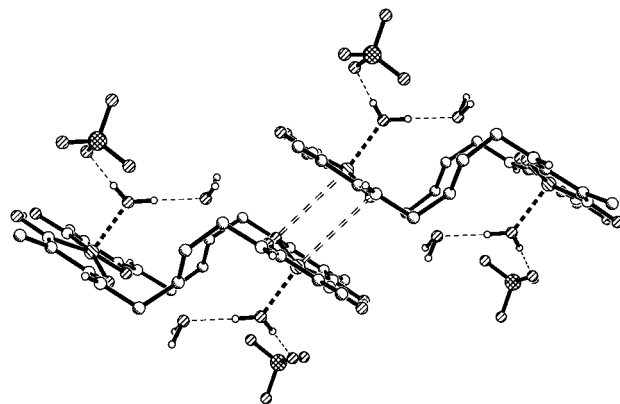


Fig. 2 Fragment of the crystal structure of complex **1** demonstrating the conformation of the dimeric units and their stacking

of only mononuclear species.¹⁰ Therefore, crystallisation of complex **1** is a good example of spontaneous self-assembly based on the formation of an intramolecular H-bond.

Acknowledgements

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