

Self-assembly of a tetranuclear macrocyclic copper(II) complex

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A dinuclear macrocyclic complex is synthesized via the one-pot reaction of dipotassium nitroacetate, formaldehyde and a linear tetraamine copper(II) complex; the X-ray crystal structure of the product reveals an association of two dinuclear complexes to form a novel tetracopper(II) species.

Reactions of metal templates such as $[M(en)_2]^{2+}$ or $[M(2,3,2-tet)]^{2+}$ ($M = Ni^{II}, Cu^{II}$; $en = ethane-1,2-diamine$, $2,3,2-tet = 1,4,8,11-tetraazaundecane$) with formaldehyde and a nitroalkane 'locking' fragment have emerged as versatile and effective synthetic routes toward pendant-armed macrocycles.¹ More recently, the range of locking fragments has been extended to include primary amines,² amides and sulfonamides³ and heterocycles.⁴ These molecules effect ring closure after reaction of formaldehyde with the coordinated primary amines to produce 14-membered macrocyclic rings based upon the well known cyclam (1,4,8,11-tetraazacyclotetradecane) framework, with the pendant groups arising from substituents on the locking fragments. In principle, this approach may be extended to bifunctional locking groups to generate alkyl-bridged dinuclear complexes, and one report of this type of chemistry is known using dinitro alkanes in this role.⁵

Here we report a new method of generating binuclear complexes via one-pot metal-directed reactions of dipotassium nitroacetate, formaldehyde and a tetraaminecopper(II) complex. An aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ was stirred while an equimolar amount of 2,3,2-tet was added dropwise. To the resulting purple solution was added aqueous formaldehyde (2 equiv.) and $K_2(O_2CCHNO_2)$ (1 equiv.). The mixture was heated with stirring at 50 °C for 20 h before being filtered. Ion-exchange chromatography of the reaction mixture yielded two products; the first being the mononuclear complex $[CuL^2][ClO_4]_2$ ($\lambda_{max} = 518 \text{ nm}$, $\epsilon = 84.2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) followed by the major product, the dimeric $[Cu_2L^1]_2[ClO_4]_3Cl_3$ ($\lambda_{max} = 510 \text{ nm}$, $\epsilon = 137 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ per Cu centre). The first crop of $[Cu_2L^1]_2[ClO_4]_3Cl_3$ was obtained in 13% yield (of solid compound), but further crops precipitated on standing. The solution properties of both products are typical of cyclam-type complexes of Cu^{II} , with respect to their visible electronic maxima and resistance to acid catalysed dissociation (3 M HCl) over a period of several weeks.

X-Ray quality crystals† of the dimer $[Cu_2L^1]_2[ClO_4]_3Cl_3 \cdot 6H_2O$ were obtained by slow evaporation of an aqueous solution of the complex containing an excess of

$NaClO_4$ and NaCl. The crystal structure analysis shows that two dicopper(II) complexes have assembled into a dimeric tetranuclear species (Fig. 1). The pairs of covalently linked macrocyclic planes are twisted relative to each other by an approximate angle of 50° and the Cu...Cu distance is 11.32 Å. Interestingly, the central C atom [C(12)] is deprotonated and the resulting nitronate group forms an intermolecular coordinate bond to an adjacent Cu^{II} centre [2.412(6) Å]. The geometry of each unique Cu^{II} ion is best described as distorted tetragonally elongated octahedral, with anions occupying the remaining coordination sites. The nitronate group and adjacent atoms [C(C)CNO₂] form a planar structure. In addition, a lengthening of the N–O bonds (*ca.* 0.1 Å) and shortening of the C–N bond (*ca.* 0.2 Å) relative to the nitro groups appended to each macrocyclic ring was found. These observations lead to the conclusion that the C–N bond in this functional group has essentially double-bond character.

The formation of $[Cu_2L^1]^{3+}$, and its crystallisation as a dimeric tetranuclear complex, is remarkable, and was unexpected. The crystallisation of $[Cu_2L^1]^{3+}$ involves the assembly of 22 different molecules $\{4 \times [Cu(2,3,2-tet)]^{2+}, 6 \times (O_2CCHNO_2)^{2-}, 12 \times CH_2O\}$ into one supramolecular unit in a one-pot reaction, which illustrates the efficiency of metal-directed reactions of this kind. Dipotassium nitroacetate $K_2(O_2CCHNO_2)$ and its derivatives are unstable toward decarboxylation in aqueous solution.⁸ In this case, condensation of three $(O_2CCHNO_2)^{2-}$ ions with two equivalents of formaldehyde followed by decarboxylation generates the molecule 1,3,5-trinitropentane *in situ*. Decarboxylation may occur either before or after the formaldehyde/nitroacetate condensation. The latter mechanism is more likely, *i.e.* 1,3,5-trinitropentane-1,3,5-tricarboxylate is initially formed as an intermediate, since metal-directed reactions of nitromethane (the decarboxylation product of nitroacetate) with formaldehyde under similar conditions do not lead to macrocyclic species. Similarly, the formation of $[CuL^2]^{2+}$ most likely involves the nitrocarboxylate substituted macrocycle as an intermediate which decarboxylates in the final step. Analogous processes have been observed in *gem*-diacid substituted tetraamine complexes.⁹

The electron paramagnetic resonance (EPR) spectra of $[CuL^2]^{2+}$ and $[Cu_2L^1]^{3+}$ [Fig. 2(a) and (c)] as frozen solutions are quite different, with the latter being consistent with a weakly

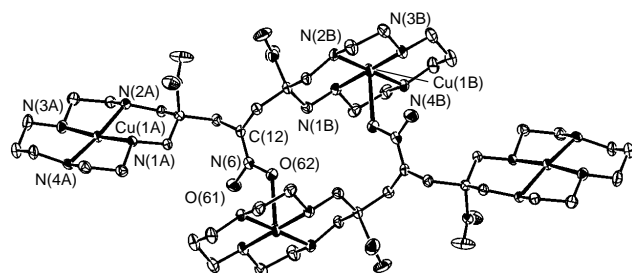
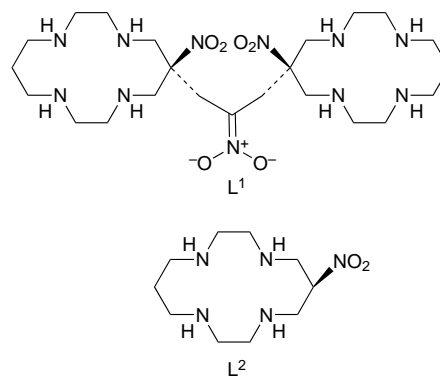


Fig. 1 Drawing of the $[Cu_2L^1]_2^{6+}$ cation (anions and H-atoms omitted); ellipsoids are drawn at the 30% probability level



dipole–dipole coupled dicopper(II) complex. Simulation of the EPR spectrum of $[\text{Cu}_2\text{L}^1]^{3+}$ [Fig. 2(b), $g_{\parallel} = 2.17$, $A_{\parallel} = 205$ G; $g_{\perp} = 2.035$, $A_{\perp} = 50$ G] was achieved with the program DISSIM,¹⁰ which also yielded a Cu...Cu separation of 11.0 Å and a twist angle between the two macrocyclic planes of 80°. The simulation indicates that the compound exists as discrete dicopper(II) complexes in solution and not as the tetranuclear dimer identified in the solid-state structure. In addition, the relative twist angle between the two macrocycles derived from the simulation is *ca.* 30° greater than that identified in the X-ray crystal structure. That is, formation of the tetranuclear dimer perturbs slightly the relative positions of the two covalently linked macrocyclic planes. The EPR spectrum of the mononuclear analogue $[\text{CuL}^2]^{2+}$ [Fig. 2(a)] is better resolved and typical of an isolated d^9 complex in a pseudo-axial ligand field. The similarity between the spectra of $[\text{Cu}_2\text{L}^1]^{3+}$ and $[\text{CuL}^2]^{2+}$ indicates that the two metal centres in $[\text{Cu}_2\text{L}^1]^{3+}$ are only weakly interacting at this internuclear separation (11 Å), and that dipole–dipole coupling merely acts to broaden what is essentially a mononuclear spectrum.

We have shown that the nitroacetate dianion is a potentially useful synthetic intermediate which, in conjunction with formaldehyde, may generate multifunctional carbon acids *in situ* capable of simultaneously cyclising and bridging two metal

centres. Furthermore, this reagent offers a route towards mono-C-substituted ($-\text{NO}_2$) macrocycles such as $[\text{CuL}^2]^{2+}$ which have been much more difficult to prepare than disubstituted ($-\text{NO}_2$, $-\text{Me}$) analogues derived from nitroethane and formaldehyde. Further work is continuing utilising this novel reagent to effect macrocyclic ring closure.

We gratefully acknowledge Mr David Hunter for his assistance with the EPR spectral measurements and we thank the Energy Research and Development Corporation and the University of Queensland for financial support.

Footnote

† *Crystal data:* $[\text{Cu}_2\text{L}^1]_2[\text{ClO}_4]_3\text{Cl}_3 \cdot 6\text{H}_2\text{O}$, $\text{C}_{46}\text{H}_{108}\text{Cl}_6\text{Cu}_4\text{N}_{22}\text{O}_{30}$, $M = 1916.4$, triclinic, space group $P\bar{1}$, $a = 9.677(1)$, $b = 13.354(1)$, $c = 15.583(2)$ Å, $\alpha = 92.170(9)$, $\beta = 90.94(1)$, $\gamma = 99.14(1)^\circ$, $U = 1986.2(4)$ Å³, $Z = 1$, $D_c = 1.602$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 13.49$ cm⁻¹, $F(000) = 996$, $T = 293$ K, final $R_1 = 0.0683$, $wR_2 = 0.1797$ for 3789 observed reflections [$|F_o| > 2\sigma|F_o|$, $2\theta < 50^\circ$], $w^{-1} = \sigma^2(F_o^2) + (0.1203P)^2 + 4.65P$, where $P = (F_o^2 + 2F_c^2)/3$. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K α radiation and employing the ω - 2θ scan method. The structure was solved by direct methods with SHELXS-86⁶ and refined by full-matrix least squares on F^2 with SHELXL-93.⁷ All non-H atoms were refined with anisotropic thermal parameters, whereas H-atoms were constrained at estimated positions.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/386.

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Received, 9th January 1997; Com. 7/00213K

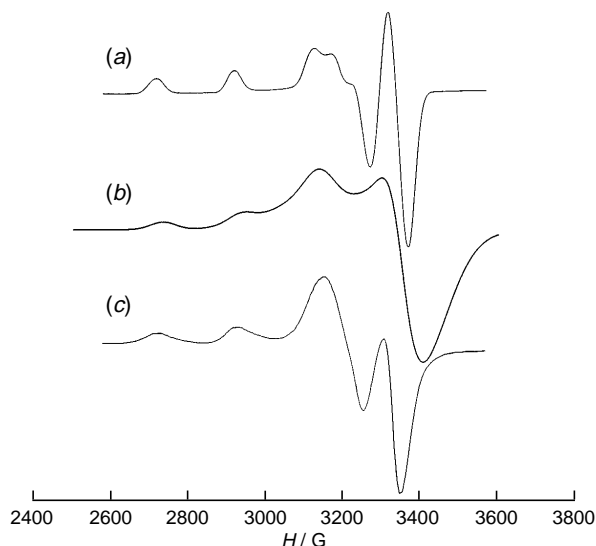


Fig. 2 (a) Experimental EPR spectrum of $[\text{CuL}^2]^{2+}$, (b) simulated EPR spectrum of $[\text{Cu}_2\text{L}^1]^{3+}$ and (c) experimental EPR spectrum of $[\text{Cu}_2\text{L}^1]^{3+}$; frequency = 9.272 GHz, $T = 77$ K, solvent water–dimethylformamide (2:1)