

The metal directed assembly of a trinuclear macrocyclic copper(II) complex

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A trinuclear macrocyclic complex is reported from the metal directed condensation between melamine, formaldehyde and the Cu^{II} complex of a linear tetraamine.

Metal directed condensation reactions of coordinated primary amines with aldehydes and dibasic acids such as nitroalkanes or primary amines offer effective and facile routes to pendent-armed macrocyclic ligands and their complexes.¹ In each case, a new six-membered chelate ring is formed across a pair of *cis* disposed primary amines, and the pendent substituents introduced *via* the acid 'locking fragment' reside at the apex of this chelate ring. The majority of examples of this type of chemistry involve the reaction of Cu^{II} polyamines with nitroethane and formaldehyde,² but other metal ions,³ aldehydes⁴ and acids⁵ have been employed successfully. Mononuclear complexes have almost invariably been the targets. There is continual interest in viable synthetic routes to oligonuclear complexes by virtue of the unusual cooperative magnetic and electronic interactions that arise when metal ions are constrained to be in proximity of one other. If a *difunctional* acid, bearing two sets of acidic methylene or primary amino groups is employed, then one may close two different ring systems connected through the locking group. However, this approach has rarely been successful, these examples involving the locking groups propane-1,3-diamine,⁶ 1,3,5-trinitropentane,⁷ 1,2-dinitroethane, 1,3-dinitropropane and 1,4-dinitrobutane.⁸ Unsuccessful attempts to bridge two metal centres using this chemistry are known⁹ where mononuclear complexes have been formed *via* intramolecular cyclisation. Herein, we describe the first example where a *trifunctional* locking group has been employed in a metal directed aldehyde/amine condensation reaction to give a trinuclear complex.

The aromatic triazine melamine possesses primary amino groups at the 2-, 4- and 6-positions and is ideally suited to act as a trifunctional locking group. In particular, the rigidity of melamine forbids intramolecular reactions that have been

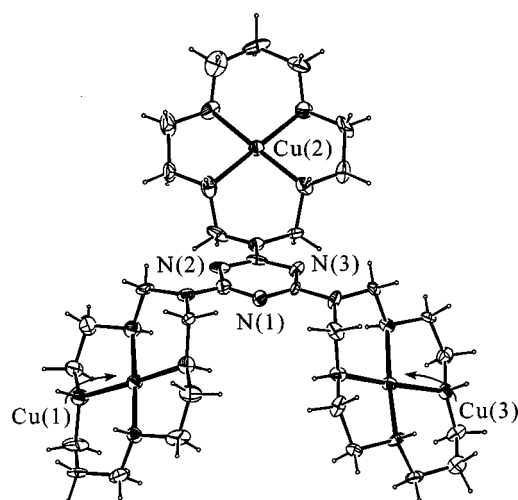
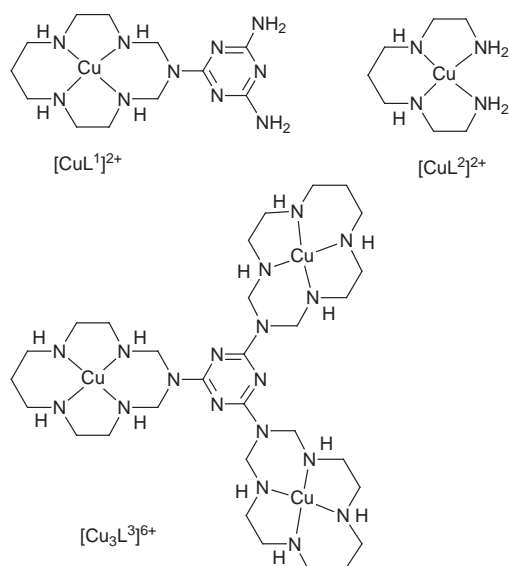


Fig. 1 View of the $[\text{Cu}_3\text{L}^3]^{6+}$ cation showing 30% probability ellipsoids. Selected bond lengths: Cu–N 1.98(2)–2.03(2) Å, N(1)–C(1), C(3) 1.33(2) Å.

observed to compete with oligonuclear complex formation in more flexible difunctional analogues. Recently we reported¹⁰ the metal-directed assembly of the mononuclear, pendent-armed macrocyclic complex $[\text{CuL}^1]^{2+}$ using melamine as a locking fragment in conjunction with formaldehyde and the Cu^{II} complex of the linear tetraamine bis-*N,N'*-(2-aminoethyl)propane-1,3-diamine (L^2). We have shown that the melamine pendent group exhibits a very strong propensity for H-bonding with other molecules and ions in the solid state, which is a feature of other crystal structures containing the melamine group or fragment.¹¹ However, it became apparent to us that the remaining two primary amino groups in $[\text{CuL}^1]^{2+}$ might also be employed as locking fragments for other macrocyclic rings. To this end, by varying the stoichiometry of the reaction, we have successfully condensed three molecules of $[\text{CuL}^2]^{2+}$ with melamine and formaldehyde to produce the new trinuclear macrocyclic complex $[\text{Cu}_3\text{L}^3][\text{ClO}_4]_6 \cdot 5\text{H}_2\text{O}$.† Single crystals of the complex were grown from a saturated aqueous solution of the complex, and we have determined the crystal structure of this compound.‡ A view of the complex ion $[\text{Cu}_3\text{L}^3]^{6+}$ is shown in Fig. 1. The three fourteen-membered macrocyclic Cu^{II} units are linked to the triazine 'hub' *via* the aromatic amino groups. Water molecules and/or perchlorate anions (not shown in Fig. 1) occupy the two axial sites of each metal centres at Cu–O distances of *ca.* 2.5 Å. The configuration of each set of four N-donors is *RSSR* (*trans*-III), which is the most commonly observed N-based isomer in fourteen-membered macrocyclic complexes. The corresponding bond lengths and angles in each macrocyclic sub-unit are the same within experimental error. However, the relative dispositions of the rings are different. Two of the macrocyclic sub-units are found on the same side of the triazine hub, while the other is on the opposite side (*syn,syn,anti*). Therefore, the overall molecular (but not crystallographic) symmetry is C_s . There are no significant intermolecular contacts between trinuclear complex units in the

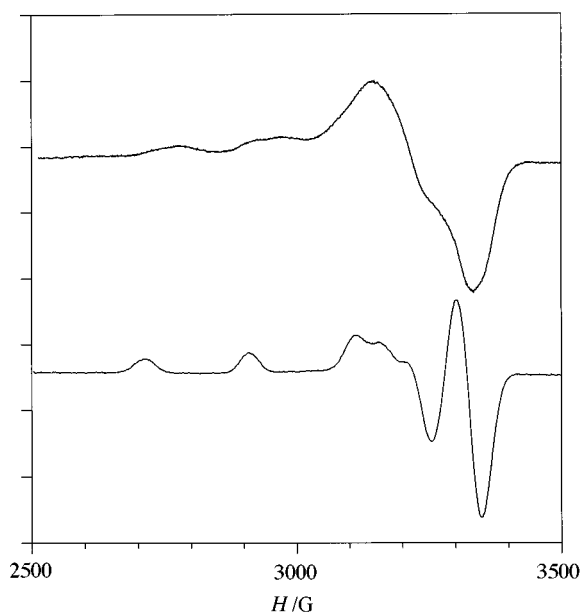


Fig. 2 EPR spectra of $[\text{Cu}_3\text{L}^3][\text{ClO}_4]_6$ (top) and $[\text{CuL}^1][\text{ClO}_4]_2$ (bottom). Experimental conditions: 1 mmol dm^{-3} solutions in DMF– H_2O (1:2), $T = 77 \text{ K}$, $\nu = 9.272 \text{ GHz}$.

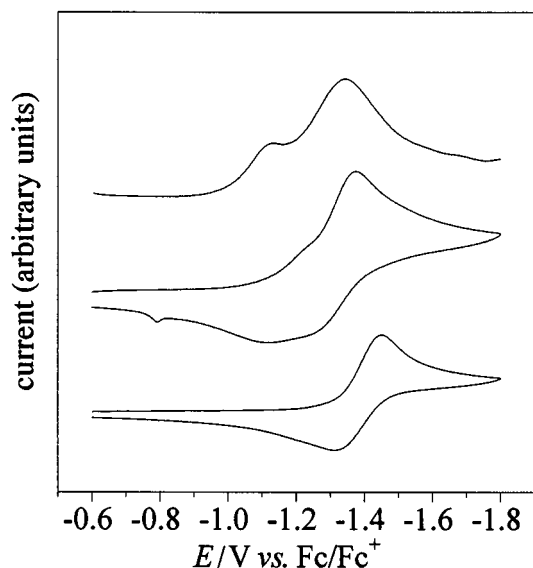


Fig. 3 Square wave voltammogram of $[\text{Cu}_3\text{L}^3][\text{ClO}_4]_6$ (top); cyclic voltammogram of $[\text{Cu}_3\text{L}^3][\text{ClO}_4]_6$ (centre) and cyclic voltammogram of $[\text{CuL}^1][\text{ClO}_4]_2$ (bottom). Experimental conditions: 5 mmol dm^{-3} solutions in MeCN, 0.1 mol dm^{-3} $n\text{-Bu}_4\text{NClO}_4$, glassy carbon working, Pt auxiliary and Au reference electrodes (potentials referenced vs. ferrocene/ferrocenium couple).

present crystal structure. The free primary amines of the protonated analogue $[\text{Cu}(\text{HL}^1)]^{3+}$ are very effective H-bond donors, and H_2O -linked macrocyclic chains result through intermolecular interactions in the solid state. By comparison, these amino groups are no longer available for H-bonding in the trinuclear analogue $[\text{Cu}_3\text{L}^3]^{6+}$, as they have each been incorporated into one of the macrocyclic rings.

The amino N-atoms in melamine are trigonal planar, as a result of conjugation of their lone pairs with the aromatic ring, so the $\text{N}(5n)\text{--C}(n)$ ($n = 1, 2, 3$) torsional angles are close to zero degrees. The conformation of the triazine-substituted six-membered chelate ring is somewhat distorted by the inclusion of a trigonal atom at the apex, which results in the melamine ring being tilted by *ca.* 40° relative to each CuN_4 plane. It is apparent that all three macrocyclic sub-units may be on the

same side (*syn,syn,syn*) of the triazine ring or one may be on the opposite side to the other two (*syn,syn,anti*). Molecular mechanics modeling found that the minimised strain energies of the two conformers differed by less than 2 kJ mol^{-1} , so steric effects evidently do not play an important role in determining the preferred conformation.

Three-way dipole–dipole coupling between the metal centres in $[\text{Cu}_3\text{L}^3]^{6+}$ was observed in the electron paramagnetic resonance spectrum of the complex in a DMF– H_2O (1:2) glass at 77 K (Fig. 2). For comparison, the EPR spectrum of the mononuclear analogue $[\text{CuL}^1]^{2+}$ is also shown. From the crystal structure analysis, the $\text{Cu}\cdots\text{Cu}$ distances in the triangular array of metal centres in $[\text{Cu}_3\text{L}^3]^{6+}$ are 7.97 \AA ($\text{Cu}(1)\cdots\text{Cu}(3)$), 9.54 \AA ($\text{Cu}(1)\cdots\text{Cu}(2)$) and 9.36 \AA ($\text{Cu}(2)\cdots\text{Cu}(3)$). These internuclear distances are within the range over which we have previously observed dipole–dipole coupling in the EPR spectra of dinuclear Cu^{II} complexes.^{7,12} Nevertheless, the EPR spectra of $[\text{Cu}_3\text{L}^3]^{6+}$ and $[\text{CuL}^1]^{2+}$ are qualitatively similar; with the former exhibiting much broader peaks. This shows that metal–metal interactions in the trinuclear complex are only a minor perturbation on the basic mononuclear spectrum.

Cyclic voltammetry of $[\text{Cu}_3\text{L}^3]^{6+}$ in MeCN solution revealed overlapping waves in the region -1.2 to $-1.4 \text{ V vs. ferrocene/ferrocenium}$ (Fig. 3). Square wave voltammetry resolved these processes into one-electron and two-electron responses at -1.14 and $-1.35 \text{ V vs. Fc/Fc}^+$ respectively. For comparison, the cyclic voltammogram of $[\text{CuL}^1]^{2+}$ is also shown, where a quasi-reversible Cu^{III} couple at $-1.40 \text{ V vs. Fc/Fc}^+$ is found. The positive shift in the Cu^{III} waves of $[\text{Cu}_3\text{L}^3]^{6+}$ relative to $[\text{CuL}^1]^{2+}$ reflect the electrostatic metal–metal interactions that facilitate reduction to the monovalent state. In aqueous solution, all of these electrochemical responses become totally irreversible due to the instability of Cu^{I} amines in water.

Magnetic coupling between the three $S = \frac{1}{2}$ centres in $[\text{Cu}_3\text{L}^3]^{6+}$ should be significant on the basis of the EPR spectroscopic results, and we are currently investigating this through low temperature magnetic moment measurements.

Acknowledgements

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Notes and references

† To a refluxing solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (7.24 g), L^2 (5.40 g), Et_3N (6.07 g), formaldehyde (6.0 cm^3 , 32%) was added a solution of melamine (1.53 g) in MeOH–water (1:1, 100 cm^3). The reaction was allowed to proceed for 5 d. Column chromatography (Sephadex C-25, 0.4 mol dm^{-3} NaClO_4) separated unreacted $[\text{CuL}^2]^{2+}$, $[\text{CuL}^1]^{2+}$ (major) then the desired product $[\text{Cu}_3\text{L}^3]^{6+}$ well behind the mononuclear complexes. The complex precipitated on concentration of the eluate to *ca.* 100 cm^3 (yield 5%) (Found: C, 22.3; H, 4.5; N, 16.1. $[\text{Cu}_3\text{L}^3][\text{ClO}_4]_6 \cdot 6\text{H}_2\text{O}$, $\text{C}_{30}\text{H}_{78}\text{Cl}_6\text{Cu}_3\text{N}_{18}\text{O}_{30}$, requires C, 22.88; H, 4.99; N, 16.02%).

‡ Crystal data: $[\text{Cu}_3\text{L}^3][\text{ClO}_4]_6 \cdot 5\text{H}_2\text{O}$, $\text{C}_{30}\text{H}_{76}\text{Cl}_6\text{Cu}_3\text{N}_{18}\text{O}_{29}$, $M = 1556.41$, monoclinic, space group $P2_1$ (no. 4), $a = 8.643(3)$, $b = 22.580(4)$, $c = 15.759(5) \text{ \AA}$, $\beta = 95.78(2)^\circ$, $U = 3057(1) \text{ \AA}^3$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 13.93 \text{ cm}^{-1}$, $T = 293 \text{ K}$, final $R_1 = 0.0644$ for 2233 observed reflections [$|F_o| > 2\sigma|F_o|$, $2\theta < 50^\circ$], $wR_2 = 0.2191$ for 5515 unique reflections ($R_{\text{int}} = 0.0813$). The structure was solved by Patterson methods with SHELXS-86¹³ and refined by full matrix least squares with SHELXL-93.¹⁴ CCDC reference number 186/1168. See <http://www.rsc.org/suppdata/dt/1998/3539/> for crystallographic files in .cif format.

- 1 P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.
- 2 P. Comba, N. F. Curtis, G. A. Lawrance, M. A. O'Leary, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1988, 2145; P. Comba, N. F. Curtis, G. A. Lawrance, A. M. Sargeson, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1986, **25**, 4260.
- 3 N. F. Curtis, G. J. Gainsford, A. Siriwardena and D. C. Weatherburn, *Aust. J. Chem.*, 1993, **46**, 755; M. Rossignoli, P. V. Bernhardt, G. A. Lawrence and M. Maeder, *J. Chem. Soc., Dalton*

- Trans.*, 1997, 323; M. Rossignoli, C. C. Allen, T. W. Hambley, G. A. Lawrence and M. Maeder, *Inorg. Chem.*, 1996, **35**, 4961.
- 4 P. V. Bernhardt and P. C. Sharpe, *Inorg. Chem.*, 1998, **37**, 1629; L. Fabbri, M. Licchelli, A. M. Lanfredi, O. Vassalli and F. Uguzzoli, *Inorg. Chem.*, 1996, **35**, 1582.
- 5 Y. D. Lampeka, A. I. Prikhod'ko, A. Y. Nazarenko and E. B. Rusanov, *J. Chem. Soc., Dalton Trans.*, 1996, 2017; P. V. Bernhardt, K. A. Byriel, C. H. L. Kennard and P. C. Sharpe, *Inorg. Chem.*, 1996, **35**, 2045.
- 6 S.-G. Kang, S.-K. Jung, J. K. Kweon and M.-S. Kim, *Polyhedron*, 1993, **12**, 353.
- 7 P. V. Bernhardt and L. A. Jones, *Chem. Commun.*, 1997, 655.
- 8 P. Comba and P. Hilfenhaus, *J. Chem. Soc., Dalton Trans.*, 1995, 3269.
- 9 M. P. Suh, S.-G. Kang, V. L. Goedken and S.-H. Park, *Inorg. Chem.*, 1991, **30**, 365.
- 10 P. V. Bernhardt and E. J. Hayes, *Inorg. Chem.*, 1998, **37**, 4214.
- 11 G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen and D. M. Gordon, *Acc. Chem. Res.*, 1995, **28**, 37.
- 12 P. V. Bernhardt, P. Comba, T. W. Hambley, S. S. Massoud and S. Stebler, *Inorg. Chem.*, 1992, **31**, 2644.
- 13 G. M. Sheldrick, *Acta. Crystallogr., Sect. A*, 1990, **46**, 467.
- 14 G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Determination, University of Göttingen, 1993.

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