

clustered, the trend of a decreasing C—O bond length with decreasing bridge angle is clearly evident.

A packing diagram is shown in Fig. 6. In general the long direction of the molecules lies perpendicular to the *b* axis with the longest dimension of the molecules lying along the diagonal of the *ac* plane. No unusual intermolecular contacts were observed.

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

I. Bis(3-aminopropyl)amine(di-2-pyridylamine)copper(II) Nitrate and Bis(3-aminopropyl)amine(2,2'-bipyridyl)copper(II) Nitrate

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The crystal structures of bis(3-aminopropyl)amine(di-2-pyridylamine)copper(II) nitrate, $C_{16}H_{26}N_8O_6Cu$ (I), and bis(3-aminopropyl)amine(2,2'-bipyridyl)copper(II) nitrate, $C_{16}H_{25}N_7O_6Cu$ (II), have been established by X-ray analysis. (I) is monoclinic, space group $P2_1/a$ with $a = 16.81$ (5), $b = 12.33$ (5), $c = 10.42$ (5) Å, $\beta = 99.5$ (5)°, $Z = 4$; and (II) is orthorhombic, space group $Pbca$ with $a = 13.96$ (5), $b = 13.02$ (5), $c = 22.58$ (8) Å, $Z = 8$. Both structures were solved by the heavy-atom method and refined to $R = 0.0707$ and 0.0739 for (I) and (II), respectively. Both structures are ionic lattices with the cations having a distorted five-coordinate square-pyramidal stereochemistry, but with significantly different angular distortions.

Introduction

A wealth of crystallographic data (Muetterties & Schunn, 1966; Hathaway & Billing, 1970) 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 present distorted geometries are involved, depending on the bite angles of the chelate ligands and the conformation of the polydentate chelate ligands (Gollogly & Hawkins, 1972). The present structures have been determined to demonstrate 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.

Experimental

The complexes $Cu(bpa)(dpyam)(NO_3)_2$ (I)* and $Cu(bpa)(bpy)(NO_3)_2$ (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(3-aminopropyl)amine and di-2-pyridylamine (for I) and 2,2'-bipyridyl (for II) in methanol (7 mmol in 25 ml). Blue-black crystals of both (I) and (II) were formed on cooling; (I), found: C = 39.18, H = 5.30, N = 23.01; $C_{16}H_{26}N_8O_6Cu$ requires: C = 39.34, H = 5.12, N = 22.95%; and (II), found: C = 40.54, H = 5.28, N = 20.91; $C_{16}H_{25}N_7O_6Cu$ requires: C = 40.46, H = 5.30, N = 20.64%.

* Bis(3-aminopropyl)amine = bpa; di-2-pyridylamine = dpyam; 2,2'-bipyridyl = bpy.

Crystal data

The crystal and refinement data for (I) and (II) are summarized in Table 1. The unit-cell parameters were determined from precession photographs, and the intensity data were collected photographically using the equi-inclination Weissenberg technique. Five-film packs were used for each layer and the intensities were estimated using the Science Research Council Microdensitometer Service (Rutherford Laboratory).

Structure solution and refinement

Both structures were solved by three-dimensional Patterson and Fourier techniques using the program *SHELX 76* (G. M. Sheldrick) with successive addition of atom positions to improve the phasing. The structures were refined by full-matrix least-squares analysis, in which $\sum w|F_o - F_c|^2$ was the function minimized, until the shift/e.s.d. ratio in any parameter was less than 0.05. Calculated H positions were used with a fixed C—H and N—H bond length of 1.08 Å (with a fixed temperature factor of 0.07 Å²), and floated on the associated C or N atom. A refined weighting scheme was used, where $w = k/[\sigma^2(F_o) + g(F_o)^2]$; see Table 1

Table 1. *Crystal and refinement data*

Compound	(I) Cu(bpa)(dpyam)- (NO ₃) ₂	(II) Cu(bpa)(bpy)- (NO ₃) ₂
<i>M_r</i>	489.97	474.72
Stoichiometry	C ₁₆ H ₂₆ N ₈ O ₆ Cu	C ₁₆ H ₂₅ N ₇ O ₆ Cu
Space group	<i>P2₁/a</i> (monoclinic)	<i>Pbca</i> (orthorhombic)
<i>a</i> (Å)	16.81 (5)	13.96 (5)
<i>b</i> (Å)	12.33 (5)	13.02 (5)
<i>c</i> (Å)	10.42 (5)	22.58 (5)
β (°)	99.5 (5)	—
<i>U</i> (Å ³)	2130.1	4104.12
<i>Z</i>	4	8
<i>D_m</i> [(floatation) g cm ⁻³]	1.54 (5)	1.56 (5)
<i>D_c</i> (g cm ⁻³)	1.53	1.54
Radiation	Cu <i>K</i> α	Cu <i>K</i> α
	($\lambda = 1.54178$ Å)	($\lambda = 1.54178$ Å)
<i>F</i> (000)	1012.0	1959.99
μ (cm ⁻¹)	17.44	17.80
Data used	<i>hk0</i> – <i>hk8</i> <i>h1l</i> – <i>h2l</i>	<i>0kl</i> – <i>11kl</i>
Number of unique reflections	818	1133
Number of parameters varied	131	138
<i>R</i> = ($\sum \Delta / \sum F_o $)	0.0707	0.0739
<i>R_w</i> = ($\sum \Delta w^{1/2} / \sum F_o w^{1/2}$)	0.0749	0.0766
<i>k</i>	3.8857	42.4570
<i>g</i>	0.001769	0.000016
Maximum final shift/e.s.d.	0.036	0.032
Residual electron density (e Å ⁻³)	0.68	0.70
Number of anisotropic atoms	1	1

for final values of *k* and *g* in the refinement. 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 no correction for absorption was made. The final atom coordinates are listed in Table 2.* H-atom positional parameters and the overall isotropic temperature factor are presented in Table 3, and the bond lengths and bond 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, along with the atom-numbering scheme used.

Discussion

The lattices of both complexes are made up of nitrate ions and discrete cations, Cu(bpa)(dpyam)²⁺ and Cu(bpa)(bpy)²⁺ for (I) and (II), respectively. There are no unusual features in either the bond lengths or the bond angles of the nitrate ions (Addison, Logan, Wallwork & Garner, 1971) or in the organic ligands

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33734 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

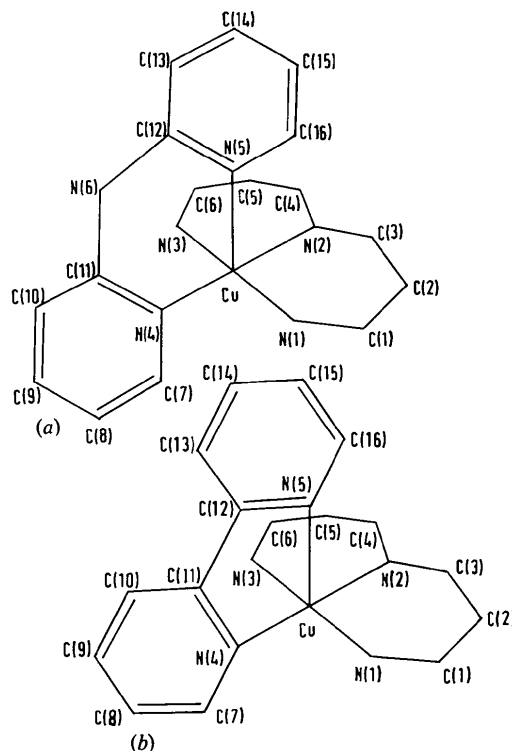


Fig. 1. The molecular structure (including atom-numbering schemes) of (a) Cu(bpa)(dpyam)(NO₃)₂ (I), (b) Cu(bpa)(bpy)(NO₃)₂ (II).

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

	(I) Cu(bpa)(dpyam)(NO ₃) ₂				(II) Cu(bpa)(bpy)(NO ₃) ₂			
	x	y	z	U	x	y	z	U
Cu	6809 (2)	6306 (2)	7150 (2)		451 (2)	1904 (2)	1590 (1)	
N(1)	7400 (9)	7621 (11)	7997 (12)	31 (3)	425 (10)	3200 (9)	1103 (5)	51 (3)
C(1)	6908 (12)	8589 (17)	8308 (17)	48 (4)	-551 (14)	3581 (14)	897 (7)	67 (5)
C(2)	6342 (12)	8250 (16)	9200 (17)	46 (4)	-1208 (15)	3767 (15)	1391 (8)	79 (6)
C(3)	5666 (14)	7570 (18)	8562 (19)	58 (5)	-1503 (14)	2823 (13)	1730 (8)	72 (6)
N(2)	5879 (9)	6456 (12)	8150 (13)	36 (3)	-722 (9)	2309 (9)	2059 (5)	48 (4)
C(4)	6037 (12)	5656 (15)	9274 (16)	38 (4)	-454 (14)	2890 (7)	2601 (7)	67 (5)
C(5)	5911 (13)	4520 (16)	8823 (19)	53 (4)	149 (15)	2331 (17)	3005 (9)	94 (7)
C(6)	6467 (14)	4113 (17)	7938 (18)	54 (5)	1005 (15)	1796 (15)	2835 (8)	85 (6)
N(3)	6375 (9)	4784 (12)	6733 (12)	32 (3)	869 (10)	1116 (10)	2324 (5)	53 (4)
N(4)	7900 (9)	5836 (11)	6741 (12)	27 (3)	1673 (9)	1483 (8)	1165 (5)	33 (3)
C(7)	8430 (11)	5509 (15)	7810 (16)	34 (4)	2509 (12)	2029 (12)	1201 (6)	48 (4)
C(8)	9202 (12)	5216 (15)	7844 (16)	34 (4)	3333 (12)	1700 (11)	932 (5)	47 (5)
C(9)	9501 (13)	5298 (16)	6622 (17)	44 (4)	3338 (13)	825 (13)	626 (7)	54 (5)
C(10)	8997 (12)	5671 (16)	5573 (17)	38 (4)	2487 (13)	258 (13)	581 (7)	59 (5)
C(11)	8216 (13)	5943 (14)	5633 (16)	33 (4)	1656 (11)	626 (11)	852 (6)	39 (4)
N(6)	7702 (9)	6323 (13)	4507 (13)	40 (4)				
C(12)	6952 (11)	6708 (13)	4230 (15)	26 (4)	745 (10)	79 (9)	813 (5)	24 (3)
C(13)	6628 (12)	6972 (15)	2909 (16)	36 (4)	609 (13)	-835 (11)	491 (6)	50 (4)
C(14)	5877 (12)	7356 (15)	2610 (16)	39 (4)	-266 (12)	-1275 (11)	467 (6)	45 (4)
C(15)	5391 (14)	7556 (17)	3565 (17)	51 (4)	-1027 (13)	-828 (12)	756 (6)	51 (4)
C(16)	5735 (13)	7211 (15)	4846 (17)	37 (4)	-863 (13)	78 (12)	1050 (7)	52 (5)
N(5)	6480 (9)	6857 (11)	5162 (12)	25 (3)	-2 (9)	536 (8)	1075 (5)	31 (3)
N(7)	8576 (10)	6330 (13)	1265 (14)	36 (3)	1723 (13)	115 (12)	7223 (6)	64 (4)
O(1)	9182 (10)	6386 (12)	725 (13)	68 (4)	2026 (10)	-606 (10)	7528 (6)	87 (4)
O(2)	7896 (9)	6561 (10)	636 (12)	51 (3)	2296 (11)	700 (11)	6985 (6)	95 (4)
O(3)	8683 (8)	6098 (10)	2452 (11)	39 (3)	878 (11)	156 (10)	7099 (6)	89 (4)
N(8)	8873 (12)	8928 (15)	6512 (17)	62 (4)	1572 (14)	1466 (13)	4590 (8)	75 (5)
O(4)	8212 (11)	8837 (13)	5846 (14)	77 (4)	1872 (11)	1986 (12)	4997 (7)	103 (5)
O(5)	9454 (9)	9315 (12)	6062 (12)	63 (4)	755 (14)	1233 (13)	4599 (7)	127 (6)
O(6)	8981 (12)	8833 (14)	7736 (16)	98 (4)	2075 (13)	1163 (13)	4213 (8)	126 (6)

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

	(I) Cu(bpa)(dpyam)(NO ₃) ₂			(II) Cu(bpa)(bpy)(NO ₃) ₂		
	x	y	z	x	y	z
H(1)	7794	7905	7348	869	3068	718
H(2)	7757	7351	8898	733	3808	1367
H(3)	6571	8901	7412	-864	2991	622
H(4)	7304	9212	8777	-465	4276	641
H(5)	6668	7795	10003	-844	4269	1698
H(6)	6100	8978	9564	-1844	4143	1226
H(7)	5373	7998	7709	-1772	2280	1409
H(8)	5247	7469	9234	-2066	3019	2038
H(9)	5339	6289	7461	-1041	1589	2192
H(10)	5642	5829	9966	-1096	3128	2829
H(11)	6657	5734	9744	-56	3560	2463
H(12)	5957	3994	9661	338	2848	3361
H(13)	5306	4485	8282	-304	1727	2698
H(14)	6305	3289	7660	1509	2379	2698
H(15)	7083	4135	8441	1298	1372	3204
H(16)	6703	4426	6031	1523	703	2227
H(17)	5744	4838	6320	314	576	2444
H(18)	8209	5504	8725	2509	2742	1446
H(19)	9570	4901	8712	3990	2133	975
H(20)	10112	5075	6547	3979	569	403
H(21)	9209	5763	4655	2470	-459	341
H(22)	7668	5621	3881			
H(23)	7000	6840	2173	1213	-1189	274
H(24)	5653	7563	1609	-368	-1980	223
H(25)	4791	7891	3328	-1728	-1179	746
H(26)	5378	7282	5614	-1460	449	1266

Table 4. Bond lengths (\AA) (*e.s.d.*'s Cu-N, 0.013-0.017; C-N and C-C, 0.016-0.027 \AA)

	(I)	(II)	(I)	(II)	
N(1)-Cu	2.025	2.014	C(10)-C(9)	1.35	1.40
N(2)-Cu	2.025	2.021	C(11)-C(10)	1.37	1.40
N(3)-Cu	2.034	2.036	N(6)-C(11)	1.42	
N(4)-Cu	2.034	2.033	C(12)-N(6)	1.33	
N(5)-Cu	2.164	2.218	C(12)-C(11)		1.46
C(1)-N(1)	1.52	1.52	C(13)-C(12)	1.43	1.41
C(2)-C(1)	1.50	1.46	N(5)-C(12)	1.36	1.34
C(3)-C(2)	1.48	1.51	C(14)-C(13)	1.34	1.35
N(2)-C(3)	1.50	1.48	C(15)-C(14)	1.41	1.38
C(4)-N(2)	1.52	1.49	C(16)-C(15)	1.43	1.37
C(5)-C(4)	1.48	1.44	N(5)-C(16)	1.32	1.34
C(6)-C(5)	1.50	1.44	O(1)-N(7)	1.24	1.24
N(3)-C(6)	1.49	1.47	O(2)-N(7)	1.25	1.22
C(7)-N(4)	1.37	1.37	O(3)-N(7)	1.25	1.23
C(11)-N(4)	1.36	1.32	O(4)-N(8)	1.21	1.22
C(8)-C(7)	1.34	1.37	O(5)-N(8)	1.25	1.18
C(9)-C(8)	1.45	1.33	O(6)-N(8)	1.26	1.17

present (Johnson, Beineke & Jacobson, 1971; Stephens, 1972), see Tables 4 and 5. In each cation the Cu^{II} ion involves a distorted five-coordinate geometry with no evidence of coordination by a sixth ligand; Cu-O(2) is 3.80 \AA in (I) and there is no interaction $< 4 \text{\AA}$ in (II); distances which are too long for appreciable coordination or semi-coordination (Hathaway & Bill-

ing, 1970). In both complexes the Cu^{II} ion is coordinated by five N ligands in a distorted square-pyramidal stereochemistry with the bis(3-aminopropyl)amine ligand occupying three of the in-plane ligand positions N(1–3) (meridional coordination) and the bidentate ligand [di-2-pyridylamine in complex (I) and 2,2'-bipyridyl in complex (II)] occupying the remaining in-plane position, N(4) and the fifth ligand position, N(5).

In both complexes the mean in-plane Cu–N distances do not differ significantly from 2.0 Å but there is a significant difference in the Cu–N(5) distance, namely, 2.164 Å in (I) and 2.218 Å in (II). This may be related to the differences in the N(4)–Cu–N(5) angle of 89.2° and 77.0° in the two complexes due to the out-of-plane bite angles of these two bidentate ligands, which involve a six-membered and a five-membered ring in (I) and (II) respectively. In both complexes the Cu^{II} ion is lifted out of the plane of the four in-plane N atoms, N(1)–N(4), by 0.32 and 0.28 Å for (I) and (II), respectively, distances which bear an inverse relationship to the Cu–N(5) bond length as suggested previously (Hathaway & Billing, 1970).

In both complexes the bpa ligand bonds as an unsymmetrical tridentate ligand with significantly different N(1)–Cu–N(2) and N(2)–Cu–N(3) bond angles of $>90^\circ$ and $<90^\circ$, respectively. The overall conformation of the two fused six-membered rings (Gollogly & Hawkins, 1972; Skelton, Waters & Curtis, 1972) in each complex, which are formed by coordination with the copper ion, is analogous to the *cis*-decalin (Eliel, Allinger, Angyal & Morrison, 1967) system [*cis* with respect to the proton of the secondary nitrogen N(2) and the Cu–N(5) bond direction] and results in angles of 70.36 and 73.69° between the normals to planes (5) and (6) (Table 6) for (I) and (II), respectively. Both six-membered rings, for each complex, are in chair conformations (Table 6). It is of note that the

coordination mode of bpa in the distorted square-based pyramidal $\text{Cu}(\text{bpa})(\text{CH}_3\text{CO}_2)(\text{ClO}_4)$ (Skelton, Waters & Curtis, 1972) involves chair and twist-boat conformations, respectively, of the six-membered rings and is, in consequence, different from (I) and (II) (Fig. 2).

While both complexes are square-based pyramidal there are significant differences: the basal plane N(1), N(2), N(3) and N(4) of complex (I) only involves a small standard deviation (0.0498 Å), while that for (II)

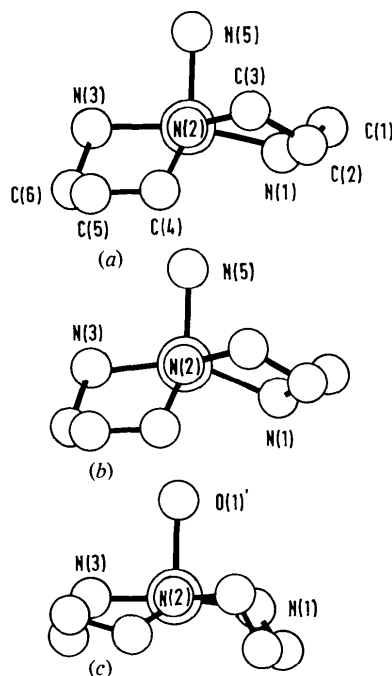


Fig. 2. The conformation of the bpa ligand viewed along the Cu–N(2) bond of (a) $\text{Cu}(\text{bpa})(\text{dpyam})(\text{NO}_3)_2$ (I), (b) $\text{Cu}(\text{bpa})(\text{bpy})(\text{NO}_3)_2$ (II), (c) $\text{Cu}(\text{bpa})(\text{CH}_3\text{CO}_2)(\text{ClO}_4)$ (Skelton, Waters & Curtis, 1972).

Table 5. Bond angles ($^\circ$) (*e.s.d.*'s N–Cu–N, 0.5–0.7; C–C–C and C–N–C, 1.0–2.2°)

	(I)	(II)		(I)	(II)	(I)	(II)
N(2)–Cu–N(1)	93.9	93.1	C(6)–C(5)–C(4)	116.0	124.2	N(5)–C(12)–N(6)	122.2
N(3)–Cu–N(1)	164.6	150.7	N(3)–C(6)–C(5)	110.1	113.3	N(5)–C(12)–C(13)	118.7
N(3)–Cu–N(2)	85.1	86.3	C(6)–N(3)–Cu	110.4	111.9	C(13)–C(12)–C(11)	124.2
N(4)–Cu–N(1)	85.7	89.0	C(7)–N(4)–Cu	113.7	123.1	N(5)–C(12)–C(11)	115.7
N(4)–Cu–N(2)	158.9	176.5	C(11)–N(4)–Cu	130.1	117.7	C(14)–C(13)–C(12)	120.0
N(4)–Cu–N(3)	89.7	90.5	C(11)–N(4)–C(7)	115.4	119.2	C(15)–C(14)–C(13)	122.2
N(5)–Cu–N(1)	101.3	112.5	C(8)–C(7)–N(4)	126.8	121.7	C(16)–C(15)–C(14)	114.5
N(5)–Cu–N(2)	111.5	104.7	C(9)–C(8)–C(7)	115.6	120.1	N(5)–C(16)–C(15)	123.7
N(5)–Cu–N(3)	93.4	95.9	C(10)–C(9)–C(8)	118.3	119.0	C(12)–N(5)–Cu	123.6
N(5)–Cu–N(4)	89.2	77.0	C(11)–C(10)–C(9)	121.8	119.4	C(16)–N(5)–Cu	115.2
C(1)–N(1)–Cu	118.5	117.0	C(10)–C(11)–N(4)	122.0	120.6	C(16)–N(5)–C(12)	120.5
C(2)–C(1)–N(1)	109.8	112.5	N(6)–C(11)–N(4)	117.8		O(2)–N(7)–O(1)	119.7
C(3)–C(2)–C(1)	113.5	115.1	N(6)–C(11)–C(10)	120.2		O(3)–N(7)–O(1)	117.7
N(2)–C(3)–C(2)	116.5	115.1	C(12)–N(6)–C(11)	136.3		O(3)–N(7)–O(2)	122.5
C(3)–N(2)–Cu	118.1	116.8	C(12)–C(11)–N(4)		117.4	O(5)–N(8)–O(4)	121.3
C(4)–N(2)–Cu	106.6	111.1	C(12)–C(11)–C(10)		121.9	O(6)–N(8)–O(4)	122.3
C(4)–N(2)–C(3)	113.2	111.6	C(13)–C(12)–N(6)	119.1		O(6)–N(8)–O(5)	115.1
C(5)–C(4)–N(2)	111.8	114.3					

Table 6. Equations of least-squares planes in the form $lX + mY + nZ = p$, where X , Y and Z are orthogonal axes, with deviations (\AA) of relevant atoms from the planes given in square brackets

	l	m	n	p
(I) Cu(bpa)(dpyam)(NO ₃) ₂				
Plane (1): N(1)–N(4) (r.m.s.d. = 0.0498 \AA) [N(1) –0.0488, N(2) 0.0491, N(3) –0.0507, N(4) –0.0504, Cu –0.3197]	0.3939	–0.4304	0.8121	5.9366
Plane (2): N(1)–N(3) (r.m.s.d. = 0.0000 \AA) [C(1) –0.5194, C(2) 0.1124, C(3) –0.3778, C(4) 1.4341, C(5) 1.6222, C(6) 1.3979]	0.4333	–0.4422	0.7854	6.0924
Plane (3): N(4), C(7)–C(11) (r.m.s.d. = 0.0361 \AA) [N(4) –0.0286, C(7) –0.0002, C(8) 0.0167, C(9) –0.0502, C(10) –0.0024, C(11) 0.0647]	0.3766	0.9175	0.1278	12.1810
Plane (4): N(5), C(12)–C(16) (r.m.s.d. = 0.0344 \AA) [N(5) 0.0328, C(12) –0.0606, C(13) 0.0038, C(14) 0.0300, C(15) 0.0236, C(16) –0.0296]	0.3293	0.9259	0.1852	11.9964
Plane (5): N(1), C(1), C(3), N(2) (r.m.s.d. = 0.0380 \AA) [N(1) 0.0342, C(1) –0.0407, C(3) 0.0415, N(2) –0.0349, Cu –0.6674, C(2), 0.7138]	0.3442	–0.1829	0.9209	8.2524
Plane (6): N(2), C(4), C(6), N(3) (r.m.s.d. = 0.0117 \AA) [N(2) –0.0112, N(3) 0.0113, C(4) 0.0121, C(6) –0.0123, Cu 1.2989, C(5) –0.6523]	0.9477	0.3107	0.0725	12.2195
Angle between normals to planes (3) and (4) is 4.29°. Angle between normals to planes (5) and (6) is 70.36°.				

(II) Cu(bpa)(bpy)(NO₃)₂

Plane (1): N(1)–N(4) (r.m.s.d. = 0.2370 \AA) [N(1) 0.2323, N(2) –0.2379, N(3) 0.2416, N(4) –0.2360, Cu –0.2758]	0.5332	0.6582	0.5315	4.1505
Plane (2): N(1)–N(3) (r.m.s.d. = 0.0000 \AA) [C(1) –0.3858, C(2) 0.1812, C(3) –0.3467, C(4) 1.4225, C(5) 1.7530, C(6) 1.4097]	0.3279	0.7091	0.6242	4.7037
Plane (3): N(4), C(7)–C(11) (r.m.s.d. = 0.0075 \AA) [N(4) 0.0097, C(7) –0.0002, C(8) –0.0062, C(9) 0.0033, C(10) 0.0059, C(11) –0.0125]	0.2427	–0.5080	0.8265	1.7498
Plane (4): N(5), C(12)–C(16) (r.m.s.d. = 0.0114 \AA) [N(5) –0.0140, C(12) 0.0181, C(13) –0.0070, C(14) –0.0078, C(15) 0.0120, C(16) –0.0013]	0.2067	–0.5188	0.8298	1.6666
Plane (5): N(1), C(1), C(3), N(2) (r.m.s.d. = 0.0076 \AA) [N(1) 0.0069, C(1) –0.0081, C(3) 0.0083, N(2) –0.0071, –0.0071, Cu –0.8030, C(2) 0.6737]	0.1306	0.8329	0.5377	4.8800
Plane (6): N(2), C(4), C(6), N(3) (r.m.s.d. = 0.0028 \AA) [N(2) 0.0027, C(4) –0.0029, C(6) 0.0030, N(3) –0.0027, Cu 1.2059, C(5) –0.4072]	0.5704	0.6058	–0.5546	–1.3362
Angle between normals to planes (3) and (4) is 2.15°. Angle between normals to planes (5) and (6) is 73.69°.				

is significantly greater, namely 0.2370 \AA , suggesting that (I) involves a more regular square-based-pyramidal stereochemistry than (II). This is reflected in the close similarity of the N(1)–Cu–N(3) and N(2)–Cu–N(4) angles of (I) (164.6 and 158.9°) which are comparable to the corresponding angles of 165 and 167° in the most regular square-based-pyramidal

complex of Cu^{II}, namely KCu(NH₃)₅(PF₆)₃ (Ray & Hathaway, 1978). In (II) the N(1)–Cu–N(3) angle (150.7°) is more distorted towards 120° and the N(2)–Cu–N(4) angle (176.5°) nearer to 180°, suggesting that (II) has a distortion away from a square-pyramidal stereochemistry towards that of a trigonal-bipyramidal system, as related by the sense of the Berry

twist (Berry, 1960) in these two stereochemistries. The more trigonal-distorted square-pyramidal stereochemistry of (II) may be related to the smaller bite angle of 77.0° of the bpy ligand (Johnson, Beineke & Jacobson, 1971) relative to that of 89.2° in the dpyam ligand (Stephens, 1972), but it is then difficult to see how the bite angle influences the smaller value of N(1)—Cu—N(3) in (I).

The pyridine rings of the dpyam and bpy ligands are reasonably planar in (I) and (II), respectively; in (I) they are inclined at an angle of 4.29° to each other while in (II) they are twisted about the C(11)—C(12) bond by an angle of 2.15°, both in reasonable agreement with previously observed values (Johnson, Beineke & Jacobson, 1971; Stephens, 1972).

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Crystal and Molecular Structure of (3,3'-Dimethyl-2,2'-bipyridyl)methylmercury(II) Nitrate; a Complex That May Have Weak Intramolecular π -Coordination

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$C_{13}H_{15}HgN_3O_3$ is monoclinic, $a = 10.521$ (5), $b = 9.310$ (5), $c = 16.570$ (8) Å, $\beta = 106.6$ (1)°, $Z = 4$, space group $P2_1/c$. The structure was solved by Patterson and Fourier techniques using 1560 counter-measured observed reflections and refined by the full-matrix least-squares method to $R = 0.061$. The complex has a bent C(1)—Hg—N(1) group [172.7 (5)°] with Hg—C(1) 2.01 (1) and Hg—N(1) 2.11 (1) Å, weak interaction between Hg and nitrate O atoms, and evidence suggesting the presence of a weak intramolecular π -interaction between Hg and the second pyridyl ring, with Hg—C(2') 3.11 (1), Hg—N(1') 3.29 (1) Å and an angle of 100.5° between the planes of the pyridyl rings.

Introduction

Methylmercury(II) forms complexes involving irregular three-coordination for Hg with 2,2'-bipyridyl (Canty, Marker & Gatehouse, 1975; Canty & Gatehouse, 1976) and methyl-substituted 2,2'-bipyridyls, except for 3,3'-dimethyl-2,2'-bipyridyl (3,3'-dmbpy) where steric interaction between 3,3'-dimethyl groups prevents

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coplanarity of the pyridyl rings required by chelation (Canty & Marker, 1976). Coordination of only one N to methylmercury(II) has been shown by ^1H NMR spectroscopy for $[\text{MeHg}(3,3'\text{-dmbpy})]\text{NO}_3$ (Canty & Marker, 1976), but ^{199}Hg NMR studies of MeHg^{11} complexes of pyridine, 2,2'-bipyridyl, and related substituted ligands suggest that there may be weak π -interaction between Hg and the second aromatic ring in this complex and also in the analogous 2-benzylpyridine complex (Canty, Marker, Barron & Healy, 1978). Chemical shifts for the Hg atom in these two complexes are approximately 90 ppm upfield from

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