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A new class of macrocycle capable of binding exogenous metals: synthesis, structure, magnetic and electrochemical properties of a Cu(II) trinuclear complex based upon 1,4,8,11-tetraazacyclotetradecane-2,3-dione [*exo*O$_2$]cyclam †

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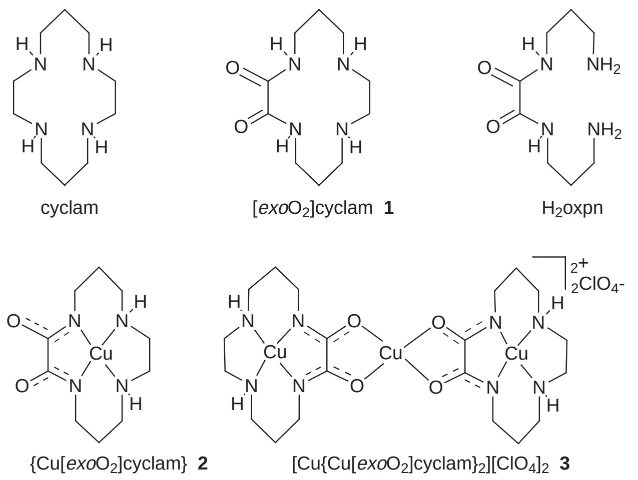
Received 8th April 1999, Accepted 12th May 1999

Synthesis of the new macrocycle 1,4,8,11-tetraazacyclotetradecane-2,3-dione [*exo*O$_2$]cyclam and its complexation with copper(II) salts results in the formation of a complex comprising two macrocycles each coordinated to a copper(II) ion *via* the tetraaza groups and linked together through a copper(II) ion coordinated to the *exo-cis* oxygen donors of each macrocycle.

The macrocycle known as cyclam and its derivatives have been the subject of an immense amount of interest to coordination chemists due to their ability to complex many of the transition metals.[1–3] Cyclam-based complexes have been used in a wide range of studies from bioinorganic[1] systems to catalytic[2] systems and as sensors;[3] a search on the Cambridge Crystallographic Data Base[4] revealed over 500 structures of cyclam and cyclam derivatives complexed with transition metals. In this communication the first example in a new class of macrocycle based on cyclam is presented. The new macrocycle, in addition to its ability to coordinate metals *via* the N$_4$ donor set of the ring, can also bind exogenous metal ions *via* the *exo-cis* oxygen atoms which form part of the oxamide groups present in the macrocycle. Oxamide-based ligands such as H$_2$oxpn have also been of great interest due to their ability to form polymetallic[5–7] and heterobimetallic[8–13] systems. Bis complexes containing copper/copper[5,7] and copper/nickel[8,12] have been found to be very strongly antiferromagnetically coupled through the oximidate bridges. However, bis complexes containing copper/gadolinium are ferromagnetically coupled.[10,11] These types of features have been exploited in the design of model magnetic systems and the formation of extended structures which utilise the fact the oxpn can adopt either a *cis* or *trans* conformation.[14] Although this flexibility can give rise to a rich variety of complexes and extended structures, it allows much less control over the final type of complex obtained.[14] We have extended this approach by producing a macrocyclic analogue of H$_2$oxpn, in which the *exo-cis* conformation of the oxygen donors is enforced (see Scheme 1). Such a system allows the controlled formation of complexes *via* the stepwise complexation of the macrocyclic and the *exo* donors. Therefore, this approach could be used to synthesise new ion sensors, heterobimetallic systems and model magnetic systems in a more controlled fashion, taking advantage of the macrocyclic effect.

The new macrocycle, [*exo*O$_2$]cyclam **1** was synthesised very simply ‡ in one step by the condensation reaction of dimethyloxalate and the tetraamine *N*,*N*′-bis(3-aminopropyl)ethylenediamine in refluxing ethanol. Although initially the synthesis was hampered by formation of higher [2 + 2] and [3 + 3] adducts and polymer, the macrocycle can be synthesised in over 60% yield if the reaction is performed at high dilution over a period of 32 h. The trinuclear complex can be synthesised § by the step-wise addition of copper(II) perchlorate in methanol to a solution of the macrocycle in methanol–water (50 : 50 v/v). (**CAUTION**: Perchlorate salts are potentially explosive and should therefore be handled with appropriate care.) It has been shown that the synthesis of the trimetallic complex **3** proceeds after the formation of a monomeric complex of the macrocycle with copper (**2**). Complex **2** § has been independently isolated presumably with the copper bound in the N$_4$ coordination environment of the macrocyclic ring.



Scheme 1

Dark red single crystals of **3** suitable for single crystal X-ray diffraction studies were obtained in 53% yield by leaving the reaction mixture standing for 4 weeks. The crystal structure¶ of the complex (Fig. 1) shows a central copper(II) ion ligated by the two *exo* oxygen groups of two [*exo*O$_2$]cyclam units. These cyclam units are also coordinated to copper(II) ions. The central copper is located on a centre of symmetry and is ligated by an O$_4$ donor set in a square planar coordination environment. The oxygen atoms of the two associated perchlorate anions are weakly interacting with the central the copper(II) and are positioned in the remaining apical sites above and below the copper(II) ion at a distance of 2.827(5) Å. The copper(II) ions ligated by the macrocycles have a square pyramidal coordination geometry with a N$_4$ donor set which forms the square base of the pyramid. The apex of the pyramid is completed by a water molecule, however there is also a perchlorate (this is present in the adjacent asymmetric unit interacting with the central copper(II) of another trimer unit) positioned in the sixth vacant coordination site with a weak copper–oxygen interaction of 2.983(6) Å.

Examination of the coordination environment of the three coppers reveals that they are all co-planar, with maximum r.m.s. deviation of 0.072, in a plane consisting of Cu(1), O(1), O(2), C(1), C(2), N(1), N(2) and Cu(2). Furthermore, the sum of the angles around C(1), C(2), N(1) and N(2) is 360.0(3)° indicating

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† *Supplementary data available*: Magnetic and electrochemical data. Available from BLDSC (No. SUP 57551, 5 pp.). See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

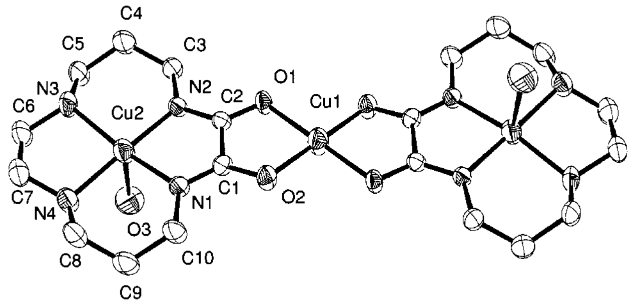

Fig. 1 Molecular structure of **3**. The two perchlorate anions are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.933(3), Cu(1)–O(2) 1.933(3), Cu(2)–N(1) 1.961(3), Cu(2)–N(2) 1.957(3), Cu(2)–N(3) 2.007(4), Cu(2)–N(4) 2.007(4), Cu(2)–O(3) 2.545(4); O(2)–Cu(1)–O(1) 86.24(11), O(2)′–Cu(1)–O(1) 93.76, O(1)′–Cu(1)–O(1) 180.0, N(2)–Cu(2)–N(1) 84.28(13), N(2)–Cu(2)–N(3) 95.06(14), N(1)–Cu(2)–N(3) 164.59(17), N(2)–Cu(2)–N(4) 175.02(16), N(1)–Cu(2)–N(4) 96.62(15).

that these atoms are trigonal planar. This implies that Cu(1)–O–C–N–Cu(2) is a delocalised unit as a result of the conjugation of electrons from the oxygen atoms and the lone pairs on the nitrogen atoms. This is further supported by the average O–C and C–N bond lengths [1.282(5) and 1.286(5) Å] which are shorter than expected for single O–C or C–N bonds [*ca.* 1.481 and 1.462 Å].

The magnetic properties of the trimer were investigated over the temperature range 1.8–300 K using a dried powder sample of **3** on a Quantum Design SQUID magnetometer. The data were found to be modelled accurately using an expression derived by Kahn *et al.*[5b] which was used to fit data from an analogous copper(II)-based trimer. The best fit of the data gave an exchange parameter, $J_1 = -364.2$ cm^{-1}, for the antiferromagnetic exchange between adjacent copper(II) ions whereas the exchange parameter for the coupling between terminal copper(II) ions (J_2) was set to zero. This is consistent with Kahn's analysis[5b] and an intermolecular exchange parameter was determined, $J_3 = -0.79$ cm^{-1}. This may be attributed to the weak interaction of the copper(II) ions of the trimer through the perchlorate anions.

The cyclic voltammogram obtained for a 1 mmol dm^{-3} solution of complex **3** at a platinum electrode in acetonitrile (with $[NBu_4]^+PF_6^-$ electrolyte, 0.1 M) shows two peaks at −1.2 and −0.67 V with respect to the ferrocene–ferrocenium couple. The peak at −1.2 V is an electrochemically irreversible reduction which then gives rise to an associated oxidation peak at −0.67 V. This peak has an approximately Lorentzian profile indicative of an electrode stripping process. Thus reduction of the trimer appears to result in the adsorption of an electroactive product onto the electrode which can be removed by reoxidation. Integration of the time *vs.* current curves associated with these peaks shows that twice as much current is passed in the reduction process than the oxidation process at all sweep rates. Preliminary electrochemical studies on **2** suggest reduction of the macrocyclic copper ions in **3** is unlikely in the range of study. Sweeping to higher potentials reveals no further significant oxidation peaks other than a very weak feature at −0.35 V which can be attributed to a very small amount of free ligand-based oxidation. The single reduction peak observed for **3** at all sweep rates between 10 and 200 mV s^{-1}, plus the electro-inactivity of **2**, combined with the charge passed during reduction suggest that only the central copper ion is reduced and deposited on the electrode in a two-electron process. In support it should be noted that the reoxidation potential is similar to that found for the oxidation of a copper electrode under the same conditions. This would suggest that the reoxidation generates a soluble copper(I) species and further studies are underway to fully characterise these processes.

There are now several examples of macrocyclic ligands which incorporate another ligand/binding unit for either a metal or organic unit but these are all connected *via* either aromatic spacer or aliphatic linking groups.[15] The system we describe in this paper however, provides the opportunity to allow direct communication from the metal ion bound in the macrocycle to the metal bound to the *exo* oxygen groups, because the groups can form a planar delocalised system. Further studies will exploit this feature by examining the possibility of using **1** as a basis to produce multicentre redox species and model magnetic systems. Furthermore, as a result of the electrochemical studies, further work will also examine the possibility of using **1** in the electrowinning of copper(II) and other redox active metal ions from solution by deposition onto an electrode surface.

Acknowledgements

We thank the Royal Society of Edinburgh/BP for a research Fellowship (N. R.) and the Leverhulme trust for financial support. We thank Andrew Harrison, University of Edinburgh for help with the SQUID measurements.

Notes and references

‡ The new macrocycle, [*exo*O$_2$]cyclam **1** was synthesised by adding solutions of dimethyloxalate (2.12 g, 18.1 mmol) in ethanol (350 cm^3) and the tetraamine, *N*,*N*′-bis(3-aminopropyl)ethylenediamine (3.14 g, 18.0 mmol) in ethanol (350 cm^3) to a solution of refluxing ethanol (50 cm^3) dropwise *via* a peristaltic pump over a period of 32 h. After 32 h addition was complete and the solution was cooled and filtered. The solution was then reduced to dryness and the white product taken up into hot propan-2-ol (100 cm^3). Filtering the hot solution and then reduction to dryness gave the desired product in 64% yield (2.5 g, 11.0 mmol), mp 141–142 °C (Found: C, 51.53; H, 8.85; N, 23.87. Calc. for $C_{10}H_{20}N_4O_2 \cdot 0.25H_2O$: C, 51.62; H, 8.88; N, 24.07%). ^{1}H NMR (CD$_3$OD, 200 MHz): δ 1.99 (q, 4 H, $^3J_{HH} = 7.7$, OCNHCH$_2$C*H*$_2$), 2.99 (t, 4H, $^3J_{HH} = 7.1$, OCNHCH$_2$CH$_2$C*H*$_2$), 3.06 (t, 4H, $^3J_{HH} = 7.5$ Hz, OCNHC*H*$_2$), 3.13 (s, 4H, NHC*H*$_2$C*H*$_2$NH). IR (cm^{-1}, KBr): 3300s, 3550–3000w, 2929m, 2875m, 1728w, 1655m, 1652s, 1521m, 1466m, 1438m, 1364w, 1288w, 1112m, 1073w, 767m, 569w. Positive ion mass spectrum (nitrobenzyl alcohol matrix): *m*/*z* 229 (MH$^+$).

§ Crystals of [Cu{Cu[*exo*O$_2$]cyclam}$_2$][ClO$_4$]$_2$ **3** were obtained by the slow addition of copper(II) perchlorate hexahydrate (0.081 g, 0.22 mmol) in methanol (*ca.* 10 cm^3) over a peroid of 2 h to a stirred solution of **1** (0.033 g, 0.15 mmol) in water (2 cm^3). (**CAUTION**: Perchlorate salts are potentially explosive.) After the addition was complete the colour of the solution had changed to dark red and on standing for 4 weeks yielded deep red crystals (0.065 g, 0.077 mmol, 53% yield), mp >160 °C (decomp.) (Found: C, 27.72; H, 4.49; N, 12.81. Calc. for $C_{20}H_{36}N_8O_{12}Cu_3Cl_2 \cdot 2H_2O$: C, 27.36; H, 4.58; N, 12.72%). IR (cm^{-1}, KBr): 3630–3000m, 3434m, 3251m, 2937m, 2872m, 1625s (br), 1433s, 1398w, 1352m, 1342m, 1316m, 1259w, 1174m, 1092s (br), 1015m, 991w, 939w, 886w, 816w, 626m, 541w, 502w. Positive ion electrospray mass spectrum (from methanol and water): *m*/*z* 742.5 ($M^+ - ClO_4^-$).

Compound **3** can also be synthesised by adding compound **2** (0.05 g, 0.17 mmol) to copper(II) perchlorate hexahydrate (0.032 g, 0.089 mmol). Compound **2** was synthesised by the addition of potassium hydroxide (0.29 g, 5.2 mmol) in water (0.5 cm^3) to solution of [*exo*O$_2$]-cyclam **1** (0.59 g, 2.58) in methanol (200 cm^3); this was followed by the addition of hexane (40 cm^3) and the slow addition of copper(II) chloride (0.34 g, 2.58 mmol) in methanol (50 cm^3) to the solution over a period of 3 h. After this time, a purple precipitate had formed and was isolated by filtration. The filtrate was dried *in vacuo* to yield the product as a fine purple powder (0.25 g, 0.859 mmol, 33.3% yield), mp >160 °C (decomp.) (Found: C, 41.19; H, 6.73; N, 18.92. Calc. for $C_{10}H_{18}N_4O_2Cu$: C, 41.49; H, 6.27; N, 19.35%). IR (cm^{-1}, KBr): 3630–3000m, 3179m, 3099m, 2894m, 2860m, 1606s, 1576s, 1478w, 1446m, 1384m, 1358m, 1341w, 1324m, 1175w, 1132w, 1109w, 1096w, 1079m, 1060w, 1028m, 1006w, 936w, 900w, 877m, 794w. Positive ion electrospray mass spectrum (from methanol and water): *m*/*z* 291 (MH$^+$).

¶ Crystal data for **3**: $C_{20}H_{40}N_8O_{14}Cl_2Cu_3 \cdot 2H_2O$, red lath, crystal dimensions 0.39 × 0.19 × 0.10 mm, monoclinic, $P2_1/n$, $a = 8.6599(17)$, $b = 16.907(4)$, $c = 12.784(3)$ Å, $\beta = 106.21(2)$°, $U = 1797.4(10)$ Å^3, $\mu = 3.986$ mm^{-1}, $Z = 2$. Data were collected at 220 K on a Stoe Stadi-4B diffractometer using graphite-monochromated Cu-Kα radiation, $\lambda = 1.54184$ Å. A total of 3746 reflections were collected in the range $8.9 \le 2\theta \le 140.14$° and the 3171 independent reflections were used in the structural analysis after an absorption correction was applied on the basis of ψ-scans ($T_{max} = 0.926$, $T_{min} = 0.653$). The structure was solved using direct methods with SIR92[16] and refinement on F^2 using SHELXL-97.[16] The structure converged satisfactorily to $R1 = 0.066$ and $wR2 = 0.1532$ on all data and $R1 = 0.055$ and $wR2 = 0.146$ for the observed data [for $2553F > 4\sigma(F)$]. Goodness-of-fit = 1.048 on all F^2

(3171); 235 parameters; 10 restraints; residuals in the final map = $+0.794/-0.761$ e Å^{-3}. CCDC reference number 186/1461. See http://www.rsc.org/suppdata/dt/1999/1925/ for crystallographic files in .cif format.

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Communication 9/02792K