Synthesis and Characterization of N,N′,N″,N‴-Tetrakis(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane and its Copper(II) Complexes

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The title ligand combines with two copper(II) ions as an octadentate ligand forming unique binuclear structures; the Cu–Br bond of the bromide complexes shows an extraordinary inertness towards hydration in aqueous solution.

It is well known that 1,4,8,11-tetra-azacyclotetradecane (so called cyclam) is a quadridentate saturated macrocyclic ligand which forms very stable complexes with transition metal ions. It is expected that the introduction of a pendant donor group such as $-[CH_2]_nNH_2$ to each nitrogen atom of this ligand will yield novel modes of co-ordination as illustrated in Figure 1. Wainwright prepared such ligands containing $-[CH_2]_2CN$, $-[CH_2]_2CONH_2$, and $-[CH_2]_3NH_2$ as pendant groups, and obtained only mononuclear complexes of type (**A**).[1,2] In this study we have synthesized the title ligand (taec), in which the pendant chain is shorter than those obtained previously, in the hope of obtaining the novel binuclear complexes such as (**B**) and (**C**).

The ligand, as its octahydrobromide (taec·8HBr, m.p. 270 °C), was synthesized from cyclam and *N*-tosylaziridine as shown in Scheme 1.

The 2 : 1 copper(II) complex, $Cu_2(taec)Br_4$, was isolated as fine blue crystals from the concentrated filtrate of the aqueous mixture of taec·8HBr with an excess of $CuCO_3$. When an excess of $NaClO_4$ was added to a concentrated aqueous solution of $Cu_2(taec)Br_4$ or to the filtered reaction mixture of taec·8HBr and $CuCO_3$, blue prisms were separated which

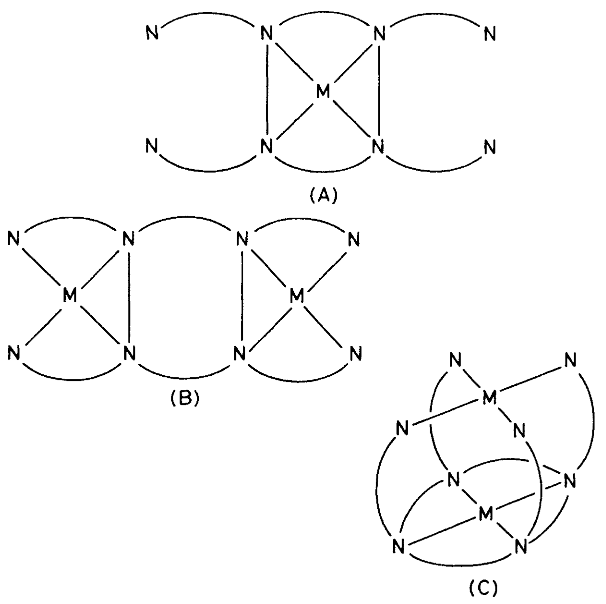
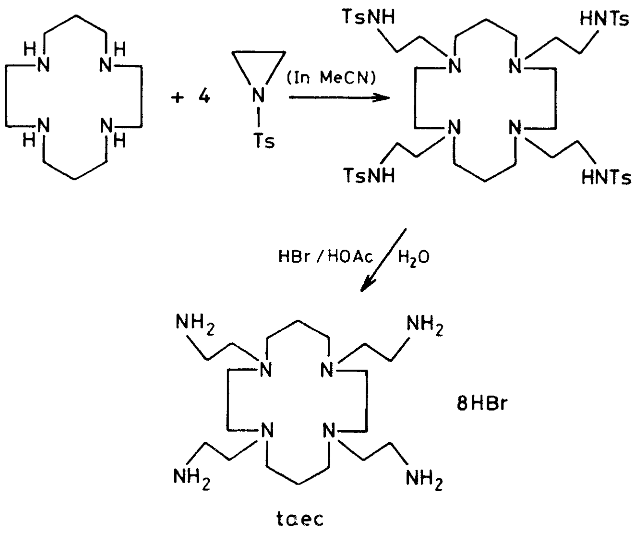


Figure 1. Possible structures for metal complexes of cyclam ($[CH_2]_nX)_4$, where X denotes a donor group such as NH_2 and $n = 2$ or 3.

were revealed to be of the formula $Cu_2(taec)Br(ClO_4)_3$ by elemental analysis. The tetraperchlorate complex $Cu_2(taec)(ClO_4)_4$ was obtained as purple needles from the tetrabromide or the bromide–triperchlorate complex by the addition of a large excess of $NaClO_4$ after the removal of bromide ions with $AgClO_4$. We have not yet been able to isolate the 1 : 1 Cu^{II} complex. Molecular models suggested that structure (**B**) is sterically more favourable than (**C**): this has been confirmed by the single crystal *X*-ray analysis for $Cu_2(taec)(ClO_4)_4$.†

A perspective view of the complex ion is shown in Figure 2. It is obvious from the figure that the co-ordination mode exactly corresponds to (**B**), and the cyclam ring assumes the *trans* III form of Bosnich *et al.*[3] The cation has a centre of symmetry and a symmetry plane (formed by C-3, Cu, O-1, C-3′, Cu′, and O-1′). The co-ordination geometry of each copper ion is an elongated square pyramid with a perchlorate oxygen at the top.

It is notable that the addition of a large excess of $NaClO_4$ into $Cu_2(taec)Br_4$ solution invariably yielded $Cu_2(taec)Br(ClO_4)_3$ and repeated trials to obtain the tetraperchlorate complex by this procedure were all unsuccessful. This suggests that the bromide ion is playing an important role in the molecular structure.



Scheme 1. Ts = Tosyl (p-$MeC_6H_4SO_2$).

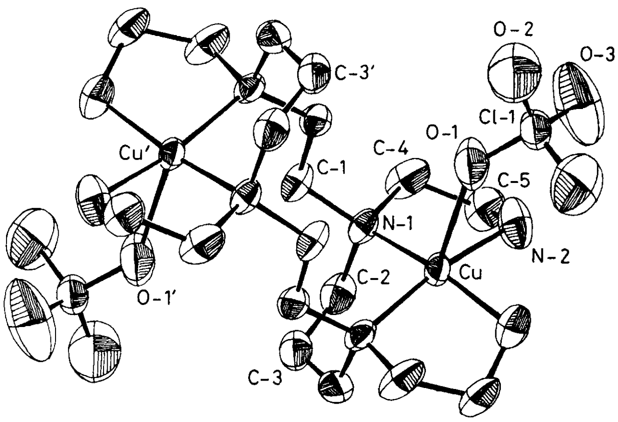


Figure 2. ORTEP drawing of $[Cu_2(taec)(ClO_4)_2]^{2+}$ (50% probability ellipsoids; hydrogen atoms are not shown). Distances (Å): Cu $\cdots$ Cu′ 5.479(1), Cu–N-1 2.066(4), Cu–N-2 2.000(6), Cu–O-1 2.562(7). Angles(°): N-1–Cu–N-2 85.3(2), N-1–Cu–O-1 107.0(1), N-2–Cu–O-1 83.4(2).

Table 1. Spectral and magnetic data.

	$\tilde{\nu}_{max.}$ (10^3 cm^{-1}) Aq. solution	Nujol	$\mu_{eff.}$(μ_B) Room temp.	θ(K)
$Cu_2(taec)Br_4$	16.3(470)[a]	16.2	1.82	−20
$Cu_2(taec)Br(ClO_4)_3$	16.3(470)	16.3	1.98	−24
$Cu_2(taec)(ClO_4)_4$	17.7(330)	19.2	1.81	−20

[a] Extinction coefficient (dm^3 mol^{-1} cm^{-1}).

The electronic spectra of the complexes of the tetrabromide and bromide–triperchlorate complexes closely resemble each other in Nujol mull and are practically the same in aqueous solution, whereas the d–d band of the tetraperchlorate is substantially shifted to a higher frequency relative to those of the bromide-containing complexes in both aqueous solution and Nujol mull (Table 1). The spectra all obey Beer's law in aqueous solution in the concentration range examined (2×10^{-3}—2.5×10^{-4} mol dm^{-3}), indicating that almost all the copper is bonded to bromide ions in the aqueous solutions. This is a surprising result considering the generally accepted view that bromo-copper(II) complexes are readily hydrolysed in aqueous solution.[4] Therefore, such an unusual inertness of Cu–Br bonding cannot be explained by simple co-ordination of bromide ions: the bromide ion may be incorporated into a

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† *Crystal data:* $C_{18}H_{44}Cl_4Cu_2N_8O_{16}$, orthorhombic, space group *Pnnm*, $a = 11.709(1)$, $b = 14.948(3)$, $c = 9.938(2)$ Å, $D_m = 1.75$, $D_c = 1.71$ g cm^{-3}, $Z = 2$. The structure was solved by direct methods and refined using 2397 unique data [$F > 3\sigma(F)$] measured on a Rigaku AFC-5 diffractometer with Mo-K_α radiation. The final R value is 0.069.

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

space in the complex such that it is bound by both copper atoms.

The magnetic moments of the complexes are slightly higher than the spin-only value at room temperature, and all the complexes obey the Curie–Weiss law with negative Weiss constants (θ), Table 1.

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