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Steric constraints imposed by triazamacrocyclic ligands. Crystal and molecular structure of two copper(II) complexes with triazamacrocyclic ligands: μ-chloro-μ-hydroxo-bis(1,5,9-triazacyclododecane)dicopper(II) perchlorate and bromo-(1,5,9-triazacyclotetradecane)copper(II) perchlorate

Paul G. Graham, David C. Weatherburn*
Department of Chemistry, Victoria University of Wellington, P.O. Box 600, Wellington (New Zealand)
Frank C. March
Computer Services Centre, Victoria University of Wellington, P.O. Box 600, Wellington (New Zealand)
and **Ward T. Robinson**
Department of Chemistry, University of Canterbury, Private Bag, Christchurch (New Zealand)

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Abstract

Crystal structures of two complexes of copper(II) with triazamacrocycles have been determined. The dimeric complex $[Cu_2(L1)_2(\mu\text{-}OH)(\mu\text{-}Cl)](ClO_4)_2$ (L1 = 1,5,9-triazacyclododecane) crystallizes in the monoclinic space group $P2_1/n$ with $a = 14.29(1)$, $b = 9.292(9)$, $c = 25.63(2)$ Å, $\beta = 102.23(6)°$, $Z = 4$. The structure has been refined to an R of 0.081 (R_w 0.0847). The coordination sphere of the copper(II) is best described as trigonal bipyramidal with two nitrogens of the macrocycle and the O atom occupying the trigonal plane. The Cu–N bond distances vary from 1.99(1)–2.06(1) Å. $[Cu(L6)Br](ClO_4)$ (L6 = 1,5,9-triazacyclotetradecane) crystallizes in the orthorhombic space group *Pnma*, $a = 14.365(4)$, $b = 11.491(6)$, $c = 10.194(3)$ Å, $Z = 4$. The data have been refined to R of 0.077 (R_w 0.075). The copper has a very distorted four-coordinate geometry, the Cu–N bond distances are equal within experimental error (2.02 Å); the bond angles around the copper range from 92–148°. Electrochemical and ESR spectral studies of the $[Cu(L6)]^{2+}$ complex are reported.

Introduction

Schaber *et al.* [1] reported that their attempts to prepare Cu(II) complexes of the ligand 1,5,9-triazacyclododecane, [12]aneN$_3$, L1, resulted in the isolation of two products; the minor product was emerald green, the major product dark brown. X-ray structural analysis showed that the green compound was a dinuclear complex $[Cu_2(L2)Br_2]^{2+}$ (L2 = 1,5,9,13,17,21-hexaazacyclotetracosane, [24]-aneN$_6$). The brown compound was the $[Cu(L1)Br_2]$ complex [1]. Formation of 2 + 2 addition products in the Richman–Atkins [2] synthesis of triazamacrocycles has been reported previously [3–5] and the conditions which lead to the formation of the large macrocycles have been discussed [4, 6]. We have reported the preparation of copper complexes of L1 and kinetic studies on the dissociation of the ligand from $[Cu(L1)]^{2+}$ in acid solution [7]. As all the complexes prepared in that work were coloured blue–green it seemed desirable to structurally characterize one of the $[Cu(L1)]^{2+}$ complexes used in our kinetic investigations. The results of such a study would also be of interest because although numerous [6, 8] structural studies have been reported for Cu(II) complexes of the macrocycles [9]aneN$_3$, L3 and Me$_3$[9]aneN$_3$, L4 and one structure of a copper complex of the macrocycle 1,4,7-triazacyclododecane, L5, has been reported [9], copper complexes of [12]aneN$_3$ have not been structurally characterised.

In the course of earlier studies on triazamacrocyclic complexes [10] we prepared a Cu(II) complex of the ligand L6, (L6 = 1,5,9-triazacyclotetradecane), which contains a fourteen-membered macrocyclic ring. This complex was formulated as a dimeric μ-bromo bridged species by analogy with other com-

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*Author to whom correspondence should be addressed.

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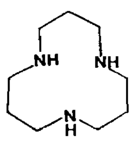
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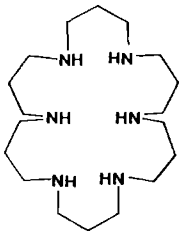
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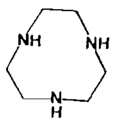
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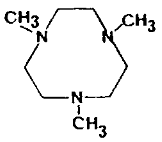
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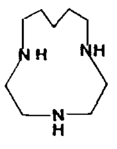
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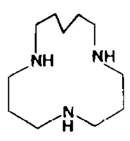
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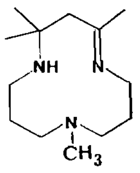
L7

TABLE 1. Crystal data and details of the structure determination of **1** and **2**

	1	**2**
Formula	$Cu_2C_{18}H_{43}N_6Cl_3O_9$	$CuC_{11}H_{25}N_3BrClO_4$
Formula weight	721.0	505.8
Space group	$P2_1/n$	*Pnma*
Crystal system	monoclinic	orthorhombic
a (Å)	14.29(1)	14.365(4)
b (Å)	9.292(9)	10.194(3)
c (Å)	25.63(2)	11.491(6)
β (°)	102.23(6)	
V (Å^3)	3326(6)	1683(1)
Z	4	4
Crystal size (mm)	0.62×0.5×0.42	0.44×0.24×0.16
Diffractometer	Nicolet Rm3	
Radiation	Mo Kα (0.71069 Å)	
Temperature (°C)	−135	−125
No. data	5519	1603
Unique data	4013	1062
Data used	1993	906
Criterion	$I>3\sigma$	
T_{max}, T_{min}	0.853, 0.530	0.966, 0.621
R, R_w	0.0812, 0.0874	0.077, 0.075
No. parameters	236	107
Obs./parameter	8.4	8.5
Max. shift/error	0.003	0.005

plexes of this type [10]. A structural investigation of this complex was of interest because it has the largest triazamacrocyclic ring size of any reported Cu(II) complex. We report the results of these studies and subsequent investigations of electrochemical and ESR studies on the $[Cu(L6)]^{2+}$ complex.

Experimental

Structure determination

Crystals of both compounds, green $[Cu_2(L1)_2(\mu\text{-}OH)(\mu\text{-}Cl)](ClO_4)_2$ (**1**) and blue–green $[Cu(L6)Br]ClO_4$ (**2**) suitable for structural studies were obtained by recrystallizing the previously reported compounds from methanol [7, 10]. Information regarding the structure determinations is presented in Table 1. Crystal stability was monitored by recording three check reflections every 100 reflections and no significant variations were observed. For **1** the structure was solved and refined using SHELXTL [11]; direct methods revealed the heavy atoms and the remaining non-hydrogen atoms were located using difference Fourier maps. Anisotropic thermal parameters were assigned to the copper, chlorine and all the oxygen atoms except O(1); all other atoms were refined isotropically. Hydrogen atoms were included at calculated positions but were not refined. The final difference map showed some evidence for a severely disordered solvent molecule which could not be refined. The function minimized in the refinement was $\Sigma w(|F_o|-|F_c|)^2$ where $w=[\sigma(F_o)+0.005F_o^2]^{-1}$.

With **2** study on the diffractometer revealed systematic absences which were consistent with either space group *Pnma* or $Pn2_1a$. The structure was solved successfully in *Pnma* using SHELXS [12] and refined using SHELX-76 [13]. Neutral atom scattering factors were used [14]. Attempts to refine the structure in $Pn2_1a$ resulted in very high correlation coefficients and an unsatisfactory geometry. The positions of the bromide and copper atoms were located from a Patterson map and all remaining non-hydrogen atoms were located in subsequent difference Fourier maps. These maps suggested that the carbon atoms of the eight-membered chelate ring were disordered across the crystallographic mirror plane at $y=0.25$. In the initial stages of the refinement the C(8) carbon was placed on the mirror plane and the C(6) and C(7) atoms were refined as separate peaks. The constraint on the C(8) atom was then removed and the C(8) positions across the mirror plane were resolved. No constraints were applied to bond distances but site occupancies of the disordered carbon atoms were fixed at 0.5. Separate positions for the C(7) and C(8) carbon atoms were resolved but separate positions for C(6) could not be resolved at the resolution of the X-ray data. At this stage the copper and bromine atoms and the perchlorate anion were refined anisotropically. Further cycles of refinement revealed that the largest peaks in the difference map were situated close to the bromine atom and close to N(5). A contoured difference Fourier map with N(5) removed revealed a non-isotropic electron density of the N(5) peak. Attempts to resolve separate positions for the N(5) atoms were not successful. The function minimized in the refinement was $\Sigma w(|F_o|-|F_c|)^2$ where $w=[\sigma(F_o)+0.000308F_o^2]^{-1}$. Hydrogen atoms were included in the final cycles of calculations at their calculated positions for the atoms which were not disordered. Final atomic coordinates for both structures are given in Table 2. See also 'Supplementary material'.

TABLE 2. Positional parameters for the non-hydrogen atoms of **1** and **2**

	x/a	*y/b*	*z/c*
1			
Cu(1)	0.2933(1)	0.7467(3)	0.1075(1)
Cu(1)′	0.0714(1)	0.7482(3)	0.1173(1)
Cl(3)	0.1479(3)	0.7912(5)	0.0425(2)
O(1)	0.2041(7)	0.7221(11)	0.1543(4)
N(1)	0.3765(10)	0.7780(13)	0.0555(5)
N(1)′	−0.0588(9)	0.7780(13)	0.0717(5)
N(2)	0.3730(9)	0.8973(14)	0.1553(5)
N(2)′	0.0424(10)	0.9054(14)	0.1691(5)
N(3)	0.3595(10)	0.5524(15)	0.1257(5)
N(3)′	0.0255(10)	0.5515(14)	0.1393(5)
C(1)	0.3704(14)	0.9221(20)	0.0361(7)
C(1)′	−0.0695(13)	0.9311(18)	0.0528(7)
C(2)	0.4178(14)	1.0281(21)	0.0792(7)
C(2)′	−0.0793(13)	1.0304(21)	0.0982(7)
C(3)	0.3773(14)	1.0389(20)	0.1265(7)
C(3)′	0.0104(13)	1.0409(20)	0.1447(7)
C(4)	0.4668(13)	0.8390(19)	0.1833(7)
C(4)′	−0.0241(12)	0.8431(18)	0.2029(7)
C(5)	0.4647(13)	0.6858(20)	0.2009(7)
C(5)′	−0.0025(13)	0.6852(19)	0.2203(7)
C(6)	0.4558(13)	0.5630(20)	0.1588(7)
C(6)′	−0.0399(12)	0.5692(19)	0.1777(6)
C(7)	0.3521(15)	0.4571(22)	0.0788(7)
C(7)′	−0.0177(14)	0.4564(20)	0.0944(7)
C(8)	0.3965(13)	0.5184(20)	0.0360(7)
C(8)′	−0.0995(13)	0.5247(20)	0.0541(7)
C(9)	0.3604(13)	0.6635(19)	0.0149(6)
C(9)′	−0.0812(12)	0.6660(18)	0.0312(6)
Cl(1)	0.6801(3)	0.7908(6)	0.0843(2)
O(11)	0.7109(9)	0.7849(14)	0.0342(5)
O(12)	0.5911(10)	0.7276(23)	0.0811(6)
O(13)	0.6662(13)	0.9446(16)	0.0972(7)
O(14)	0.7544(9)	0.7441(18)	0.1247(5)
Cl(2)	0.2255(4)	0.3023(6)	0.2007(2)
O(21)	0.1963(9)	0.3065(15)	0.1429(5)
O(22)	0.3143(9)	0.3738(15)	0.2174(5)
O(23)	0.1549(9)	0.3719(16)	0.2242(5)
O(24)	0.2327(10)	0.1478(18)	0.2182(6)
2			
Br(1)	0.2014(1)	0.2500	0.1241(2)
Cu(1)	0.2530(1)	0.2500	0.3212(2)
N(1)	0.3785(11)	0.2500	0.3996(14)
N(5)	0.2220(6)	0.0591(12)	0.3513(9)
C(2)	0.4325(9)	0.1312(14)	0.3679(12)
C(3)	0.3863(9)	0.0056(15)	0.4051(11)
C(4)	0.3025(9)	−0.0285(17)	0.3342(12)
C(6)	0.1752(9)	0.0397(16)	0.4678(13)
C(7A)	0.0829(18)	0.0991(35)	0.4803(25)
C(7B)	0.1406(18)	0.3319(32)	0.5222(23)
C(8)′	0.0739(14)	0.2632(89)	0.4442(17)
Cl(1)	0.4180(3)	0.2500	0.7358(4)
O(12)	0.3835(10)	0.1390(16)	0.6774(11)
O(11)	0.3872(11)	0.2500	0.8548(12)
O(13)	0.5172(10)	0.2500	0.7342(15)

Other measurements

Cyclic voltammograms of $[Cu(L6)Br]^+$ were obtained in acetonitrile solution under an argon atmosphere in a cell comprising a Pt wire working electrode, a 1 cm^2 Pt counter electrode with 0.1 M $LiClO_4$ as the electrolyte. A calomel electrode connected by a salt bridge was used as the reference and the ferrocene/ferrocenium$^+$ couple was used as an internal standard.

Results

Description of the structure of 1

Our original formulation of $[Cu_2(L1)_2(\mu\text{-}OH)(\mu\text{-}Cl)](ClO_4)_2$ is correct. The crystal consists of an ordered arrangement of the cation $[Cu_2(L1)_2(\mu\text{-}OH)(\mu\text{-}Cl)]^{2+}$ and two perchlorate anions. The latter display no unusual features and are not discussed further. The structure of the cation and the labelling of the atoms in the cation is shown in Fig. 1. Selected interatomic distances and bond angles are collected in Table 3. The copper atoms have what is best described as a distorted trigonal bipyramidal coordination geometry with O(1) and N(1) (N(1′)) as the axial groups. The axial Cu–N bond is slightly shorter than the equatorial Cu–N bonds. The variation in the bond distances to the macrocycle is much smaller than that observed in the square pyramidal [Cu[9]aneN$_3$] complexes [15–21] or in the $[Cu[24]aneN_6Br_2]^{2+}$ complex [1] all of which have one long Cu–N bond. The Cu–Cu′ distance is 3.223 Å. Distances within the macrocyclic ring are normal, nitrogen–carbon bond lengths range from 1.43–1.53 Å (average 1.48 ± 0.03 Å) while the carbon–carbon bond distances range is 1.45–1.56 Å (average 1.52 ± 0.03 Å). Angles within the macrocyclic ring are uniformly greater than the tetrahedral value, they range from 119.6 (C(4)–C(5)–C(6)) to 110.4° (N(1′)–C(1′)–C(2′)).

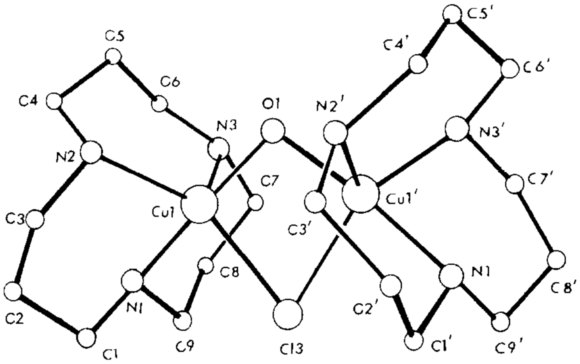

Fig. 1. PLUTO drawing of the structure of the cation of 1. Hydrogen atoms have been omitted for clarity.

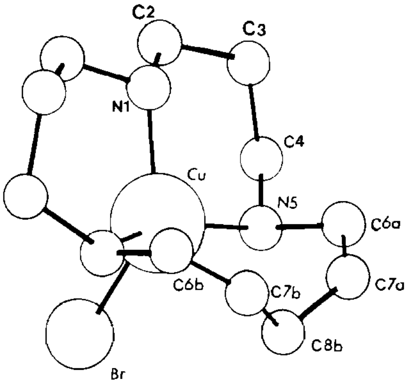

Fig. 2. PLUTO drawing of the structure of 2. For clarity only one possibility for the disordered carbons of the methylene chain is shown and the hydrogen atoms are not included.

Structure of 2

Our original formulation of 2 as a dimeric species is not correct. The crystal consists of the cation $[Cu(L6)Br]^+$ and the perchlorate anion which displays no unusual features. The structure of the cation and the labelling of the atoms is shown in Fig. 2. The bromine, copper, and N(1) atoms of the cation and the chlorine and two oxygen atoms (O(12) and O(13)) of the perchlorate anion lie on the crystallographic mirror plane at $z=\frac{1}{4}$. Selected bond distances and angles are presented in Table 3. The copper atom is four coordinate, with a very irregular geometry. The Cu(1)–N bond distances are equal within experimental error and are similar to those in 1. The very irregular nature of the geometry is shown by the bond angles around the copper. The N(5)–Cu(1)–N(1) bond angles are 96.9° and the N(5)–Cu(1)–N(5) bond angle is 147.9°. The pentamethylene chain carbon atoms C(7) and C(8) are disordered across the crystallographic mirror plane. This model gives reasonable isotropic thermal parameters for all the carbon atoms. The individual distances within the macrocyclic ring are normal; carbon–nitrogen distances average 1.49 ± 0.02 Å and carbon–carbon bond distances are 1.49 ± 0.04 Å. Angles within the ring are equal to or greater than tetrahedral (average 114.9 ± 1.9Å).

Discussion

Structures have been determined for Cu(II) complexes with the macrocyclic ligands L3 [15–17] and L4 [18–21]. Comparison of the reported structures of the copper complexes with these ligands reveals little variation in the Cu–N bond distances and angles in the different structures. In all the structures the geometry is best described as square pyramidal with one long axial Cu–N bond (2.20 Å) and two shorter Cu–N bonds (2.05 Å). This geometry apparently results from rigid steric requirements of the small $[9]aneN_3$ ligands. It has been suggested that L1 does not have the same rigid structural requirements as the smaller macrocycle, L3 [1]. The structure of 1 confirms this suggestion in that the coordination geometry changes to the extent that it is best described as distorted trigonal bipyramidal. Of greater significance is the fact that the Cu–N bond distances are equal within experimental error and do not show the pronounced variation present in Cu(L3) and Cu(L4) complexes. This is not simply a function of macrocyclic ring size. Structures of two other Cu(II) complexes with twelve-membered macrocyclic ligands are known; the monomeric complex $[Cu(L5)NO_3]NO_3$ [9] and the dimeric complex $[Cu_2(L7)_2(\mu\text{-}CO_3)]^{2+}$ (L7 = 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene) [22, 23]. $[Cu(L5)(NO_3)]^+$ has a distorted five-coordinate structure with a bidentate nitrate ligand. The Cu–N bond distances are not equivalent, however the variation in the distances is smaller than is observed in the Cu(L3)/Cu(L4) complexes. The $[Cu_2(L7)_2(\mu\text{-}CO_3)]^{2+}$ complex has a 'square pyramidal' structure similar to the $[9]aneN_3$ complexes in that there are two short Cu–N bonds ~2.0 Å and a longer (2.20 Å) axial Cu–N bond to the tertiary amine nitrogen [22]. Clearly the factors which influence the geometry adopted in any particular case are subtle.

Increasing the macrocyclic ring size from the twelve-membered ring in 1 to the fourteen-membered ring in 2 does not lead to major changes in the Cu–N bond lengths but does result in a very unusual coordination geometry. The N–Cu–N bond angles in the six-membered chelate rings (96°) are larger than in 1; the N–Cu–N bond angle for the eight-membered ring (148°) is extraordinary. This angle is much larger than the corresponding angle previously observed for other chelate rings of this type which range from 104–135° [9, 24]. In common with

TABLE 3. Selected bond distances and angles for **1** and **2**

Bond distances **1**			
Cu(1)–Cu(1)′	3.233(5)	Cl(3)–Cu(1)	2.407(5)
Cl(3)–Cu(1)′	2.432(5)	O(1)–Cu(1)	1.940(12)
O(1)–Cu(1)′	1.947(10)	N(1)–Cu(1)	1.986(14)
N(1)′–Cu(1)′	1.996(12)	N(2)–Cu(1)	2.041(13)
N(2)′–Cu(1)′	2.074(14)	N(3)–Cu(1)	2.045(14)
N(3)′–Cu(1)′	2.060(14)		
Bond distances **2**			
Br(1)–Cu(1)	2.383(3)	Cu(1)–N(1)	2.016(16)
Cu(1)–N(5)	2.026(16)		
Bond angles **1**			
Cl(3)–Cu(1)–O(1)	82.2(3)	Cl(3)–Cu(1)′–O(1)	81.4(3)
Cl(3)–Cu(1)–N(1)	93.6(4)	Cl(3)–Cu(1)′–N(1)′	92.0(4)
Cl(3)–Cu(1)–N(2)	126.0(4)	Cl(3)–Cu(1)′–N(2)′	124.9(4)
Cl(3)–Cu(1)–N(3)	126.8(4)	Cl(3)–Cu(1)′–N(3)′	125.7(4)
O(1)–Cu(1)–N(1)	175.7(4)	O(1)–Cu(1)′–N(1)′	173.4(5)
O(1)–Cu(1)–N(2)	93.8(5)	O(1)–Cu(1)′–N(2)′	94.7(5)
O(1)–Cu(1)–N(3)	95.1(5)	O(1)–Cu(1)′–N(3)′	95.1(5)
N(1)–Cu(1)–N(2)	88.0(5)	N(1)′–Cu(1)′–N(2)′	89.4(5)
N(1)–Cu(1)–N(3)	88.2(6)	N(1)′–Cu(1)′–N(3)′	88.4(5)
N(2)–Cu(1)–N(3)	107.2(5)	N(2)′–Cu(1)′–N(3)′	109.3(6)
Bond angles **2**			
Br(1)–Cu(1)–N(1)	134.6(5)	Br(1)–Cu(1)–N(5)	95.4(3)
N(1)–Cu(1)–N(5)	96.9(3)	N(5)–Cu(1)–N(5)	147.9(6)

other chelate rings of this type the pentamethylene chain in **2** is disordered. The model used to describe this disorder across the crystallographic mirror plane gives reasonable bond lengths, bond angles and isotropic thermal parameters. There is no evidence for the strain in the pentamethylene chain found in the $[Cu(L5)NO_3]^{2+}$ complex. The model used in **2** would suggest that the C(6) atom is disordered as well as C(7) and C(8) but we were unable to resolve this disorder at the resolution of the X-ray data. The asymmetric nature of the N(5) peak in the difference map suggests that N(5) may display some disorder as well. Comparison of the disorder models of the structurally characterized eight-membered chelate rings in macrocyclic complexes does not reveal a regular behaviour and such rings must be particularly flexible.

Redox behaviour

A distorted tetrahedral environment for Cu(II) is of considerable interest as such a geometry occurs in the blue copper proteins. The electrochemistry and the ESR spectral behaviour of **2** were consequently investigated. Solutions of $[Cu(L6)Br]^+$ gave quasi-reversible voltammograms showing reduction to Cu(I) at −0.69 V and oxidation to Cu(III) at +1.53 V versus calomel. Attempts to prepare solid complexes of $[Cu(L6)]^+$ were not successful. Solutions of $Cu(L6)^+$ prepared by the reaction of $CuClO_4$ in acetonitrile with a solution of the ligand under a nitrogen atmosphere were extremely sensitive to traces of oxygen and displayed autoxidation behaviour. A recent report by Chaudhuri and Oder [25] has shown that under different experimental conditions stable copper(I) complexes of triazamacrocycles can be prepared and their stability constants have been determined [5].

ESR and visible spectra

The visible spectra of CuL6 complexes have not previously been reported. In aqueous solution the complex (presumably $[Cu(L6)H_2O]^{2+}$) has a maximum absorbance at 694 nm ($\epsilon = 119$). The ESR spectrum of $[Cu(L6)Br](ClO_4)$ was measured in frozen DMF. The spectrum shows a typical nearly axial Cu(II) pattern with $g_{\parallel} = 2.436$, 2.300; $A_{\parallel}$ 156 G; $g_{\perp}$ 2.080, 2.006; $A_{\perp}$, 113 G. This spectrum is very similar in appearance and the parameters are almost identical to those reported for the $Cu(L5)^{2+}$ complex in aqueous DMSO [9].

Supplementary material

Tables of complete details of structure determination, the bond distances and angles, the thermal parameters, torsion angles and the positional parameters of the hydrogen atoms of **1** and **2** and of the observed and calculated structure factors have been deposited with the Cambridge X-ray Crystallographic Data Base and are available from the authors on request.

Acknowledgements

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