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The Crystal Structures of Mixed-Ligand Copper(II) Complexes.

II. Bis(2-aminoethyl)amine(2,2'-bipyridyl)copper(II) Nitrate Dihydrate and Bis(2-aminoethyl)amine(1,10-phenanthroline)copper(II) Nitrate

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Abstract

The crystal structures of bis(2-aminoethyl)amine-(2,2'-bipyridyl)copper(II) nitrate dihydrate, $C_{14}H_{21}CuN_5^+ \cdot 2NO_3^- \cdot 2H_2O$, $[Cu(C_4H_{13}N_3)(C_{10}H_8N_2)](NO_3)_2 \cdot 2H_2O$, (I), and bis(2-aminoethyl)amine(1,10-phenanthroline)copper(II) nitrate, $C_{16}H_{21}CuN_5^+ \cdot 2NO_3^-$, $[Cu(C_4H_{13}N_3)(C_{12}H_8N_2)](NO_3)_2$, (II), have been established by X-ray crystallographic analysis with photographic techniques. (I) crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.29$ (5), $b = 7.60$ (5), $c = 28.59$ (5) Å, $\beta = 106.9$ (5)°, $Z = 4$, and (II) in the monoclinic space group $C2/c$, with $a = 25.97$ (5), $b = 8.13$ (5), $c = 19.72$ (5) Å, $\beta = 100.0$ (5)°, $Z = 8$. Both structures were solved by the heavy-atom method and refined to $R = 0.0640$ and 0.0933 , respectively. Both structures are ionic, the cations involving a distorted five-coordinate square-pyramidal CuN_5 chromophore stereochemistry with closely comparable bond lengths and angles. The structure of (I) is atypical in that the 2,2'-bipyridyl ligand has an angle of twist of only 1.3° .

the conformation of the polydentate chelate ligands (Gollogly & Hawkins, 1972). The present structures have been determined in order to establish how the stereochemistry about the Cu^{II} ion varies with pairs of closely related ligands and ultimately to relate these to the detailed electronic properties of the Cu^{II} ion present.

Preparation

The complexes $Cu(\text{bea}^*)(\text{bpy}^*)(NO_3)_2 \cdot 2H_2O$, (I), and $Cu(\text{bea}^*)(\text{phen}^*)(NO_3)_2$, (II), were prepared by mixing a hot solution of $Cu(NO_3)_2 \cdot 3H_2O$ in methanol (7 mmol in 5 ml) with an equimolar stoichiometric mixture of bis(2-aminoethyl)amine and 2,2'-bipyridyl (for I) and 1,10-phenanthroline (for II) in methanol (7 mmol in 25 ml). Blue-black crystals of (I) and (II) were formed on cooling. (I), found: C = 35.28, H = 5.20, N = 19.82, Cu = 13.06; $C_{14}H_{21}N_7O_8Cu$ requires: C = 34.82, H = 5.22, N = 20.30, Cu = 13.15%; and (II), found: C = 39.04, H = 4.44, N = 20.04, Cu = 12.79; $C_{16}H_{21}N_7O_6Cu$ requires: C = 39.30, H = 4.71, N = 20.0, Cu = 12.99%.

Experimental

The crystal and refinement data for (I) and (II) are summarized in Table 1. The unit-cell parameters were

* bea = bis(2-aminoethyl)amine; bpy = 2,2'-bipyridyl; phen = 1,10-phenanthroline.

A wealth of crystallographic data (Muetterties & Schunn, 1966; Hathaway & Billing, 1970; Ray & Hathaway, 1978) has established the existence of the five-coordinate square-based pyramidal and trigonal-bipyramidal stereochemistries for the Cu^{II} ion, especially in mixed-ligand complexes. Due to the nature of the ligands, distorted geometries are involved, depending on the bite angles of the chelate ligands and

Table 1. *Crystal and refinement data*

	(I)	(II)
Compound	Cu(beat)(bpy)(NO ₃) ₂ · 2H ₂ O	Cu(beat)(phen)(NO ₃) ₂
<i>M_r</i>	482.93	470.92
Stoichiometry	C ₁₄ H ₂₃ N ₇ O ₈ Cu	C ₁₆ H ₂₁ N ₇ O ₆ Cu
Space group	<i>P</i> 2 ₁ / <i>c</i> (monoclinic)	<i>C</i> 2/ <i>c</i> (monoclinic)
<i>a</i> (Å)	10.29 (5)	25.97 (5)
<i>b</i> (Å)	7.60 (5)	8.13 (5)
<i>c</i> (Å)	28.59 (5)	19.72 (5)
β (°)	106.9 (5)	100.0 (5)
<i>Z</i>	4	8
<i>U</i> (Å ³)	2140.83	4100.34
<i>D_m</i> [(floatation) Mg m ⁻³]	1.513	1.566
<i>D_c</i> (Mg m ⁻³)	1.498	1.525
<i>F</i> (000)	996.0	1928.0
μ (mm ⁻¹)	1.781	1.781
Radiation ($\lambda = 1.541$ Å) Cu <i>K</i> α		Cu <i>K</i> α
Main axis data	(0–8) <i>kl</i>	<i>h</i> (0–6) <i>l</i>
Cross reference data	<i>h</i> (0–2) <i>l</i>	(0–2) <i>kl</i>
Number of unique reflections	1564	806
Number of anisotropic atoms	11	1
<i>N</i>	1552	976
<i>NP</i>	177	127
<i>N/NP</i>	8.77	7.7
<i>R</i>	0.0640	0.0933
<i>R_w</i>	0.0690	0.0988
<i>R_s</i>	0.0903	0.1207
<i>k</i>	1.00	134.0632
<i>g</i>	0.01616	0.000028
Maximum final shift/e.s.d.	0.13	0.006
Residual electron density (e Å ⁻³)	0.35	0.55

determined from precession photographs, and the intensities collected photographically by the equi-inclination Weissenberg technique. Five-film packs were used for each layer and the intensities were estimated by the Science Research Council Microdensitometer Service (Rutherford Laboratory).

Structure solution and refinement

Both structures were solved by three-dimensional Patterson and Fourier techniques with *SHELX 76* (G. M. Sheldrick) with successive addition of atom positions to improve the phasing for all the non-hydrogen atoms. The structures were refined by full-matrix least squares in which $\sum w|F_o - F_c|^2$ was minimized. Calculated H positions were used with a fixed C–H and N–H bond length of 1.08 Å, a fixed temperature factor of 0.07 Å², and floated on the associated C or N atom. The weighting scheme was $w = k/[\sigma^2(F_o) + g(F_o)^2]$; see Table 1 for final values of *k* and *g*. Complex neutral-atom scattering factors were used for the non-hydrogen atoms (Cromer & Waber, 1965; Cromer & Liberman, 1970). Lorentz and polarization corrections were applied, but none for absorption. The final atom coordinates are listed in

Table 2.* H atom parameters are presented in Table 3, and the bond lengths and angles for the non-hydrogen atoms in Tables 4 and 5. Table 6 lists the data for some relevant mean planes. Fig. 1 shows the molecular structures of the two cations, with the atom-numbering scheme.

Discussion

Both structures are made up of nitrate ions and discrete cations, Cu(beat)(bpy)²⁺ and Cu(beat)(phen)²⁺ for (I) and (II), respectively. There are no unusual features in the dimensions of the nitrate ions (Addison, Logan, Wallwork & Garner, 1971) or in the organic ligands (Stephens, 1969, 1972; Nakai & Noda, 1978), but the e.s.d.'s of (II) are appreciably higher than those of (I) due to the lower number of reflections available in (II).

In both structures the cations assume a distorted five-coordinate CuN₅ chromophore, involving a square-pyramidal stereochemistry with no evidence of coordination by a sixth ligand in (I), but there is a nitrate O atom at 2.99 Å from Cu in (II), offset from the normal to the basal plane by 2.48°, a distance consistent with weak semi-coordination of a sixth ligand (Hathaway & Billing, 1970). The bis(2-aminoethyl)amine ligands are involved in a planar coordination to the Cu^{II} ion, N(1–3); the fourth in-plane ligand N(4) involves a 2,2'-bipyridyl N atom in (I) and a 1,10-phenanthroline N atom in (II). The four in-plane Cu–N distances are in the range 1.98–2.06 Å and are not considered significantly different. The fifth coordinate position is occupied by the second 2,2'-bipyridyl and 1,10-phenanthroline N atoms in (I) and (II) respectively, such that both ligands are involved in out-of-plane chelation (Fig. 1) with Cu–N = 2.192 and 2.224 Å, in (I) and (II) respectively, a difference of 0.032 Å that may not be significant, especially in view of the respective bite angles of 78.4 and 77.8° for N(4)–Cu–N(5). The Cu^{II} ion is out of the plane of the four in-plane ligands N(1)–N(4) by a distance $\rho = 0.24$ Å towards N(5) for both complexes, but as the r.m.s. deviation for these planes [planes (1) of Table 6] are relatively high, 0.115 and 0.155 Å respectively, implying that the N(1)–N(4) atoms do not form a well-defined plane, the significance of this ρ value as a criterion of a square-based pyramidal stereochemistry (Hathaway & Billing, 1970) may be in some doubt for this pair of complexes. Due to the bite angle N(4)–Cu–N(5), the apical N atoms are offset from the normal to the N(1)–N(4) planes by 15.77 and 15.84° respectively. The tetragonality (*T*²) (Hathaway & Billing, 1970) of both complexes are

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34037 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates ($\times 10^4$) for non-hydrogen atoms and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	(I) Cu(bea)(bpy)(NO ₃) ₂ ·2H ₂ O				(II) Cu(bea)(phen)(NO ₃) ₂			
	x	y	z	U	x	y	z	U
Cu	-1820 (1)	814 (2)	-1300 (0)		3617 (1)	32 (6)	3770 (2)	
N(1)	-2808 (6)	-479 (8)	-1916 (2)	48 (1)	3951 (8)	-1975 (24)	4253 (10)	46 (6)
C(1)	-2499 (8)	396 (10)	-2340 (3)	60 (2)	4489 (12)	-2196 (41)	4030 (16)	78 (10)
C(2)	-1045 (8)	1012 (10)	-2171 (3)	59 (1)	4454 (13)	-1617 (39)	3352 (15)	76 (10)
N(2)	-846 (6)	2091 (8)	-1715 (2)	46 (1)	4242 (9)	60 (35)	3302 (11)	71 (7)
C(3)	596 (7)	2405 (10)	-1423 (3)	48 (1)	4078 (16)	377 (56)	2569 (20)	134 (16)
C(4)	557 (8)	2998 (10)	-920 (3)	51 (1)	3662 (15)	1468 (47)	2513 (19)	108 (13)
N(3)	-207 (6)	1645 (8)	-735 (2)	48 (1)	3267 (8)	1326 (25)	2969 (10)	50 (6)
N(4)	-2605 (6)	-692 (8)	-870 (2)	43 (1)	2971 (7)	-255 (23)	4232 (8)	31 (5)
N(5)	-3518 (6)	2442 (8)	-1236 (2)	42 (1)	3793 (8)	1723 (26)	4667 (10)	47 (6)
C(5)	-2034 (8)	-2274 (10)	-687 (3)	53 (1)	2538 (10)	-1107 (30)	3959 (13)	44 (7)
C(6)	-2628 (8)	-3322 (11)	-401 (5)	61 (1)	2139 (12)	-1190 (34)	4375 (15)	62 (9)
C(7)	-3786 (8)	-2778 (10)	-332 (3)	58 (1)	2175 (11)	-566 (30)	4962 (14)	51 (8)
C(8)	-4385 (8)	-1179 (9)	-498 (3)	52 (1)	2612 (10)	414 (29)	5238 (12)	46 (8)
C(9)	-3752 (7)	-144 (9)	-777 (3)	41 (1)	3004 (8)	508 (24)	4835 (11)	26 (6)
C(10)	-4289 (7)	1632 (9)	-990 (3)	40 (1)	3439 (10)	1539 (29)	5082 (13)	36 (6)
C(11)	-5483 (8)	2388 (10)	-936 (3)	56 (1)	3511 (12)	2346 (36)	5735 (15)	64 (9)
C(12)	-5871 (9)	4026 (10)	-1145 (3)	66 (2)	3945 (12)	3370 (37)	5931 (14)	60 (8)
C(13)	-5125 (8)	4868 (11)	-1389 (3)	59 (1)	4267 (12)	3625 (36)	5502 (16)	68 (9)
C(14)	-3919 (8)	4038 (10)	-1449 (3)	50 (1)	4212 (13)	2825 (39)	4859 (17)	78 (10)
C(15)					2667 (12)	1134 (32)	5938 (14)	55 (8)
C(16)					3086 (12)	1992 (34)	6127 (14)	60 (8)
N(6)	3477 (7)	4918 (10)	2822 (3)		1823 (9)	825 (30)	2022 (13)	57 (6)
O(1)	4160 (7)	5940 (9)	3147 (3)		1557 (7)	129 (28)	1528 (9)	68 (5)
O(2)	4029 (7)	4018 (10)	2581 (3)		2136 (8)	-48 (32)	2416 (10)	95 (6)
O(3)	2197 (7)	4918 (12)	2744 (3)		1834 (8)	2282 (25)	2151 (10)	69 (6)
N(7)	-2092 (7)	2243 (10)	327 (3)		4553 (16)	-2072 (48)	5990 (19)	115 (12)
O(4)	-2112 (8)	935 (9)	587 (3)		4087 (12)	-2446 (32)	5872 (13)	109 (8)
O(5)	-2925 (8)	3404 (10)	321 (4)		4644 (15)	-844 (49)	5691 (18)	180 (14)
O(6)	-1271 (8)	2400 (12)	106 (3)		4864 (13)	-2701 (41)	6406 (17)	151 (12)
O(7)	996 (6)	1257 (8)	6788 (3)					
O(8)	-1729 (6)	2553 (8)	1545 (2)					

Table 3. Hydrogen atom coordinates ($\times 10^4$)The overall isotropic temperature factor is 0.07 \AA^2 .

	(I) Cu(bea)(bpy)(NO ₃) ₂ ·2H ₂ O			(II) Cu(bea)(phen)(NO ₃) ₂		
	x	y	z	x	y	z
H(1)	-3884	-466	-1956	3710	-3035	4093
H(2)	-2455	-1823	1895	3988	-1818	4803
H(3)	-2638	-517	-2640	4595	-3482	4069
H(4)	-3175	1501	-2455	4780	-1485	4364
H(5)	-819	1819	-2449	4189	-2412	3018
H(6)	-368	104	-2094	4833	-1642	3198
H(7)	-1282	3375	-1820	4520	987	3520
H(8)	1166	1199	-1398	3924	-724	2302
H(9)	1049	3410	-1592	4403	829	2347
H(10)	42	4247	-942	3851	2639	2639
H(11)	1574	3114	-675	3452	1496	1990
H(12)	452	536	-601	3141	2500	3139
H(13)	-571	2158	-444	2933	663	2699
H(14)	-1116	-2680	-768	2510	-1691	3462
H(15)	-2149	-4538	-246	1781	-1819	4160
H(16)	-4269	-3603	-114	1870	777	5262
H(17)	-5310	-729	-432	2368	953	6248
H(18)	-6099	1700	-747	3019	2333	6634
H(19)	-6766	4659	1099			
H(20)	-5442	6133	1556			
H(21)	3320	4673	-1654			

comparable, 0.92 and 0.90 respectively (where $T = R_s$, the mean in-plane bond length/ R_L , the mean out-of-plane bond length) but that for (II) is considerably reduced if the presence of the semicoordinating O atom at 2.99 \AA is included, giving $T^6 = 0.77$.

In both complexes the bea coordinates as a planar symmetrical tridentate ligand with two fused five-membered rings (Gollogly & Hawkins, 1972) involving comparable N(1)-Cu-N(2) and N(2)-Cu-N(3) angles $85 \pm 1.4^\circ$ and a kk^1 configuration of the five-membered rings approximately related as mirror images in the Cu, N(2), N(5) plane as seen in the view down the N(2)-Cu direction shown in Fig. 2 and in the deviation from the mean planes (5) and (6) of Table 6.

The distortion from a regular square-based pyramidal stereochemistry for the Cu^{II} ion lies in the values of the angles N(1)-Cu-N(3) and N(2)-Cu-N(4) of 156.6 ± 1.2 and $173.4 \pm 0.8^\circ$, respectively, which compare with $166 \pm 1^\circ$ for the corresponding angles in the most regular square-pyramidal complex of the Cu^{II} ion, $\text{KCu}(\text{NH}_3)_5(\text{PF}_6)_3$ (Duggan, Ray & Hathaway, 1978). In both complexes N(1)-Cu-N(3)

Table 4. Bond lengths (Å), *e.s.d.*'s in parentheses

	(I)	(II)
Cu—N(1)	2.017 (6)	2.008 (19)
Cu—N(2)	2.011 (6)	2.002 (22)
Cu—N(3)	2.050 (6)	1.983 (20)
Cu—N(4)	2.012 (6)	2.058 (18)
Cu—N(5)	2.192 (6)	2.224 (20)
Cu—O(3)		2.99 (—)
C(1)—N(1)	1.50 (1)	1.55 (3)
C(1)—C(2)	1.51 (1)	1.41 (4)
C(2)—N(2)	1.50 (1)	1.47 (4)
N(2)—C(3)	1.49 (1)	1.46 (4)
C(3)—C(4)	1.52 (1)	1.39 (4)
C(4)—N(3)	1.48 (1)	1.48 (4)
N(4)—C(9)	1.35 (1)	1.33 (2)
N(4)—C(5)	1.37 (1)	1.35 (3)
C(5)—C(6)	1.40 (1)	1.43 (4)
C(6)—C(7)	1.34 (1)	1.25 (3)
C(7)—C(8)	1.39 (1)	1.42 (3)
C(8)—C(9)	1.41 (1)	1.40 (3)
C(9)—C(10)	1.52 (1)	1.42 (3)
C(10)—C(11)	1.41 (1)	1.43 (3)
C(11)—C(12)	1.39 (1)	1.40 (4)
C(12)—C(13)	1.34 (1)	1.30 (4)
C(13)—C(14)	1.45 (1)	1.41 (4)
N(5)—C(14)	1.37 (1)	1.41 (3)
N(5)—C(10)	1.35 (1)	1.34 (3)
C(8)—C(15)		1.48 (3)
C(11)—C(16)		1.48 (4)
C(15)—C(16)		1.29 (3)
N(6)—O(1)	1.26 (1)	1.23 (2)
N(6)—O(2)	1.22 (1)	1.24 (4)
N(6)—O(3)	1.27 (1)	1.21 (2)
N(7)—O(4)	1.25 (1)	1.23 (4)
N(7)—O(5)	1.23 (1)	1.20 (4)
N(7)—O(6)	1.20 (1)	1.17 (4)

is more distorted towards a trigonal angle of 120° , while N(2)—Cu—N(4) is distorted in the opposite sense towards 180° , directions which are related to the mechanistic pathway of the Berry twist (Berry, 1960) connecting the trigonal and square-pyramidal stereochemistries of the Cu^{II} ion. The square-pyramidal stereochem-

istry is also distorted in the sense that Cu—N(5) is not perpendicular to the N(1)—N(4) plane as N(1)—Cu—N(5) and N(3)—Cu—N(5) are comparable in each structure, namely, 97.2 ± 0.7 and $106.0 \pm 2.0^\circ$, but do not equal 90° ; this asymmetry is seen in Fig. 2.

The pyridine rings of the 2,2'-bipyridyl and 1,10-phenanthroline ligands in (I) and (II) respectively are reasonably planar (Table 6); they are inclined at 1.3 and 7.69° to each other in (I) and (II) respectively. In (I) the rings are twisted about C(9)—C(10), but to a much smaller extent than has been reported (Stephens, 1972) in other 2,2'-bipyridyl structures, but the C(9)—

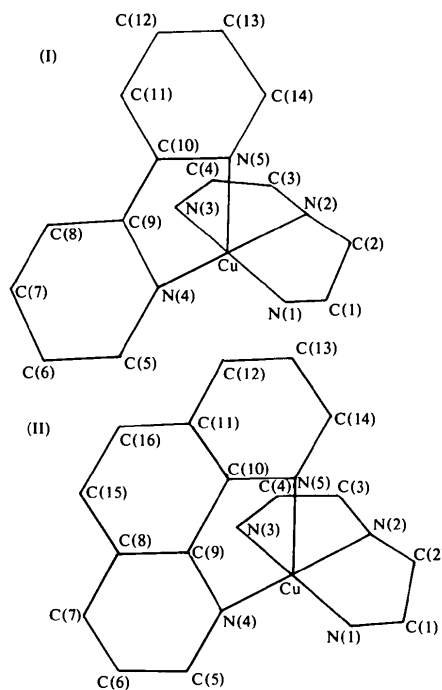


Fig. 1. The molecular structures and atom numbering of (I) Cu(II)(bpy)(NO₃)₂·2H₂O and (II) Cu(II)(phen)(NO₃)₂.

Table 5. Bond angles (°), *e.s.d.*'s in parentheses

	(I)	(II)		(I)	(II)		(I)	(II)
N(1)—Cu—N(2)	86.1 (2)	84.8 (10)	C(3)—C(4)—N(3)	107.1 (6)	121.0 (33)	C(11)—C(12)—C(13)	121.0 (8)	119.5 (28)
N(1)—Cu—N(3)	157.8 (3)	155.4 (8)	C(4)—N(3)—Cu	108.9 (5)	104.7 (19)	C(12)—C(13)—C(14)	119.6 (8)	122.3 (30)
N(2)—Cu—N(3)	83.6 (2)	85.6 (9)	Cu—N(4)—C(9)	118.3 (5)	114.3 (14)	C(13)—C(14)—N(5)	119.6 (7)	119.1 (28)
N(1)—Cu—N(4)	93.8 (2)	91.0 (8)	Cu—N(4)—C(5)	121.9 (5)	124.6 (16)	C(8)—C(15)—C(16)		115.0 (27)
N(2)—Cu—N(4)	172.7 (2)	174.1 (10)	C(5)—N(4)—C(9)	119.8 (6)	121.1 (19)	C(15)—C(16)—C(11)		128.4 (29)
N(3)—Cu—N(4)	94.1 (2)	96.6 (8)	N(4)—C(5)—C(6)	120.6 (7)	115.5 (24)	C(7)—C(8)—C(15)		121.4 (25)
N(1)—Cu—N(5)	97.9 (2)	96.5 (8)	C(5)—C(6)—C(7)	118.8 (8)	124.4 (31)	C(9)—C(8)—C(15)		123.0 (23)
N(2)—Cu—N(5)	108.8 (2)	106.8 (10)	C(6)—C(7)—C(8)	122.1 (8)	120.6 (30)	C(12)—C(11)—C(16)		127.5 (28)
N(3)—Cu—N(5)	104.0 (2)	107.9 (8)	C(7)—C(8)—C(9)	117.7 (7)	115.3 (22)	C(10)—C(11)—C(16)		112.8 (26)
N(4)—Cu—N(5)	78.4 (2)	77.8 (8)	C(8)—C(9)—C(10)	123.3 (6)	116.8 (22)	Cu—N(5)—C(14)	127.5 (5)	130.5 (19)
Cu—N(1)—C(1)	108.6 (5)	107.3 (16)	C(8)—C(9)—N(4)	120.9 (7)	122.8 (20)	Cu—N(5)—C(10)		112.9 (5)
N(1)—C(1)—C(2)	107.7 (7)	108.5 (25)	N(4)—C(9)—C(10)	115.7 (6)	120.3 (21)	O(1)—N(6)—O(2)	120.7 (7)	116.7 (25)
C(1)—C(2)—N(2)	108.6 (6)	109.7 (26)	C(9)—C(10)—C(11)	123.3 (7)	123.5 (24)	O(1)—N(6)—O(3)	117.3 (8)	127.2 (28)
C(2)—N(2)—Cu	106.4 (5)	106.4 (19)	C(9)—C(10)—N(5)	114.4 (6)	116.3 (21)	O(2)—N(6)—O(3)	121.9 (8)	116.0 (27)
C(2)—N(2)—C(3)	115.7 (6)	105.8 (27)	C(10)—C(11)—C(12)	118.1 (8)	119.6 (27)	O(4)—N(7)—O(5)	116.7 (7)	112.5 (45)
Cu—N(2)—C(3)	109.4 (4)	109.8 (22)	C(10)—N(5)—C(14)	119.3 (6)	119.1 (23)	O(4)—N(7)—O(6)	122.0 (8)	124.3 (45)
N(2)—C(3)—C(4)	106.3 (6)	106.3 (34)	N(5)—C(10)—C(11)	122.3 (7)	120.2 (24)	O(5)—N(7)—O(6)	121.2 (8)	122.6 (48)

Table 6. Equations of the planes of best fit given in the form $lX + mY + nZ + p = 0$ with reference to the cell axes and with p in Å

The deviations (Å) of the most relevant atoms from the planes are given in square brackets, r.m.s. deviations of the planes and the angles between them are given where relevant.

(a) (I) Cu(beatbpy)(NO₃)₂·2H₂O

	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
Plane (1): N(1)–N(4) (r.m.s.d. = 0.1147 Å) [Cu 0.2407, N(1) –0.1143, N(2) 0.1239, N(3) –0.1148, N(4) 0.1052]	–0.6378	0.7534	0.1601	–0.8608
Plane (2): N(4), C(5)–C(9) (r.m.s.d. = 0.0079 Å) [N(4) –0.0036, C(5) –0.0056, C(6) 0.0130, C(7) –0.0113, C(8) 0.0018, C(9) 0.0057]	0.5407	0.4603	0.7041	2.8283
Plane (3): N(5), C(10)–C(14) (r.m.s.d. = 0.0089 Å) [N(5) 0.0091, C(10) 0.0011, C(11) –0.0046, C(12) –0.0020, C(13), 0.0117, C(14) –0.0153]	0.5345	0.4439	0.7192	2.8201
Plane (4): N(4), N(5), C(5)–C(14) (r.m.s.d. = 0.0144 Å) [N(4) –0.0226, N(5) 0.0149, C(5) –0.0100, C(6) 0.0266, C(7) 0.0049, C(8) 0.0036, C(9) –0.0104, C(10) –0.0060, C(11) –0.0166, C(12) –0.0051, C(13) 0.0215, C(14) –0.0008]	0.5386	0.4497	0.7125	2.8128
Plane (5): Cu, N(1), N(2) [C(1) –0.2507, C(2) 0.4378]	0.7111	–0.7031	–0.0004	1.7082
Plane (6): Cu, N(2), N(3) [C(3) –0.4122, C(4) 0.3158]	–0.4961	0.8377	0.2284	–0.6833

Angles between planes (1) and (4) = 83.7° and between (2) and (3) = 1.3°.

(b) (II) Cu(beatphen)(NO₃)₂

	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
Plane (1): N(1)–N(4) (r.m.s.d. = 0.1549 Å) [Cu 0.2418, N(1) –0.1579, N(2) 0.1681, N(3) –0.1512, N(4) 0.1410]	0.3775	0.7254	0.5756	–6.6097
Plane (2): N(4), C(5)–C(9) (r.m.s.d. = 0.0195 Å) [N(4) –0.0234, C(5) 0.0094, C(6) 0.0188, C(7) –0.0308, C(8) 0.0154, C(9) 0.0106]	–0.4292	0.8221	–0.3741	6.0286
Plane (3): N(5), C(10)–C(14) (r.m.s.d. = 0.0197 Å) [N(5) 0.0293, C(10) –0.0218, C(11) –0.0046, C(12) 0.0241, C(13) –0.0167, C(14) –0.0102]	0.5456	–0.7682	0.3349	6.6967
Plane (4): N(4), N(5), C(5)–C(16) (r.m.s.d. = 0.0673 Å) [Cu 0.3442, N(4) 0.1187, N(5) 0.0437, C(5) 0.0070, C(6) –0.1063, C(7) –0.0771, C(8) –0.0411, C(15) 0.0237, C(16) 0.0607, C(11) 0.0423, C(12) –0.0079, C(13) –0.1013, C(14) –0.0749, C(9) 0.0473, C(10) 0.0654]	0.4963	–0.7986	0.3405	–6.2025
Plane (5): Cu, N(1), N(2) [C(1) 0.1188, C(12) –0.5208]	0.4865	0.5769	0.6561	–8.3233
Plane (6): Cu, N(2), N(3) [C(3) –0.5024, C(4) –0.0504]	0.3123	0.8470	0.4303	–5.4075

Angles between planes (1) and (4) = 78.7° and between (2) and (3) = 7.69°.

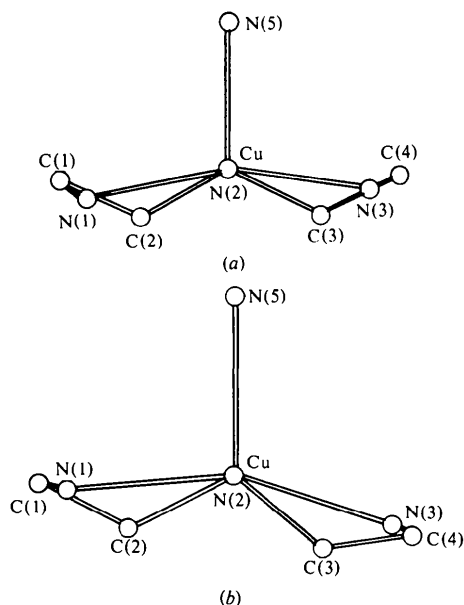


Fig. 2. The conformation of the coordinated bis(2-aminoethyl)-amine ligand along Cu–N(2) for (a) (I) Cu(beatbpy)(NO₃)₂·2H₂O and (b) (II) Cu(beatphen)(NO₃)₂.

C(10) distance of 1.517 Å is not exceptional. In (II) the 1,10-phenanthroline ligand is surprisingly non-planar [plane (6), Table 6(b)] (Nakai & Noda, 1978) and may partly account for the above angle of 7.69°, but this probably arises from the high e.s.d.'s of the bond lengths and angles in this structure.

The stereochemistries of (I) and (II) are surprisingly similar in view of the differences in the rigidity of the two bidentate ligands, but the unusually low angle of twist (1.3°) between the two pyridine rings of the 2,2'-bipyridyl ligand may account for the comparable behaviour of the two ligands in these otherwise similar structures. Both chromophores involve a comparable square-pyramidal stereochemistry, distorted in the sense of the Berry twist towards a trigonal-bipyramidal

Table 7. Electronic reflectance spectra (10² mm⁻¹)

The relative intensities of the spectra are indicated in parentheses on an arbitrary scale of 1–10.

(I)	17.3 (10)	13.0 (8)
(II)	17.5 (9)	12.3 (7)

stereochemistry, a comparability that is reflected in the similarity of the electronic reflectance spectra, Table 7.

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The Crystal and Molecular Structure of Aquabis[L-(+)-*threo*-2-amino-1-phenyl-1,3-propanediolato-*N,O*¹]copper(II) Tetrahydrate

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Abstract

The crystal structure of $\text{Cu}(\text{C}_9\text{H}_{12}\text{NO}_2)_2(\text{H}_2\text{O}) \cdot 4\text{H}_2\text{O}$, $\text{C}_{18}\text{H}_{26}\text{CuN}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$, has been refined to $R = 0.036$ for 1747 counter reflections: $a = 12.582(9)$, $b = 26.076(15)$, $c = 6.954(8)$ Å, space group $P2_12_12_1$, $Z = 4$. The structure consists of aquabis[L-(+)-*threo*-2-amino-1-phenyl-1,3-propanediolato-*N,O*¹]copper(II) neutral complexes and water molecules linked by hydrogen bonds. The coordination polyhedron of Cu is a square pyramid whose base is formed by two N atoms [Cu–N = 1.989(7), 1.995(7) Å] and two O atoms from hydroxylate groups [Cu–O = 1.915(4), 1.927(4) Å] which are adjacent to the phenyl groups, belonging to two chelating ligands. A water molecule is at the apex of the pyramid [Cu–O_w = 2.440(8) Å].

Introduction

Equilibria studies of L-(+)-*threo*-2-amino-1-phenyl-1,3-propanediol with protons and Cu^{II} ions in aqueous

solutions (Braibanti, Mori & Dallavalle, 1978) indicate the existence of several kinds of Cu^{II} complexes. In addition to that formed by the neutral (H₂L) ligand, others are formed by the deprotonated organic ligand involving the ionization of an OH group (HL⁻), probably that adjacent to the phenyl group. These complexes should contain five-membered chelate rings, with amine N and hydroxylate O as donor atoms. An analysis of the complex $\text{Cu}(\text{HL})_2 \cdot 5\text{H}_2\text{O}$ has been carried out to confirm the type of coordination in these complexes.

Experimental

Preparation

Crystals of the complex were obtained from an aqueous alkaline solution of copper chloride treated with an excess of ligand and gently heated. Blue-violet crystals separated on standing.