

## Bis-copper(II) Complexes of Binucleating Linear Octaaza Ligands

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### Abstract

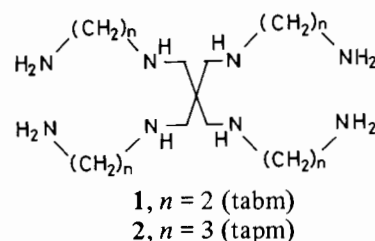
The synthesis and characterization of biscopper(II) complexes of the octaaza ligands 5,5-bis(4'-amino-2'-azabutyl)-1,9-diamino-3,7-diazanonane (tabm) and 6,6-bis(5'-amino-2'-azapentyl)-1,11-diamino-4,8-diazaundecane (tapm) is described. The structure of one of the complexes,  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ , has been determined by single crystal X-ray diffraction techniques – ( $R = 0.079$ ), space group  $P2_1/a$ , with  $a = 12.656(3)$ ,  $b = 15.411(6)$ ,  $c = 16.426(5)$  Å and  $Z = 4$ . The copper(II) ions adopt a tetragonally distorted octahedral geometry with the O–Cu–O axes nearly perpendicular. For the  $\text{Cu}_2(\text{tapm})(\text{NO}_3)_4$  analogue a structure is proposed in which a non-orthogonal arrangement of the O–Cu–O axes is possible. The ESR spectrum (77 K, DMF) of both complexes is discussed and related to the observed and proposed structures and the observed magnetic susceptibilities ( $\mu_{\text{eff}} = 1.8\text{--}1.9$ , 298 K).

### Introduction

Many examples of macrocyclic and multidentate ligands capable of simultaneously complexing two metal ions have been reported (e.g. [1–10]). Of continuing interest have been binucleating systems with two distinct complexation sites and a connecting link effectively limiting face to face interactions thereby constraining the relative orientations of the chelating sites. Examples of this type of binucleating ligand are: (i) the double ring octaaza macrocycles, in which two dioxocyclam units are connected through two tetrahedral carbon atoms [11–13], (ii) Schiff bases derived from 2,2-diaminomethyl-1,3-diaminopropane, in which the two potentially

tetradentate units are separated by a tetrahedral carbon atom [14], and (iii) multiloop macrocycles in which two crown-ether macrocycles are connected by a spiro carbon atom [15, 16].

We wish to report on two octaaza ligands which are dimeric analogues of the linear tetraamines 1,9-diamino-3,7-diazanonane(2,3,2-tet) [17] and 1,11-diamino-4,8-diazaundecane(3,3,3-tet) [18]. The octaaza ligands 5,5-bis(4'-amino-2'-azabutyl)-1,9-diamino-3,7-diazanonane (tabm) (1), and 6,6-bis(5'-amino-2'-azapentyl)-1,11-diamino-4,8-diazaundecane (tapm) (2) function as binucleating ligands in which two tetraamine moieties are connected by a tetrahedral carbon atom.



### Experimental

The ligands tabm and tapm were synthesized by reacting benzenesulfonated pentaerythritol [19] and 1,2-diaminoethane or 1,3-diaminopropane, respectively, employing previously described procedures for similar multidentate polyamine ligands [20–22]. Heavy oils were obtained which could not be distilled or crystallized. Addition of a methanolic solution of copper(II) nitrate to a solution of tabm or tapm in the same solvent resulted, after cooling, in the precipitation of purple solids, which were recrystallized from concentrated aqueous solutions. *Anal.* Found: C, 19.8; H, 6.2; N, 20.7. *Calc.* for  $\text{Cu}_2\text{C}_{13}\text{H}_{36}\text{N}_{12}\text{O}_{12} \cdot 6\text{H}_2\text{O}$ : C, 19.8; H, 6.1;

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N, 21.3%. Found: C, 26.8; H, 6.1; N, 21.4. Calc. for  $\text{Cu}_2\text{C}_{17}\text{H}_{44}\text{N}_{12}\text{O}_{12} \cdot 2\text{H}_2\text{O}$ : C, 26.5; H, 6.3; N, 21.8%.

The tapm complex was also crystallized as the extremely insoluble dithionate salt. *Anal.* Found: C, 23.8; H, 5.7; N, 12.8; S, 15.0. Calc. for  $\text{Cu}_2\text{C}_{17}\text{H}_{44}\text{N}_8\text{S}_2\text{O}_{12} \cdot 2.5\text{H}_2\text{O}$ : C, 23.9; H, 5.8; N, 13.1; S, 15.0%.

Crystals of the complex  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ , suitable for structure determination were obtained from warm aqueous solution upon standing.

#### Crystal Data

$\text{C}_{13}\text{H}_{48}\text{Cu}_2\text{N}_{12}\text{O}_{18}$ ,  $M_r = 787.7$ , monoclinic,  $a = 12.656(3)$ ,  $b = 15.411(6)$ ,  $c = 16.426(5)$  Å,  $\beta = 100.05(2)^\circ$ ,  $V = 3155(1)$  Å<sup>3</sup>,  $D_m = 1.63$  g cm<sup>-3</sup>,  $D_c = 1.66$  g cm<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 1608$ , space group  $P2_1/a$  (variant of  $P2_1/c$ ,  $C_{2h}^5$  (No. 14)).

#### Data Collection, Structure Solution and Refinement

Intensity data for  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  were collected at 293 K from a crystal measuring  $0.24 \times 0.20 \times 0.08$  mm, using a Nicolet R3m four-circle diffractometer equipped with a graphite monochromated Mo  $K\alpha$  X-radiation source ( $\lambda = 0.71069$  Å). 3190 unique reflections were collected up to  $2\theta_{\text{max}} = 42^\circ$  and of these, 1573 with  $I > 2.5\sigma(I)$  were considered observed and used in structure analysis without correction for absorption. Data were processed using the learnt profile fitting procedure of Diamond [23]. The positions of the two independent copper atoms were located using the centrosymmetric direct methods of SHELX-76 [24] and verified in a sharpened Patterson synthesis. The remaining non-hydrogen atoms were subsequently found using weighted difference methods. Blocked-matrix least-squares refinement with only the atoms of the coordination polyhedra anisotropic gave a final  $R = [(\sum \|F_o\| - |F_c|) / \sum |F_o|] = 0.079$  and  $R_w = [(\sum w \|F_o\| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.082$  with  $w = 1.37 / (\sigma^2 F_o + 3.7 \times 10^{-3} F_o^2)$ . A number of hydrogens were located from a difference-Fourier syntheses and were included in the refinement at fixed positions with their isotropic  $U$  values set invariant at  $0.05$  Å<sup>2</sup>. Neutral element scattering factors and terms for anomalous dispersion correction were taken from ref. 25. Final positional parameters are given in Table I while interatomic distances and angles are listed in Tables II and III.

Electrochemical studies were performed in 0.1 M aqueous sodium nitrate solutions using a conventional three electrode cell with a Ag/AgCl reference electrode and a platinum bead auxiliary electrode. A Metrohm hanging mercury drop electrode (HMDE) was employed as the working electrode for cyclic voltammetry and a dropping mercury electrode (DME) for d.c. polarography. The electrochemical apparatus consisted of a Metrohm Herisau E506 Polarecord and a Bausch and Lomb series 2000 Omnigraphic recorder.

TABLE I. Atomic Coordinates ( $\times 10^4$ ) and Isotropic/Equivalent isotropic Thermal Parameters (Å<sup>2</sup>,  $\times 10^3$ ),  $U_{\text{eq}}^*$  defined as  $(U_{11}U_{22}U_{33})^{1/3}$

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}^*/U_{\text{iso}}$
Part A				
N(1)	86(11)	2037(11)	6578(9)	47(10)*
N(2)	-1412(9)	1037(8)	7111(7)	20(3)
C(1)	-1036(14)	2011(13)	6066(11)	40(5)
C(2)	-1795(14)	1834(13)	6678(11)	43(5)
O(1)	230(11)	-2324(8)	8519(8)	52(9)*
O(2)	521(11)	-3422(10)	7996(9)	65(4)
O(3)	95(14)	-3500(12)	9201(11)	100(6)
N(3)	150(13)	-3091(12)	8568(11)	56(5)
C(21)	-2086(13)	824(12)	7723(10)	29(4)
Part B				
N(1)	1767(11)	1400(9)	7924(8)	35(4)
N(2)	275(10)	288(10)	8403(8)	27(9)*
C(1)	2153(13)	674(12)	8517(10)	37(5)
C(2)	1248(14)	512(13)	9016(11)	43(5)
O(1)	603(10)	2(9)	6610(8)	57(9)*
O(2)	358(12)	-1100(11)	5770(9)	77(5)
O(3)	-965(10)	-262(9)	5848(8)	58(4)
N(3)	49(12)	-427(11)	6106(9)	45(4)
C(21)	-668(12)	165(11)	8826(9)	26(4)
Part C				
N(1)	-5407(11)	-1345(9)	8015(9)	37(10)*
N(2)	-3642(9)	-288(8)	8444(7)	15(8)*
C(1)	-5458(14)	-684(13)	8650(11)	43(5)
C(2)	-4322(13)	-530(12)	9089(10)	27(4)
O(1)	-4808(10)	8(10)	6604(8)	66(10)*
O(2)	-4979(12)	1075(11)	5757(9)	77(5)
O(3)	-3575(10)	289(9)	5859(8)	56(4)
N(3)	-4466(12)	448(11)	6068(9)	42(4)
C(21)	-2528(12)	-175(11)	8868(9)	28(4)
Part D				
N(1)	-4367(10)	-2068(9)	6646(8)	35(4)
N(2)	-2616(10)	-1001(9)	7121(7)	24(3)
C(1)	-3530(13)	-2019(12)	6077(10)	37(5)
C(2)	-2486(14)	-1799(13)	6646(11)	42(5)
O(1)	-3077(10)	-2318(8)	8526(9)	46(9)*
O(2)	-3002(12)	-3535(11)	9194(10)	81(5)
O(3)	-4071(11)	-3411(10)	8021(9)	65(4)
N(3)	-3383(13)	-3093(11)	8555(10)	52(5)
C(21)	1639(12)	-802(11)	7734(9)	25(4)
Others				
Cu(1)	175(2)	1198(2)	7493(1)	30(1)*
Cu(2)	-4012(2)	-1182(2)	7546(1)	31(1)*
C(1)	-1723(12)	12(12)	8279(9)	30(4)
Ow(1)	7305(11)	918(10)	3344(8)	65(4)
Ow(2)	6605(11)	3341(10)	5414(8)	66(4)
Ow(3)	6454(11)	1683(10)	4566(8)	69(4)
Ow(4)	766(11)	2265(10)	632(8)	64(4)
Ow(5)	-3073(11)	-868(10)	3374(9)	69(4)
Ow(6)	2812(12)	2588(11)	9307(9)	81(5)

Magnetic susceptibilities were determined using the Gouy method, with  $\text{Ni}(\text{en})_3(\text{S}_2\text{O}_3)$  being employed as calibrant. The susceptibilities were corrected

TABLE II. Interatomic Bond Distance (Å) for  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ 

Coordination sphere				
Cu(1)–N(1A)	1.97(1)	Cu(2)–N(1C)	2.06(1)	
Cu(1)–N(1B)	2.04(1)	Cu(2)–N(1D)	2.00(1)	
Cu(1)–N(2A)	2.01(1)	Cu(2)–N(2C)	2.01(1)	
Cu(1)–N(2B)	2.04(1)	Cu(2)–N(2D)	2.03(1)	
Cu(1)–O(1A)	2.53(1)	Cu(2)–O(1C)	2.50(1)	
Cu(1)–O(1B)	2.46(1)	Cu(2)–O(1D)	2.53(1)	
Intraligand				
	Part (A)	Part (B)	Part (C)	Part (D)
C(1)–C(21)	1.56(2)	1.50(2)	1.56(2)	1.55(2)
C(21)–N(2)	1.46(2)	1.49(2)	1.47(2)	1.48(2)
N(2)–C(2)	1.46(2)	1.49(2)	1.52(2)	1.48(2)
C(2)–C(1)	1.53(3)	1.54(3)	1.51(2)	1.52(2)
C(1)–N(1)	1.52(2)	1.51(2)	1.47(2)	1.53(2)
O(1)–N(3)	1.27(2)	1.19(2)	1.22(2)	1.26(2)
N(3)–O(2)	1.23(2)	1.27(2)	1.23(2)	1.27(2)
N(3)–O(3)	1.23(2)	1.30(2)	1.27(2)	1.22(2)

for the diamagnetism of the constituting atoms by the use of Pascal's constants [26]. ESR spectra were recorded on a Bruker ER200D X-band spectrometer as frozen dimethylformamide (DMF) solutions (77 K).

## Results and Discussion

The structure of  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  consists of two tetragonally distorted  $\text{CuN}_4\text{O}_2$  octahedral units linked through a spiro carbon atom (Fig 1). Each copper(II) ion is bound equatorially by four amine donors and apically by coordination of two monodentate nitrate groups. The two O–Cu–O axes are orthogonal. The copper–nitrogen distances range from 1.97(1)–2.06(1) Å, with an average of 2.02(1) Å, and are in the range observed previously for the copper–nitrogen distances in  $\text{Cu}(\text{en})_2(\text{NO}_3)_2$  (2.03 Å) [27], and  $\text{Cu}(2,3,2\text{-tet})(\text{ClO}_4)_2$  (2.02 Å) [28]. The Cu–O distance (average 2.50 Å) is clearly indicative of a tetragonally distorted  $\text{CuN}_4\text{O}_2$  chromo-

TABLE III. Interatomic Bond Angles (degrees) for  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ 

(a) Coordination sphere				
N(1)A–Cu(1)–N(1)B		94.9(5)	N(1)C–Cu(2)–N(1)D	95.5(6)
N(1)A–Cu(1)–N(2)A		85.5(5)	N(1)C–Cu(2)–N(2)C	85.1(5)
N(1)A–Cu(1)–N(2)B		177.5(6)	N(1)C–Cu(2)–N(2)D	178.0(5)
N(1)A–Cu(1)–O(1)A		93.8(5)	N(1)C–Cu(2)–O(1)C	92.4(5)
N(1)A–Cu(1)–O(1)B		91.8(5)	N(1)C–Cu(2)–O(1)D	90.8(5)
N(1)B–Cu(1)–N(2)A		177.2(5)	N(1)D–Cu(2)–N(2)C	179.4(6)
N(1)B–Cu(1)–N(2)B		85.4(5)	N(1)D–Cu(2)–N(2)D	86.4(5)
N(1)B–Cu(1)–O(1)A		88.1(5)	N(1)D–Cu(2)–O(1)C	91.7(5)
N(1)B–Cu(1)–O(1)B		90.7(5)	N(1)D–Cu(2)–O(1)D	91.0(5)
N(2)A–Cu(1)–N(2)B		94.3(5)	N(2)C–Cu(2)–N(2)D	93.0(5)
N(2)A–Cu(1)–O(1)A		89.1(5)	N(2)C–Cu(2)–O(1)C	88.2(5)
N(2)A–Cu(1)–O(1)B		92.0(5)	N(2)C–Cu(2)–O(1)D	89.1(5)
N(2)B–Cu(1)–O(1)A		88.7(5)	N(2)D–Cu(2)–O(1)C	88.1(5)
N(2)B–Cu(1)–O(1)B		85.7(5)	N(2)D–Cu(2)–O(1)D	88.6(5)
O(1)A–Cu(1)–O(1)B		174.4(5)	O(1)C–Cu(2)–O(1)D	175.6(4)
(b) Intraligand				
	Part A	Part B	Part C	Part D
Cu–N(1)–C(1)	109(1)	107(1)	109(1)	109(1)
N(1)–C(1)–C(2)	106(1)	106(1)	107(1)	105(1)
C(1)–C(2)–N(2)	106(1)	106(1)	108(1)	110(1)
C(2)–N(2)–C(21)	110(1)	110(1)	108(1)	112(1)
C(2)–N(2)–Cu	106(1)	106(1)	105(1)	105(1)
C(21)–N(2)–Cu	119(1)	118(1)	121(1)	188(1)
N(2)–C(21)–C(1)	115(1)	116(1)	114(1)	115(1)
Cu–O(1)–N(3)	124(1)	132(1)	133(1)	125(1)
O(1)–N(3)–O(2)	128(2)	125(2)	121(2)	118(1)
O(1)–N(3)–O(3)	117(2)	123(2)	122(1)	122(2)
O(2)–N(3)–O(3)	121(2)	112(2)	117(2)	120(2)
C(21)A–C(1)–C(21)B	111(1)	C(21)B–C(1)–C(21)C	105(1)	
C(21)A–C(1)–C(21)C	111(1)	C(21)B–C(1)–C(21)D	109(1)	
C(21)A–C(1)–C(21)D	111(1)	C(21)C–C(1)–C(21)D	109(1)	

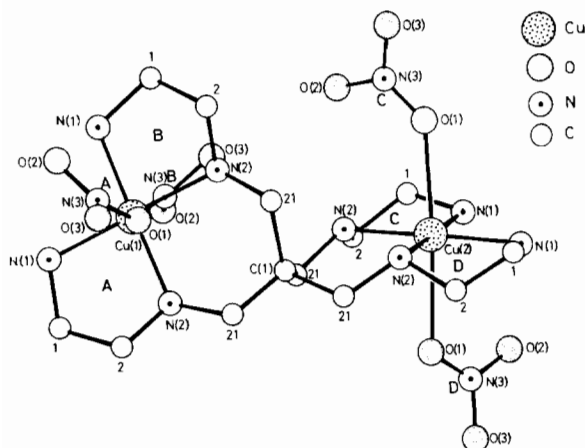


Fig. 1. Molecular configuration and atom labelling scheme for  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ .

phore, and is in line with similar long Cu–O bonds; e.g. 2.59 Å in  $\text{Cu}(\text{en})_2(\text{NO}_3)_2$  [27] 2.68 Å in  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}$  [29] and 2.59 Å in  $\text{Cu}(2,3,2\text{-tet})(\text{ClO}_4)_2$  [28]. Shorter copper–oxygen bond distances have, however, been reported for other copper–nitrate complexes – 2.016 Å and 2.039 Å for bis(3,5-dimethyl-1-phenylpyrazole)dinitratocopper(II) [30] and 2.183 Å in nitrate(1,4,7,10-tetraazacyclododecane)copper(II) nitrate [31]. In both instances bidentate coordination is suggested.

The two O–Cu–O axes are inclined at  $175.6^\circ$  towards the six membered rings containing the spiro carbon atom. These six membered rings adopt the stable chair configuration and, as a consequence the two secondary nitrogen donors adopt the *R,S* configuration in each  $\text{CuN}_4$  unit. The two sets of five-membered rings adopt the *gauche* configuration. The N–Cu–N bond angles [ $177.5(6)^\circ$ ,  $178.0(5)^\circ$ ,  $177.2(5)^\circ$ ,  $179.4(6)^\circ$ ] are close to  $180^\circ$  and the two  $\text{CuN}_4$  units are almost planar. The two copper(II) ions are separated by 6.4 Å.

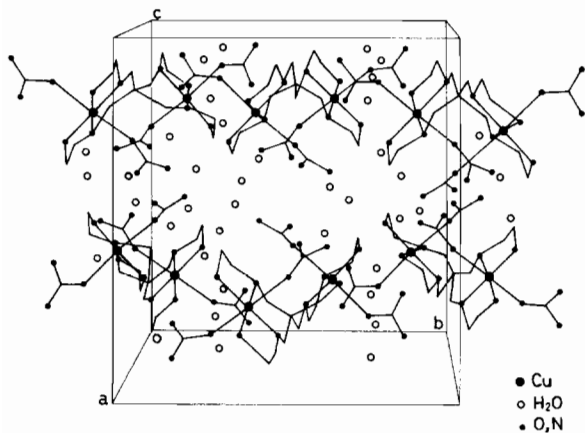


Fig. 2. Packing of  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  in the unit cell.

The packing of the  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$  molecules in the unit cell (Fig. 2) is influenced by the presence of a number of intermolecular associations between the coordinated nitrate groups and the six lattice waters. This results in both alternating stacks of waters and nitrates down the *a* direction in the unit cell and in inter-complex links in the *c* cell direction.

Structurally, each copper–tetraamine half of the dimer  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$  exhibits bond lengths and bond angles which are very similar to those reported for  $\text{Cu}(2,3,2\text{-tet})(\text{ClO}_4)_2$  [28]. A preliminary account of the structure of the  $\text{Cu}(3,3,3\text{-tet})(\text{ClO}_4)_2$  complex has been reported. The complex displays a distorted  $\text{CuN}_4$  unit, although the Cu–N distances lie in the expected range (2.02–2.04 Å) [28]. The influence of the six membered rings in promoting distortion from planarity in the  $\text{CuN}_4$  unit has been discussed previously for similar tetraamine–copper(II) complexes [32].

The visible spectra of aqueous solutions of the bis-copper(II) complexes exhibit a broad d–d band characteristically displayed by similar pseudo- $D_{4h}$  tetraamine–copper(II) complexes [33]. The position of the band maxima and the intensity [530 nm,  $\epsilon = 120 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  for  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$ , and 596 nm,  $\epsilon = 237 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  for  $\text{Cu}_2(\text{tapm})(\text{NO}_3)_4$ ] parallel the effects of ligand field strength for the analogous ligands (2,3,2-tet > 3,3,3-tet) [34] and distortion from  $D_{4h}$  symmetry (3,3,3-tet > 2,3,2-tet) observed for the monomeric copper(II) complexes [32]. The extinction coefficients observed for the bis-copper(II) complexes are slightly less than twice those reported for the monomeric analogues.

At 298 K the bis-copper(II) complexes exhibit magnetic moments of 1.8–1.9 BM per copper indicating isolated copper(II)  $d^9$  sites. For  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$ , the observed orthogonality of the two donor sets and the non planarity of the adjoining six membered rings precludes an exchange pathway [35–37] and preliminary molar susceptibility *versus* temperature data (298–4.2 K) confirm this [38]. Similarly for  $\text{Cu}_2(\text{tapm})(\text{NO}_3)_4$  the absence of a suitable exchange pathway is predicted.

The ESR spectra of  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$  and  $\text{Cu}_2(\text{tapm})(\text{NO}_3)_4$  (Fig. 3) measured as DMF glasses (77 K) exhibit complex multiplets quite unlike the spectra displayed by  $\text{Cu}(2,3,2\text{-tet})(\text{ClO}_4)_2$  ( $g_{\parallel} = 2.195$ ,  $A_{\parallel}^{\text{Cu}} = 207 \times 10^{-4} \text{ cm}^{-1}$ ) and  $\text{Cu}(3,3,3\text{-tet})(\text{NO}_3)_2$  ( $g_{\parallel} = 2.216$ ,  $A_{\parallel}^{\text{Cu}} = 188 \times 10^{-4} \text{ cm}^{-1}$ ) and are indicative of magnetic dipole interaction between the two copper sites [39]. The influence of both the separation between the two metal centres and the angle between the principal ESR axes on the spectra displayed by magnetically dipole coupled systems has been examined in detail previously [39]. For  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$  the structural data confirms the

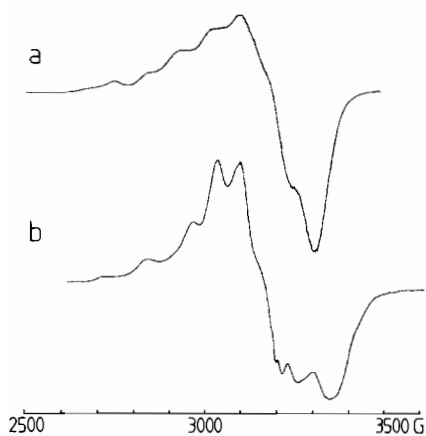


Fig. 3. ESR spectra (frozen DMF 77 K) of (a)  $\text{Cu}_2(\text{tapm})(\text{NO}_3)_4$  and (b)  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$ .

orthogonality of the O–Cu–O axes, whilst for  $\text{Cu}_2(\text{tapm})(\text{NO}_3)_4$  Dreiding models indicate that the presence of the three six-membered rings around each copper(II) permits greater flexibility and as a consequence, nonorthogonal arrangements are possible.

If the magnetic interaction is assumed to be purely dipolar [40] an estimation of the Cu–Cu distance may be obtained from the dipolar zero field interaction [39] [ $A_{\parallel} = 122 \times 10^{-4} \text{ cm}^{-1}$ ,  $D_{\parallel} = 92 \times 10^{-4} \text{ cm}^{-1}$ , Cu–Cu *ca.* 7 Å for  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$ , and  $A_{\parallel} = 93 \times 10^{-4} \text{ cm}^{-1}$ ,  $D_{\parallel} = 117 \times 10^{-4} \text{ cm}^{-1}$ , Cu–Cu *ca.* 6.5 Å for  $\text{Cu}_2(\text{tapm})(\text{NO}_3)_4$ ]. From the structural data the Cu–Cu distance for  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$  was determined as 6.4 Å and Dreiding models indicated that the Cu–Cu distance for the analogous six membered ring tapm complex was comparable. In both instances the difference between frozen solution lattice conditions (ESR) and those present in pure crystalline samples (X-ray) must be taken into consideration.

Figure 4 depicts the cyclic voltammogram of  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$  in aqueous sodium nitrate solution. The complex shows two reductions at

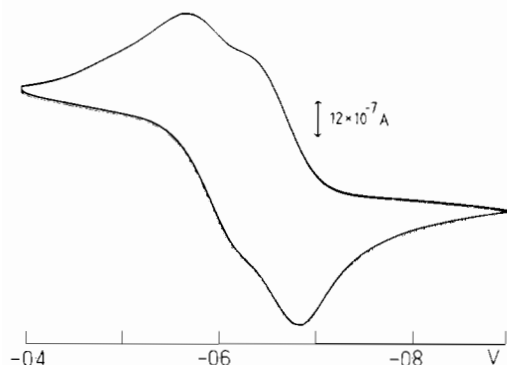


Fig. 4. Cyclic voltammogram (HMDE). (Ag/AgCl reference) of an aqueous sodium nitrate solution of  $\text{Cu}_2(\text{tabm})(\text{NO}_3)_4$ .

–0.62 and –0.68 V and two reoxidations at –0.64 and –0.57 V, at a sweep rate of  $500 \text{ mV s}^{-1}$ . The dependence of peak potentials on the sweep rate indicates non-reversible behaviour for the two couples [41]. Differential pulse polarography provides resolution of the two waves with  $E_{1/2}^1 = -0.58$  and  $E_{1/2}^2 = -0.66$  V. The cyclic voltammogram of  $\text{Cu}_2(\text{tapm})(\text{NO}_3)_4$  recorded under similar conditions indicates totally irreversible behaviour.

The irreversible nature of the reductions is fully consistent with the chemistry of similar copper(II)–tetraamine complexes. For example, the cyclic voltammogram of an acetonitrile solution of  $\text{Cu}(2,3,2\text{-tet})(\text{ClO}_4)_2$  and tetraethylammonium perchlorate, recorded employing a hanging mercury drop electrode, displays a two electron irreversible reduction [42]. Similar irreversible behaviour is observed in aqueous sodium nitrate solution. The copper(I) complex,  $\text{Cu}(2,3,2\text{-tet})^+$ , could not be obtained upon controlled potential coulometry at either platinum or mercury electrodes in acetonitrile solution [42]. From comparison of the electrochemical behaviour of  $[\text{Cu}(2,3,2\text{-tet})]^{2+}$ , particularly comparison of the d.c. polarograms of aqueous sodium nitrate solutions, it is apparent that the  $[\text{Cu}_2(\text{tabm})]^{4+}$  complex undergoes successive two electron irreversible reductions.

The chemistry of the copper(II) complexes of tabm and tapm binucleating octaaza ligands closely parallels the analogous tetraaza analogues. The synthetic elaboration of the octaaza ligands to produce binucleating macrocyclic species will be reported in a subsequent publication.

### Supplementary Material

Observed and calculated structure factors, hydrogen atom coordinates and anisotropic thermal parameters are available from the authors on request.

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