

Co-ordination to Copper(II) by Only Three Nitrogen Atoms of a Tetra-azamacrocyclic Ligand functionalised with Two Pendant Acetate-arms. X-Ray Structure of $[\text{Cu}(\text{L}^1\text{H}_2)\text{Cl}]\text{Cl}$, where L^1 is 3,11-Diacetato-7-methyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene

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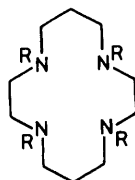
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The tetrahydrochloride salt of the new ligand 3,11-diacetato-7-methyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1-(17),13,15-triene, L^1 , has been prepared, and found to react in aqueous solution with copper(II) sulphate to give $[\text{Cu}(\text{L}^1\text{H}_2)\text{Cl}]\text{Cl}$ in which the copper(II) has a distorted trigonal bipyramidal geometry, with co-ordination to L^1 through only three of the four nitrogen atoms and only one of the two acetate-arms.

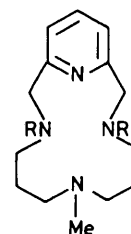
There is considerable current interest in the isomerisation reactions of metal complexes of tetra-azamacrocyclic ligands such as $[\text{Ni}(\text{tmc})]^{2+}$ [$\text{tmc} = 1,4,8,11$ -tetramethyl-1,4,8,11-tetra-azacyclotetradecane (**1**)].¹⁻³ These isomerisation reactions involve nitrogen-inversions, and it has been postulated that intermediates must be formed in which one or more of the metal-nitrogen bonds are broken to allow nitrogen-inversion to occur.^{1,2} However, no evidence has been found so far for the existence of such an intermediate in which one of the nitrogen atoms is unco-ordinated, and we report the first example of the isolation and characterisation of such a structure.

Until recently only the *endo*-mode of co-ordination had been found for potentially quadridentate tetra-azamacrocycles of the type shown in structure (A) ($\text{X} = \text{NR}$; $\text{R} = \text{Me}$

or H). In contrast, for tetrathiamacrocycles ($\text{X} = \text{S}$) the *exo* structures (B)⁴ and (C)⁵ have been found as possible modes of co-ordination. The ability of these tetrathiamacrocycles to



(1) $\text{R} = \text{Me}$ (tmc)
(2) $\text{R} = [\text{CH}_2]_2\text{NH}_2$



L^1 ; $\text{R} = \text{CH}_2\text{CO}_2^-$
 L^2 ; $\text{R} = \text{H}$

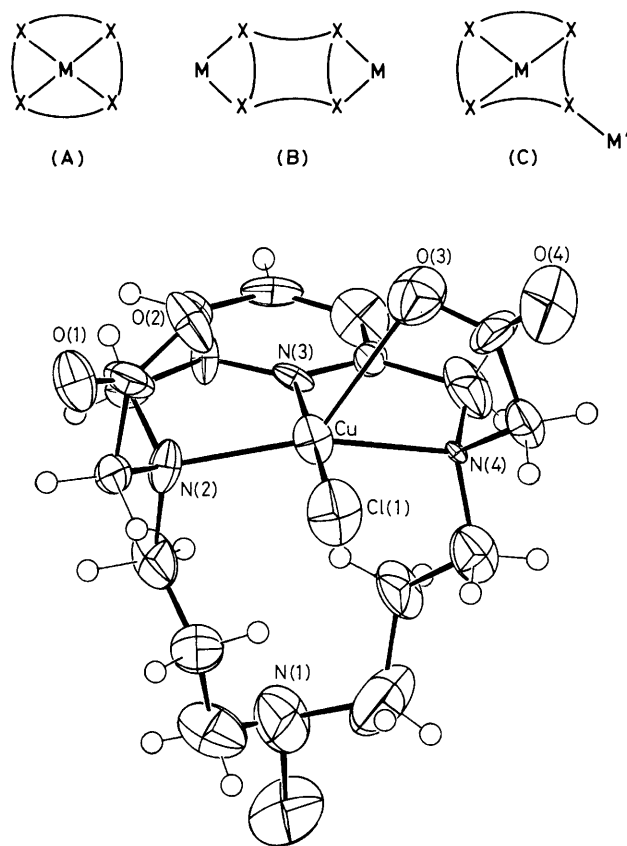


Figure 1. Molecular structure of $[\text{Cu}(\text{L}^1\text{H}_2)\text{Cl}]^+$. Bond lengths (pm) and bond angles ($^\circ$) are as follows: Cu–N(3) 195(2), Cu–N(2) 213(2), Cu–N(4) 212(2), Cu–Cl 220(1), Cu–O(3) 259(2); Cl–Cu–O(3) 90.5(5), Cl–Cu–N(2) 100.2(6), O(3)–Cu–N(2) 136.2(7), Cl–Cu–N(3) 178.6(6), O(3)–Cu–N(3) 90.9(7), N(2)–Cu–N(3) 78.9(8), Cl–Cu–N(4) 97.0(6), O(3)–Cu–N(4) 69.2(7), N(2)–Cu–N(4) 146.6(8), N(3)–Cu–N(4) 83.3(8).

give *exo*-structures is believed to be due to the larger size of the sulphur-donor atoms which reduces the macrocycle cavity size and produces greater repulsions between the sulphur lone-pairs. Recently an example of a structure of type (B) was reported for the binuclear copper(II) complex of the functionalised aza-macrocycle, (2).⁶ We report here the first example of bonding to a tetra-azamacrocycle of type (C) ($\text{M} = \text{Cu}^{\text{II}}$; $\text{M}' = \text{H}^+$; $\text{X} = \text{NR}$). This type of bonding has only been found previously in a polymeric copper(I) complex of a tetrathiamacrocycle ($\text{M}, \text{M}' = \text{Cu}^{\text{I}}$; $\text{X} = \text{S}$).⁵

As part of a project to prepare new functionalised macrocyclic ligands,⁷ we recently synthesised the new ligand L^1 by the reaction of L^2 with two moles of 2-bromoacetic acid using a published method.⁸ L^2 was prepared by a template method analogous to those reported previously.^{9,10} L^1 was isolated as a tetrahydrochloride, and a solution of $\text{L}^1 \cdot 4\text{HCl}$ (0.255 g) in water (75 cm³) was treated with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.1 g) in water (75 cm³). The mixture was warmed to 60 $^\circ\text{C}$ for 1 h, filtered whilst hot, and the solution allowed to evaporate slowly for several days. During this time deep green crystals deposited, which were filtered off and air dried. The visible spectrum of the aqueous solution showed a band at 624 nm which is close to the value reported for the $[\text{Cu}(\text{NH}_3)_3(\text{H}_2\text{O})_3]^{2+}$ ion (λ_{max} 625 nm),¹¹ and indicated that not all four N atoms of L^1 were co-ordinated.

Crystal data: $\text{C}_{18}\text{H}_{28}\text{Cl}_2\text{CuN}_4\text{O}_4 \cdot 4\text{H}_2\text{O}$, $M = 570.9$ crystallises as small green plates which are monoclinic, space group

$P2_1/n$, with $a = 14.695(9)$, $b = 12.955(6)$, $c = 13.831(6)$ Å, $\beta = 91.84(4)^\circ$, $U = 2632$ Å³, $Z = 4$, $D_x = 1.44$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $\mu = 11.0$ cm⁻¹ (no absorption correction). The crystals were poorly diffracting, and showed some decay under X-ray irradiation. 3796 Reflections were collected with a Syntex $P2_1$ diffractometer [1102 with $I/\sigma(I) \geq 3.0$], and the structure solved by the heavy-atom method and refined to a final R value of 0.091 (anisotropic temperature factors were used for all non-hydrogen atoms apart from four solvent water molecules). The results of the structure analysis are shown in Figure 1. The Me–N group, and one of the two acetate-arms of L^1 are clearly protonated and non-co-ordinating. The copper(II) complex is approximately trigonal bipyramidal, with apical co-ordination to Cl^- and the N (pyridine) atom, and with equatorial co-ordination to the other two nitrogen atoms and one acetate-arm of L^1 . The bond lengths and angles are shown in Figure 1. As is usual for tetra-azamacrocycles which contain a pyridine moiety, the Cu–N(pyridine) bond length (194.9 pm) is significantly shorter than the other two Cu–N bond lengths (average 212.4 pm). The Cl–Cu–N(pyridine) bond angle (178.6 $^\circ$) is close to the ideal for a trigonal bipyramidal structure, and the other three donor atoms and the copper(II) are approximately coplanar. However, the pendant-arm chelate ring forms an acute angle of only 69 $^\circ$ at copper(II), and this significantly distorts the trigonal bipyramidal structure. The non-co-ordinating acetate-arm is on the same side of the azamacrocyclic plane as the co-ordinating acetate-arm, which prevents ready co-ordination in an idealised *trans*-six-co-ordinate structure.[†]

The significant feature of the structure is the non-co-ordination of the Me–N group, giving rise to bonding mode (C) ($\text{M}' = \text{H}^+$), which has not been reported previously for a tetra-azamacrocycle. We conclude that it is reasonable to postulate the presence of similar intermediates in the isomerisation reactions of $[\text{Ni}(\text{tmc})]^{2+}$ and other complexes of tetra-azamacrocycles.^{1,2}

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[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.