Unexpected rearrangement of a novel pendent-arm tetraazamacrocyclic complex

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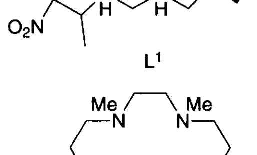
The copper(II) complex of *trans*-5(*S*),7(*S*),12(*R*),14(*R*)-tetramethyl-1,4,8,11-tetraazacyclotetradecane-6,13-dione dioxime (L^2) is synthesised and its X-ray crystal structure is reported; it has a *trans*-II (*R*,*R*,*S*,*R*) arrangement of the four coordinated secondary amines within the fourteen-membered macrocycle.

In a recent paper, we reported the metal template directed synthesis of the new functionalised tetraazamacrocycle L^1 as its copper(II) complex.[1] This complex is novel in that it possesses nitro groups appended to secondary C atoms within the macrocyclic ring. That is, the relatively acidic nitro-substituted C atoms are reactive and potentially nucleophilic sites, so this new class of compound provides a new route toward C-functionalised azamacrocycles. In this work, we report the product of a mild reduction of $[CuL^1]^{2+}$ in basic solution to form the novel dioxime derivative $[CuL^2]^{2+}$.

A solution of $[CuL^1][ClO_4]_2$ (4.0 g) in water (100 cm³) was treated with K_2CO_3 (16.0 g) for 15 min at *ca.* 0 °C. Hydrogen peroxide (30%, 26 cm³) was added dropwise, then the reaction mixture was brought to room temp. and neutralised by the addition of aqueous HCl. Purification was achieved by cation exchange chromatography, giving two N-based isomers of the complex $[CuL^2]^{2+}$; the major isomer is blue and the other purple. The blue complex was isolated as its chloride salt, and the purple isomer was crystallised as its perchlorate salt. The IR spectra of both isomers display intense resonances characteristic of an oxime ($\bar{\nu}_{C=N}$ 1636 cm^{-1}), with no evidence of nitro group stretching vibrations at 1550 or 1360 cm^{-1}, showing that no starting material remained. The aqueous solution electronic spectrum of the blue isomer of $[CuL^2]^{2+}$ exhibits a single visible maximum at 556 nm (ε 191 dm³ mol^{-1} cm^{-1}), whereas the purple isomer yielded a visible maximum at 510 nm. By comparison, the purple starting material $[CuL^1]^{2+}$ displays a single visible maximum at λ_{max} 519 nm (ε 59.6 dm³ mol^{-1} cm^{-1}). If solutions of the blue isomer are acidified with dilute $HClO_4$, their colour changes to purple over a few days and the product exhibits a visible spectrum identical to that of the purple isomer of $[CuL^2]^{2+}$.

Recrystallisation of $[CuL^2]Cl_2$ from aqueous solution in the presence of excess $NaBF_4$ afforded crystals of $[Cu(L^2)Cl]BF_4 \cdot H_2O$ suitable for X-ray work.† A view of the complex cation appears in Fig. 1. A distorted square-pyramidal coordination geometry of four amines and one apical chloro ligand is defined. The Cu atom is displaced by 0.270 Å from the least-squares N_4 plane towards the chloro ligand. The two pendent oxime groups are apparent, and their C–N and N–O bond lengths are consistent with a ketoxime as opposed to the C-nitroso tautomer. This results in the relevant macrocyclic C atoms becoming sp² hybridised compared with their tetrahedrally coordinated geometry in the precursor complex. A remarkable feature of this structure is the (*R*,*R*,*S*,*R*) configuration of the four secondary amine N atoms, commonly referred to as *trans*-II.[4] In this configuration, three of the four amine H atoms are on the same side of the macrocyclic plane. The Cu–N bond lengths in this complex are significantly longer than those found in the centrosymmetric precursor $[CuL^1][ClO_4]_2$ complex, where an (*R*,*R*,*S*,*S*) or *trans*-III configuration was defined.[1] The *trans*-III configuration is dominant for fourteen-membered macrocyclic complexes, where pairs of amine H atoms (attached to the same six-membered chelate ring) are on the same side of the ring but opposite to that of the remaining pair of H atoms. The marked differences between the energies and intensities of the visible maxima of $[CuL^1]^{2+}$ and the *trans*-II isomer of $[CuL^2]^{2+}$ are explained by reference to their crystal structures. The significantly longer Cu–N bond lengths in *trans*-II $[CuL^2]^{2+}$ and out of plane distortion of the CuN_4 group significantly lowers the effective ligand-field strength relative to the planar $[CuL^1]^{2+}$ analogue.[1] In addition, the lower symmetry of the highly distorted *trans*-II $[CuL^2]^{2+}$ chromophore results in a fourfold increase in intensity relative to its centrosymmetric precursor. By comparison, the high-energy visible electronic maximum of the purple isomer of $[CuL^2]^{2+}$ strongly suggests a *trans*-III configuration, although no structural data are available at present to confirm this.

The crystal structural analysis of $[CuL^2(Cl)]BF_4 \cdot H_2O$ defines the first example of a *trans*-II configuration in a coordinated fourteen-membered macrocyclic secondary tetraamine. The only examples where a *trans*-II coordination geometry has been observed in a tetradentate coordinated ligand are in the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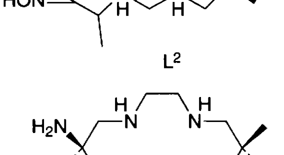
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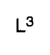
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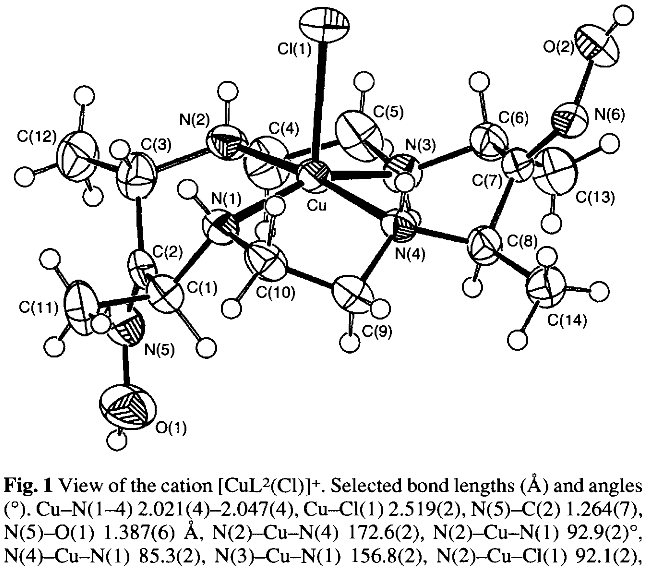


Fig. 1 View of the cation $[CuL^2(Cl)]^+$. Selected bond lengths (Å) and angles (°). Cu–N(1–4) 2.021(4)–2.047(4), Cu–Cl(1) 2.519(2), N(5)–C(2) 1.264(7), N(5)–O(1) 1.387(6) Å, N(2)–Cu–N(4) 172.6(2), N(2)–Cu–N(1) 92.9(2)°, N(4)–Cu–N(1) 85.3(2), N(3)–Cu–N(1) 156.8(2), N(2)–Cu–Cl(1) 92.1(2), N(3)–Cu–Cl(1) 101.0(2).

complexes *trans*-[RuO(L^3)Cl]$^+$ and *trans*-[RuL^3(NCMe)(N_3)]$^+$,[5,6] where the methyl groups impart kinetic stability to the tertiary amines with respect to N-inversion. Pentadentate coordination of the macrocycle L^4 in [Co(HL^4)Cl]$^{3+}$ ion also results in a *trans*-II configuration,[7] but chelation by one of the pendent groups dictates the configuration for two of the four chirotopic N-donors. It is also notable that these earlier examples involve stabilisation of this unusual configuration by inert metal ions, in contrast to the labile copper(II) ion in [Cu(L^2)Cl]$^+$.

Cyclic voltammetry of *trans*-II [CuL^2]$^{2+}$ (Fig. 2) resulted in a totally reversible Cu^{II}–Cu^I couple (E^0 −0.74 *vs*. SCE). There was no diminution in the intensity of the anodic wave even at slow scan rates (*ca*. 20 mV s^{-1}), indicating that the copper(I) complex is remarkably stable in aqueous solution. This behaviour is unprecedented for a macrocyclic secondary amine complex of Cu^{II}. By comparison, the *trans*-III isomers of [CuL^1]$^{2+}$ and [CuL^4]$^{2+}$ exhibit totally irreversible electrochemical behaviour under the same conditions,[8] with dissociation of their respective copper(I) complexes occurring rapidly before reoxidation can take place. The reversible electrochemical behaviour of the *trans*-II isomer of [CuL^2]$^{2+}$ appears to be a consequence of the rather distorted, non-planar CuN_4 coordination geometry of this configuration, which facilitates the expansion of the Cu–N bond lengths and tetrahedral distortion of the CuN_4 group upon reduction. By contrast, the *trans*-III analogues cannot adapt to the considerable changes in coordination geometry on going from Cu^{II} to Cu^I and simply dissociates.

The existence of [CuL^2]$^{2+}$ in the unexpected *trans*-II configuration must arise through inversion of one coordinated secondary amine going from the (*R,R,S,S*) (*trans*-III) isomer of the precursor to the (*R,R,S,R*) (*trans*-II) of the product. Electrochemistry of [CuL^1]$^{2+}$ shows that reductions of the metal centre and the nitro group occur at similar potentials, so reduction of the metal during the conversion of [CuL^1]$^{2+}$ to [CuL^2]$^{2+}$ is almost certain. Reoxidation of the copper(I) complex is presumably achieved by aerial oxygen. Therefore, the present N-inversion must be occurring upon reduction to Cu^I, as proposed in Scheme 1. It is likely that a temporary break of one Cu–N bond occurs upon reduction of the metal centre in order that N-inversion be facilitated. However, the putative three-coordinate [CuL^2]$^+$ does not dissociate, but survives for a sufficiently long period to allow N-inversion, recoordination in a *trans*-II configuration and reoxidation to Cu^{II}. As shown by electrochemical experiments, subsequent reduction of *trans*-II [CuL^2]$^{2+}$ will be reversible, without significant rearrangement.

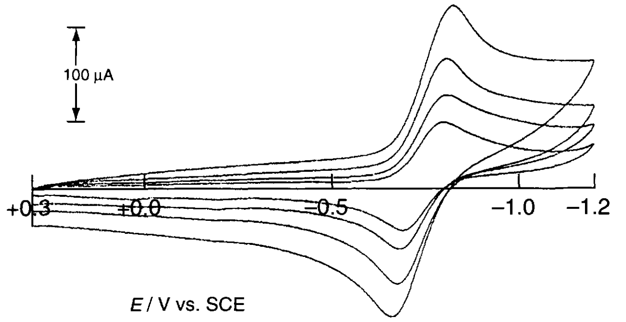
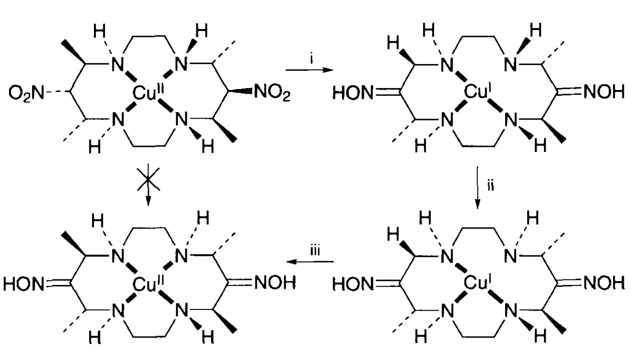


Fig. 2 Cyclic voltammograms of [CuL^2]$^{2+}$: (glassy carbon electrode, aqueous 0.1 mol dm^{-3} $NaClO_4$, scan rates 50, 100, 200 and 400 mV s^{-1})



Scheme 1 *Reagents*: i, H_2O_2, K_2CO_3; ii, N-inversion; iii, O_2

The stabilisation of pendant oxime groups was unexpected. Ketoximes are usually hydrolysed to the corresponding ketone under the basic conditions employed in this reaction.[9] The use of hydrogen peroxide in basic solution is recommended for the conversion of nitro groups to carbonyl groups,[10] where mild (two-electron) reduction of the nitro group is generally followed by facile hydrolysis of the intermediate oxime.

More forcing hydrolytic conditions should lead to the diketone derivative of L^2, which will add a new class of reactive functionalised macrocycle. We are currently exploring further derivatives of the complexes [CuL^1]$^{2+}$ and the novel oxime relative [CuL^2]$^{2+}$.

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Footnote

† *Crystal data*: $C_{14}H_{32}BClCuF_4N_6O_3$, M = 518.26, monoclinic, space group $P2_1/c$, a = 16.581(4), b = 7.8704(4), c = 18.740(4) Å, β = 114.563(8)°, Z = 4, D_c 1.548 g cm^{-3}, μ(Mo-Kα) = 11.63 cm^{-1}, F(000) = 1076, T = 296 K, final R_1 = 0.0446, wR_2 = 0.1044 for 2220 independent observed reflections [$|F_o| > 2\sigma(|F_o|)$, $2\theta < 50°$], $w^{-1} = \sigma^2(F_o)^2 + (0.0562P)^2 + 2.34P$ where $P = (F_o^2 + 2F_c^2)/3$. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation and employing the ω–2θ scan method. The structure was solved by direct methods with SHELXS-86[2] and refined by full-matrix least squares with SHELXL-93.[3] 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 Crystallograpic 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 182/59.

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