The Structure of Bis(2,2'-bipyridyl)peroxodisulphatocopper(II) Monohydrate

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Abstract

Bis(2,2'-bipyridyl)peroxodisulphatocopper(II) monohydrate, $[Cu(C_{10}H_8N_2)_2(S_2O_8)]$. H_2O, $C_{20}H_{16}CuN_4O_8S_2.H_2O$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.612$ (2), $b = 9.684$ (2), $c = 15.557$ (4) Å, $\alpha = 100.64$ (5), $\beta = 82.03$ (5), $\gamma = 96.81$ (5)°, $Z = 2$. Final $R = 0.0407$. The structure involves a distorted five-coordinate square-pyramidal CuN_4O chromophore with a disordered peroxodisulphate anion involved in semi-coordination to the Cu atom, plus a molecule of lattice water. The structure contrasts with the more usual distorted trigonal-bipyramidal stereochemistry of a $[Cu(bpy)_2X]Y$ complex and represents the extreme A-type distortion of the mechanistic pathway of the Berry twist.

Introduction

The stability of the $[Cu(bpy)_2]^{2+}$ cation to reducing anions has been illustrated in the crystal structures of $[Cu(bpy)_2(S_4O_6)]$ (Harrison & Hathaway, 1978) and $[Cu(bpy)_2(H_2O)]S_2O_6$ (Harrison & Hathaway, 1979); however, it is equally stable in the presence of oxidizing anions such as nitrate (Nakai, Ooi & Kuroya, 1970), perchlorate (Nakai, 1971) and peroxodisulphate. In view of the formal similarity of the $O_3S.O.O.SO_3^{2-}$ and $O_3S.S.S.SO_3^{2-}$ anions the crystal structure of $[Cu(bpy)_2(S_2O_8)].H_2O$ (I) has been determined.

Experimental

Potassium peroxodisulphate was dissolved in a hot solution of $CuCl_2.2H_2O$ containing 2.2 mol of bpy and a turquoise microcrystalline precipitate was formed on cooling. Recrystallization from hot water yielded small, well formed crystals of $[Cu(bpy)_2(S_2O_8)].H_2O$. Found: C, 40.78; H, 3.18; N, 9.64; S, 10.74; Cu, 10.80%; calculated for $C_{20}H_{18}CuN_4O_9S_2$: C, 40.99; H, 3.09; N, 9.64; S, 10.84; Cu, 10.94%.

Crystal data

$C_{20}H_{18}CuN_4O_9S_2$, $M_r = 586.06$, triclinic, $a = 7.612$ (2), $b = 9.684$ (2), $c = 15.557$ (4) Å, $\alpha = 100.64$ (5), $\beta = 82.03$ (5), $\gamma = 96.81$ (5)°, $U = 1111.07$ Å^3, $D_m = 1.787$ (by flotation), $D_c = 1.751$ Mg m^{-3}, $Z = 2$, $F(000) = 598$, Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), μ(Mo $K\alpha$) = 1.176 mm^{-1}, space group $P\bar{1}$. Cell dimensions were determined and intensities collected on a Philips PW 1100 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. A θ–2θ scan mode was used and reflections with $3.0 < \theta < 35°$ in one quadrant were examined. A constant scan speed of 0.05° s^{-1} and a variable scan width of (0.7 + 0.1 tan θ)° were used. With an acceptance criterion of $I > 2.5\sigma(I)$, 4579 reflections were retained. Lorentz and polarization corrections were applied, but none for absorption. The structure was solved by Patterson and Fourier techniques and refined by blocked-matrix least squares with anisotropic temperature factors for all non-H atoms. The positions of the H atoms were calculated geometrically assuming C—H and O—H = 1.08 Å, a fixed temperature factor of 0.07 Å^2 and atoms floated on the adjacent C or O atoms. The refinement converged when the maximum shift/e.s.d. was <0.042, with a refined weighting scheme $w = 0.2306[\sigma^2(F_o) + 0.008419(F_o)^2]$, and yielded a maximum residual electron density of 0.58 e Å^{-3} with $R = 0.0407$ and $R_w = 0.0517$. Complex scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970) and the Cu atom was corrected for anomalous dispersion. All calculations were carried out with *SHELX* 76 and *XANADU* (G. M. Sheldrick), *PLUTO* (S. Motherwell) and *XPUB* (R. Taylor), on an IBM 370/138 computer. The final non-H atomic coordinates are given in Table 1,* bond lengths in Table 2, bond angles in Table 3 and some relevant mean planes in Table 4. Fig. 1 illustrates the local molecular structure of the $[Cu(bpy)_2O]$ cation and the

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* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35025 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## Table 1. Fractional coordinates (×10⁴) for non-hydrogen atoms, with e.s.d.'s in parentheses

Nearest neighbours to H₂O H(10) and H(11) >2·4 Å.

	x	y	z
Cu	−1258 (1)	−139 (1)	−2303 (1)
N(1)	−1081 (3)	−1509 (2)	−1533 (1)
C(1)	−329 (4)	−2737 (3)	−1784 (2)
C(2)	−268 (4)	−3649 (3)	−1212 (2)
C(3)	−998 (4)	−3295 (3)	−348 (2)
C(4)	−1705 (4)	−2014 (3)	−71 (2)
C(5)	−1712 (3)	−1123 (3)	−678 (2)
C(6)	−2375 (3)	289 (3)	−450 (2)
C(7)	−3098 (4)	855 (3)	394 (2)
C(8)	−3713 (4)	2186 (4)	533 (2)
C(9)	−3608 (4)	2892 (4)	−156 (2)
C(10)	−2868 (4)	2266 (3)	−991 (2)
N(2)	−2249 (3)	992 (2)	−1134 (2)
N(3)	−1078 (3)	1247 (2)	−3091 (2)
C(11)	−401 (4)	2604 (3)	−2908 (2)
C(12)	−405 (4)	3541 (3)	−3475 (2)
C(13)	−1088 (5)	3057 (4)	−4267 (2)
C(14)	−1723 (5)	1652 (3)	−4466 (2)
C(15)	−1688 (3)	759 (3)	−3871 (2)
C(16)	−2271 (4)	−761 (3)	−4031 (2)
C(17)	−2944 (4)	−1445 (4)	−4796 (2)
C(18)	−3450 (5)	−2891 (4)	−4890 (2)
C(19)	−3293 (5)	−3584 (4)	−4218 (2)
C(20)	−2616 (4)	−2834 (3)	−3463 (2)
N(4)	−2077 (3)	−1454 (2)	−3380 (2)
S(1)	3263 (1)	267 (1)	−2704 (1)
S(2)	4195 (1)	4228 (1)	−2208 (1)
O(1)	1734 (3)	627 (2)	−2067 (1)
O(2)	4567 (4)	−333 (4)	−2370 (2)
O(3)	2808 (5)	−421 (3)	−3547 (2)
O(4)	3881 (5)	1758 (4)	−3125 (2)
O(5)	5037 (5)	2669 (4)	−2529 (3)
OH(2)	2130 (5)	−3498 (4)	−3819 (2)
O(4')	3957 (8)	2738 (6)	−2974 (3)
O(5')	4758 (6)	1666 (5)	−2642 (4)
O(6)	2777 (4)	3959 (3)	−1544 (2)
O(7)	5846 (5)	4787 (4)	−1930 (4)
O(8)	3672 (6)	4892 (5)	−2843 (3)

Table 2. Bond lengths (Å) with e.s.d.'s in parentheses

N(1)—Cu	1·972 (4)	C(15)—C(14)	1·383 (6)
N(2)—Cu	2·039 (4)	C(16)—C(15)	1·472 (5)
N(3)—Cu	1·959 (5)	C(17)—C(16)	1·384 (5)
N(4)—Cu	2·032 (4)	N(4)—C(16)	1·347 (5)
O(1)—Cu	2·367 (4)	C(18)—C(17)	1·394 (6)
C(1)—N(1)	1·350 (5)	C(19)—C(18)	1·366 (7)
C(5)—N(1)	1·349 (4)	C(20)—C(19)	1·391 (6)
C(2)—C(1)	1·373 (6)	N(4)—C(20)	1·339 (5)
C(3)—C(2)	1·380 (5)	O(1)—S(1)	1·451 (3)
C(4)—C(3)	1·382 (5)	O(2)—S(1)	1·409 (5)
C(5)—C(4)	1·393 (5)	O(3)—S(1)	1·426 (4)
C(6)—C(5)	1·478 (5)	O(4)—S(1)	1·684 (6)
C(7)—C(6)	1·390 (5)	O(5')—S(1)	1·660 (7)
N(2)—C(6)	1·353 (5)	O(5)—S(2)	1·674 (6)
C(8)—C(7)	1·393 (6)	O(4')—S(2)	1·703 (7)
C(9)—C(8)	1·362 (6)	O(6)—S(2)	1·422 (4)
C(10)—C(9)	1·399 (5)	O(7)—S(2)	1·401 (5)
N(2)—C(10)	1·343 (5)	O(8)—S(2)	1·397 (6)
C(11)—N(3)	1·347 (4)	O(5)—O(4)	1·467 (6)
C(15)—N(3)	1·344 (4)	O(5')—O(4')	1·467 (10)
C(12)—C(11)	1·378 (6)	H(17)—OH(2)	0·814 (60)
C(13)—C(12)	1·384 (6)	H(18)—OH(2)	0·747 (52)
C(14)—C(13)	1·382 (6)		

Table 3. Bond angles (°) with e.s.d.'s in parentheses

N(2)—Cu—N(1)	81·4 (2)	C(14)—C(15)—N(3)	120·8 (3)
N(3)—Cu—N(1)	172·2 (1)	C(16)—C(15)—N(3)	115·0 (4)
N(3)—Cu—N(2)	101·6 (2)	C(16)—C(15)—C(14)	124·2 (3)
N(4)—Cu—N(1)	100·7 (2)	C(17)—C(16)—C(15)	123·0 (4)
N(4)—Cu—N(2)	141·0 (1)	N(4)—C(16)—C(15)	115·0 (3)
N(4)—Cu—N(3)	81·7 (2)	N(4)—C(16)—C(17)	121·9 (4)
O(1)—Cu—N(1)	84·8 (2)	C(18)—C(17)—C(16)	118·9 (4)
O(1)—Cu—N(2)	93·0 (2)	C(19)—C(18)—C(17)	119·0 (4)
O(1)—Cu—N(3)	87·8 (2)	C(20)—C(19)—C(18)	119·3 (4)
O(1)—Cu—N(4)	126·0 (2)	N(4)—C(20)—C(19)	122·0 (4)
C(1)—N(1)—Cu	125·6 (3)	C(16)—N(4)—Cu	112·6 (3)
C(5)—N(1)—Cu	115·3 (3)	C(20)—N(4)—Cu	128·1 (3)
C(5)—N(1)—C(1)	119·0 (4)	C(20)—N(4)—C(16)	118·8 (3)
C(2)—C(1)—N(1)	122·5 (4)	O(2)—S(1)—O(1)	114·2 (3)
C(3)—C(2)—C(1)	118·8 (4)	O(3)—S(1)—O(1)	113·9 (3)
C(4)—C(3)—C(2)	119·5 (4)	O(3)—S(1)—O(2)	115·5 (3)
C(5)—C(4)—C(3)	119·2 (4)	O(4)—S(1)—O(1)	103·4 (3)
C(4)—C(5)—N(1)	120·9 (3)	O(4)—S(1)—O(2)	118·0 (3)
C(6)—C(5)—N(1)	115·2 (3)	O(4)—S(1)—O(3)	88·9 (3)
C(6)—C(5)—C(4)	123·8 (3)	O(5')—S(1)—O(1)	107·7 (3)
C(7)—C(6)—C(5)	123·4 (4)	O(5')—S(1)—O(2)	82·9 (3)
N(2)—C(6)—C(5)	114·6 (3)	O(5')—S(1)—O(3)	119·0 (3)
N(2)—C(6)—C(7)	122·0 (4)	O(6)—S(2)—O(5)	103·5 (3)
C(8)—C(7)—C(6)	118·6 (4)	O(7)—S(2)—O(5)	88·1 (3)
C(9)—C(8)—C(7)	119·6 (4)	O(7)—S(2)—O(6)	117·2 (4)
C(10)—C(9)—C(8)	119·2 (4)	O(6)—S(2)—O(4')	101·4 (3)
N(2)—C(10)—C(9)	122·0 (4)	O(7)—S(2)—O(4')	122·5 (4)
C(6)—N(2)—Cu	113·3 (3)	O(8)—S(2)—O(4')	84·3 (4)
C(10)—N(2)—Cu	127·9 (3)	O(8)—S(2)—O(5)	118·8 (3)
C(10)—N(2)—C(6)	118·6 (3)	O(8)—S(2)—O(6)	112·7 (3)
C(11)—N(3)—Cu	125·3 (3)	O(8)—S(2)—O(7)	114·1 (4)
C(15)—N(3)—Cu	115·2 (3)	O(5)—O(4)—S(1)	107·0 (4)
C(15)—N(3)—C(11)	119·5 (4)	O(4)—O(5)—S(2)	108·5 (4)
C(12)—C(11)—N(3)	122·1 (4)	O(5')—O(4')—S(2)	105·1 (5)
C(13)—C(12)—C(11)	118·6 (4)	O(4')—O(5')—S(1)	105·3 (5)
C(14)—C(13)—C(12)	119·1 (4)	H(18)—OH(2)—H(17)	112·8 (58)
C(15)—C(14)—C(13)	119·8 (4)	S(1)—O(1)—Cu	124·1 (2)
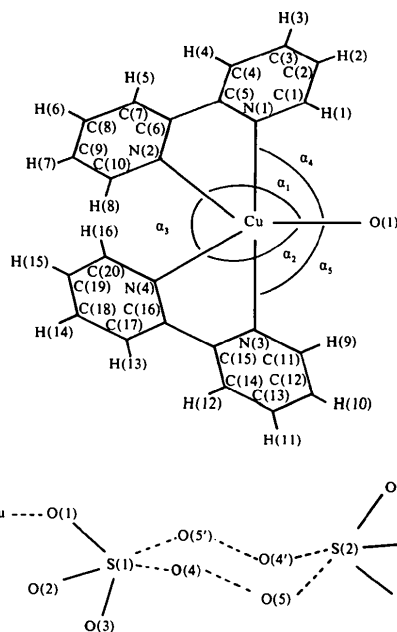
Fig. 1. The molecular structure of the Cu(bpy)₂O and S₂O₈ groups, the atom numbering and the angle notation.

disordered peroxodisulphate anion and the atom numbering.

Discussion

The structure of (I) involves molecules of [Cu(bpy)$_2$-(S$_2$O$_8$)] and uncoordinated molecules of water. The local molecular structure of (I) involves a five-coordinate CuN$_4$O chromophore with four short Cu—N

Table 4. *Equations of the plane of best fit given in the form: lX + mY + nZ + p = 0, X = a*, Y = a × c*, Z = c and p is in Å*

The deviations (Å) of the most relevant atoms from the planes are given in square brackets. The r.m.s. deviation of the planes and the angles between them are given where relevant. (E.s.d.'s 0·006–0·016 Å.)

	l	m	n	p
Plane (1): N(1), C(1)—C(5)	0·8936	0·3641	0·2626	1·7811
(r.m.s.d. = 0·0157) [N(1) −0·0246, C(3) −0·0185, C(5) 0·0168]				
Plane (2): C(6)—C(10), N(2)	0·9046	0·3407	0·2562	1·7138
(r.m.s.d. = 0·0034) [N(2) 0·0054, C(10) −0·0040]				
Plane (3): N(1), C(1)—C(10), N(2)	0·9043	0·3394	0·2590	1·7246
(r.m.s.d. = 0·0228) [N(1) −0·0482, C(2) 0·0420, C(5) 0·0264]				
Plane (4): N(3), C(11)—C(15)	0·9095	−0·3197	−0·2658	−0·2491
(r.m.s.d. = 0·0126) [N(3) −0·0213, C(11) 0·0132]				
Plane (5): N(4), C(16)—C(20)	0·9227	−0·2838	−0·2609	−0·2569
(r.m.s.d. = 0·0092) [N(4) 0·0153, C(20) −0·0105]				
Plane (6): N(3), C(11)—C(20), N(4)	0·9196	−0·2920	−0·2628	−0·2857
(r.m.s.d. = 0·0243) [N(3) −0·0464, C(12) 0·0396, C(15) −0·0325]				
Plane (7): S(1), O(4), O(5)	−0·7968	0·4898	0·3538	3·3243
Plane (8): O(4), O(5), S(2)	−0·5404	0·2912	−0·7894	−5·7436
Plane (9): S(1), O(5'), O(4')	−0·4161	0·3789	0·8266	4·2431
Plane (10): O(5'), O(4'), S(2)	0·8844	0·1800	−0·4305	−5·0677

Angles† between planes (1) and (2) = 1·5, (4) and (5) = 2·2, (3) and (6) = 48·4, (7) and (8) = 124·6, (9) and (10) = 131·0°.

† E.s.d.'s 0·4–1·5°.

distances and one long Cu—O distance. With the nomenclature of Fig. 1 for a trigonal-bipyramidal [Cu(bpy)$_2$X]Y system, the out-of-plane Cu—N(1) and Cu—N(3) distances are only just significantly different (mean 1·965 Å) and almost linear, with N(1)—Cu—N(3) = 172·2°. The two in-plane Cu—N distances are not significantly different (average 2·036 Å) and are longer than the out-of-plane Cu—N distance by 0·071 Å, only slightly less than the difference of 0·1 Å previously observed in trigonal-bipyramidal Cu^{II} complexes (Huq & Skapski, 1971). The in-plane Cu—O(1) distance of 2·367 Å suggests a significant elongation compared with a normal Cu—O distance of ca 2·00 Å (Hathaway & Hodgson, 1973). In (I), the out-of-plane angular distortions are 90 ± 10°, as obtained previously for [Cu(bpy)$_2$X]Y systems involving a near trigonal-bipyramidal chromophore stereochemistry (Harrison, Hathaway & Kennedy, 1979), but they differ in that N(1)—Cu—O(1) (a_4) and N(3)—Cu—O(1) (a_5), 84·8 and 87·8° respectively, are significantly less than 90°, whereas these angles are normally equal to or greater than 90° in [Cu(bpy)$_2$X]Y systems (Table 5), with two exceptions: a_4 for [Cu(bpy)$_2$I]I (Barclay, Hoskins & Kennard, 1963) and [Cu(bpy)$_2$(H$_2$O)]S$_5$O$_6$ (Harrison, Hathaway & Kennedy, 1979) of 89·1 and 89·0°, respectively. Only three complexes have both a_4 and a_5 less than 90°, namely, [Cu(bpy)$_2$(H$_2$O)]S$_2$O$_6$, [Cu(bpy)$_2$(NO$_3$)]NO$_3$ (Nakai, Ooi & Kuroya, 1970) and (I) (see later).

The in-plane angles of (I) show very significant deviations from the 120° necessary for regular trigonal-bipyramidal stereochemistry. O(1)—Cu—N(4) (a_2), 126·0°, and N(2)—Cu—N(4) (a_3), 141·0°, are greater than 120° and N(2)—Cu—O(1) (a_1), 93·0°, is signifi-

Table 5. *Some bond angles (°) for [Cu(bpy)$_2$X]Y systems (see Fig. 1 for notation)*

	Space group	Complex	a_1	a_2	a_3	$a_1 - a_2$	a_4	a_5	
1	Pnan	[Cu(bpy)$_2$Cl]Cl.6H$_2$O	118·7	118·6	122·8	0·1	90·9	90·9	Stephens & Tucker (1973)
2	P1̄	[Cu(bpy)$_2$Cl].CuCl$_2$	133·4	111·1	115·5	22·3	91·0	93·5	Kaiser, Brauer, Schröder, Taylor & Rasmussen (1974)
3	P2$_1$/c	[Cu(bpy)$_2$Cl]NO$_3$.2H$_2$O	127·7	123·5	108·8	4·2	92·2	93·0	Kennedy, Ray, Sheahan & Hathaway (1980)
4	C1̄	[Cu(bpy)$_2$Cl]$_2$S$_5$O$_6$.6H$_2$O	130·5	122·1	107·3	8·4	92·0	93·3	Harrison, Hathaway & Kennedy (1979)
5	P2$_1$/c	[Cu(bpy)$_2$Cl]ClO$_4$	137·1	126·4	96·5	10·7	93·4	92·1	Kennedy, Ray, Sheahan & Hathaway (1980)
6	P2$_1$/c	[Cu(bpy)$_2$Br]BF$_4$	134·5	126·2	99·4	8·3	93·0	91·2	Hathaway & Murphy (1980)
7	P1̄	[Cu(bpy)$_2$I](ClO$_4$)	122·9	122·8	114·3	0·1	93·8	91·0	Hathaway & Murphy (1980)
8	P1̄	[Cu(bpy)$_2$I]I	124·4	121·9	113·8	2·5	89·1	91·5	Barclay, Hoskins & Kennard (1963)
9	P2$_1$/c	[Cu(bpy)$_2$(NH$_3$)](BF$_4$)$_2$	129·5	122·3	108·2	7·2	92·7	91·6	Stephens (1972)
10	C2/c	[Cu{(bpy)$_2$(NCS)}]BF$_4$	138·2	117·2	104·2	22·6	94·9	91·8	Hathaway (1980)
11	P2$_1$/n	[Cu(bpy)$_2$(CN)]NO$_3$.2H$_2$O	138·0	126·5	95·4	11·5	94·5	94·5	Hathaway (1980)
12	P2$_1$/c	[Cu(bpy)$_2${SC(NH$_2$)$_2$}](ClO$_4$)$_2$	125·1	124·4	110·5	0·7	93·4	92·3	Ferrari, Corradi, Fava, Palmieri, Nardelli & Pelizzi (1973)
13	P2$_1$/c	[Cu(bpy)$_2$(H$_2$O)]S$_5$O$_6$	143·6	104·9	111·4	28·7	89·0	91·4	Harrison, Hathaway & Kennedy (1979)
14	C2/c	[Cu(bpy)$_2$(H$_2$O)]S$_2$O$_4$	115·0	115·0	129·8	0·0	87·3	87·3	Harrison & Hathaway (1979)
15	P1̄	[Cu(bpy)$_2$(NO$_3$)]NO$_3$	127·7	91·9	140·4	35·8	85·9	85·4	Nakai, Ooi & Kuroya (1970)
16	P1̄	[Cu(bpy)$_2$(S$_2$O$_8$)].H$_2$O	126·0	93·0	141·0	32·3	84·8	87·8	This work

cantly less than 120°. Thus, relative to a regular trigonal-bipyramidal CuN_4O chromophore, the Cu–O(1) bond shows a significant elongation, α_3 a significant increase (21°) above 120°, and there is a difference of 33° between α_1 and α_2.

The first two types of distortion have been observed in the local molecular stereochemistry of $[Cu(bpy)_2(H_2O)]S_2O_6$ [Fig. 2(b)] (Harrison & Hathaway, 1979) in which Cu–O(1) is elongated to 2·158 Å, α_3 is increased to 129·8° and α_1 and α_2 are decreased symmetrically to 115·0°. In (I) there is a further lenghtening of Cu–O(1) to 2·367 Å and a further increase in α_3 to 141·0°, but, in addition, there is an unsymmetrical distortion of α_1 and α_2, such that the former increases to 126·0° and the latter decreases to 93·0°, a difference of 33°. A comparable stereochemistry has been observed in $[Cu(bpy)_2(NO_3)]$-NO_3 (Nakai, Ooi & Kuroya, 1970), described as trigonal bipyramidal, but without a full appreciation of the in-plane angular distortions involved. The local molecular stereochemistry of $|Cu(bpy)_2(NO_3)|NO_3$ is, nevertheless, very similar to that of (I), but as the data were only refined to an R of 0·13, there is little value in a detailed comparison with the more accurate data of (I). The three structures of Fig. 2 are characterized in that α_3 is significantly above the

Fig. 2. The local molecular stereochemistries of (a) $|Cu(bpy)_2$-$(S_2O_8)|.H_2O$; (b) $[Cu(bpy)_2(H_2O)]S_2O_6$ and (c) $[Cu(bpy)_2$-$(NO_3)]NO_3$. (Distances are in Å, angles in degrees.)

Fig. 3. Correlation between the N(1)–Cu–O(1) (α_4) (●) and N(3)–Cu–O(1) (α_5) (O) angles and N(2)–Cu–N(4) (α_3) angles.

Table 6. *Equations for the mean plane through* N(1), N(2), N(3), N(4) *(see Table 4 for notation) for* $[Cu(bpy)_2(S_2O_8)].H_2O$, $[Cu(bpy)_2(NO_3)]NO_3.H_2O$, *and* $|Cu(bpy)_2(H_2O)|S_2O_6$

See Table 4 for e.s.d.'s on $|Cu(bpy)_2(S_2O_8)|.H_2O$.

	l	m	n	p
(a) $|Cu(bpy)_2(S_2O_8)|.H_2O$	0·9994	0·0250	0·0243	1·3074
(r.m.s.d. = 0·4068) [N(1) 0·4075, N(2) −0·4050, N(3) 0·4062, N(4) −0·4087, Cu 0·2729]				
(b) $|Cu(bpy)_2(NO_3)|NO_3.H_2O$	0·7515	0·5719	0·3288	−3·5782
(r.m.s.d. = 0·4323) [N(1) −0·4430, N(2) 0·4215, N(3) −0·4213, N(4) 0·4428, Cu −0·2627]				
(c) $|Cu(bpy)_2(H_2O)|S_2O_6$	1·0000	0·0000	0·0000	−10·2418
(r.m.s.d. = 0·4737) [N(1) −0·4737, N(2) 0·4737, N(1') −0·4737, N(2') 0·4737, Cu −0·3801]				

trigonal angle of 120°, an angle which is opposite the Cu–O(1) elongated bond of the square-pyramidal description of this stereochemistry, with N(1)–N(4) forming the basal plane. Because of the angular distortions present, the mean basal plane, Table 6, has a high r.m.s. deviation with N(1) and N(3) lying on the same side of the plane as the Cu^{II} atom and N(2) and N(4) on the opposite side, reflecting the near-linear N(1)–Cu–N(3) angle and the near-trigonal, 141·0°, α_3 angle. But, in addition, the Cu atom lies nearer to the mean plane than do N(1) and N(3), in accordance with the above comment (Table 5) that in the three complexes of Fig. 2 α_4 and α_5 are significantly less than 90°. This suggests that there may be a significant correlation between the magnitude of α_3 and those of α_4 and α_5, as illustrated in Fig. 3. For $[Cu(bpy)_2X]Y$ complexes with an approximately trigonal-bipyramidal stereochemistry, for values of α_3 *below* 120°, the values of α_4 and α_5 lie *above* 90°, while for complexes with values of α_3 *above* 120°, the out-of-plane angles are *less* than 90°.

The sense of these distortions, Fig. 2, can be rationalized in terms of the Berry twist mechanistic pathway (Berry, 1960) which describes the inter-conversion of a regular trigonal-bipyramidal stereochemistry to a regular square-pyramidal stereochemistry *via* the bonding modes of vibration of an MX_5 chromophore of C_{2v} symmetry, Fig. 4. With five equivalent ligands, only one square-pyramidal stereochemistry is involved, but with non-equivalent ligands, as in the CuN_4X chromophore of the $[Cu(bpy)_2X]Y$ system, different stereoisomers of the square-pyramidal stereochemistry arise depending on which ligand atom is involved in the elongation of the fifth coordinate position, Fig. 5, *via* the *A*, *B* and *C* distortion pathways of the Berry twist. The elongation is *via* the Cu–*X*, −N(4) and −N(2) bonds respectively for the *A*, *B* and *C* routes, with the *B* and *C* routes equivalent due to the equivalence of the two bpy ligands. The various five-coordinate structures of the $[Cu(bpy)_2X]Y$ complexes, Table 5, then represent different structural distortions of the two alternative reaction pathways

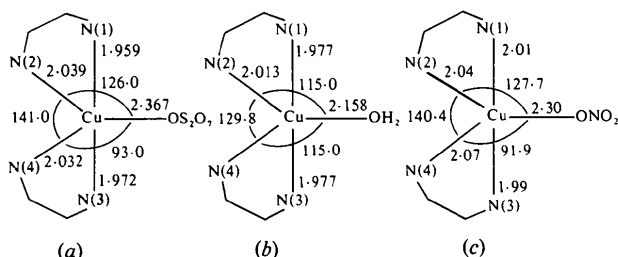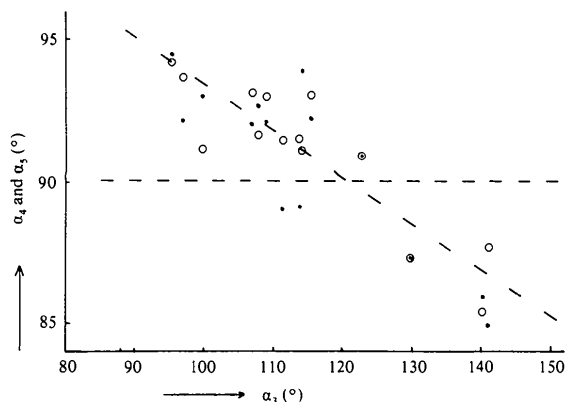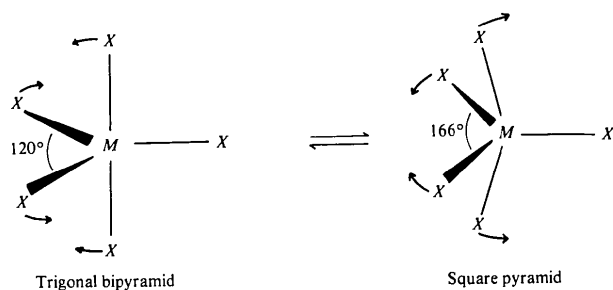Fig. 4. The Berry twist mechanism for interconversion of a regular trigonal bipyramid to a square pyramid *via* the *e* mode of vibration.
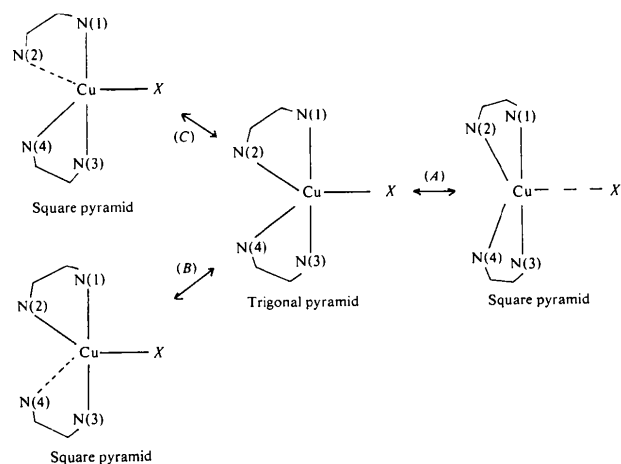

Fig. 5. The mechanistic reaction pathway for the CuN_4X chromophore of the $[Cu(bpy)X]Y$ complexes for distortion from trigonal bipyramid to square pyramid, involving three alternative pathways.

Fig. 6. The correlation of $(\alpha_1 - \alpha_2)$ and α_3 (see Table 5 for notation).

available, with the precise geometry determined by van der Waals and lattice-packing factors associated with each crystal lattice and yielding a range of distorted $[Cu(bpy)_2X]Y$ stereochemistries, each representing one structural point in the mechanistic pathway of the Berry twist. The angular distortions in the CuN_4X chromophores are more crystallographically significant than the bond-length distortions, particularly those involving the in-plane trigonal angles α_1, α_2, and α_3. Fig. 6 shows a plot of α_3 against $(\alpha_1 - \alpha_2)$ for all the five-coordinate $[Cu(bpy)_2X]Y$ complexes. The bulk of these are in section D of Fig. 6 with $\alpha_1 - \alpha_2 < 15°$ and $\alpha_3 = 95-130°$, and are best considered as trigonal bipyramidal with near C_{2v} symmetry. The most regular is $[Cu(bpy)_2Cl]Cl.6H_2O$ and only $[Cu(bpy)_2(H_2O)]-S_2O_6$ has α_3 significantly greater than $120°$ ($129·8°$). Section E contains three complexes with $\alpha_3 < 120°$ and $\alpha_1 - \alpha_2 > 20°$. These are best considered as distorted trigonal bipyramidal with the square-pyramidal distortion described by route B (or C) of Fig. 5, such that the Cu—N(4) direction is the elongation axis. Section F of
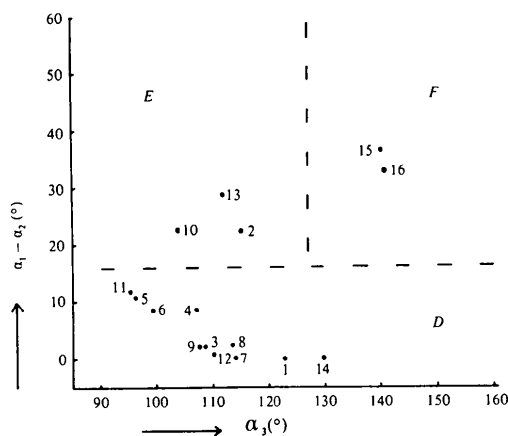
Fig. 6 only contains two complexes, including (I), and has $\alpha_3 > 120°$ and $\alpha_1 - \alpha_2 > 20°$; the complexes are best described as intermediate in stereochemistry between trigonal bipyramidal and square pyramidal with the sense of the square-pyramidal distortion represented by route A of Fig. 5.

The five-coordinate $[Cu(bpy)_2X]Y$ complexes of Table 5 then represent a series of closely graded stereochemistries of the CuN_4X chromophore, which nicely illustrate the plasticity effect (Gazo *et al.*, 1976) in the stereochemistry of the Cu^{II} ion and with which it is hoped to establish, elsewhere, a correlation between the electronic properties of the complexes and the stereochemistries, particularly where cation distortion isomers are involved (Ray, Hulett, Sheahan & Hathaway, 1978).

The pyridine rings of (I) are reasonably planar, Table 4, and the angles of twist of the pyridine rings of the individual bpy ligands are small ($1·52$ and $2·21°$, Table 4) and consistent with the angles previously reported for the bpy ligand in $[Cu(bpy)_2X]Y$ complexes ($0·0-11·6°$; Stephens, 1969, 1972). The low values, $<3°$, are consistent with the small differences in the Cu—N distances to the individual bpy ligands of $0·067$ and $0·073$ Å for the N(1), N(2) and N(3), N(4) bpy ligands respectively, differences which represent near-symmetrical coordination of the bpy ligands, and are reflected in the near equivalence of the bite angles N(1)—Cu—N(2) and N(3)—Cu—N(4) of $81·4$ and $81·7°$, respectively, and must represent one of the least-strained pairs of bpy ligands in the $[Cu(bpy)_2X]Y$ series (Anderson, 1972).

The structure of the $S_2O_8^{2-}$ anion is complicated by the presence of disorder in the peroxo group in the anion, the sense of which is illustrated in Fig. 1. The disorder is restricted to the peroxo group and does not extend to the terminal SO_3 groups. The site-occupation factor of the disordered peroxo group, initially $0·5$, refined to a value of $0·57$ and was fixed. At this point

the terminal SO_3 groups were checked for disorder but none was found. Because of the disorder, the bond lengths and angles of the $S_2O_8^{2-}$ group are not too reliable. The bond lengths in the SO_3 groups are 1·40–1·45 Å with the longest, S(1)—O(1) = 1·451 (3), which is significantly different from the rest, consistent with the involvement of O(1) in semi-coordination to the Cu^{II} atom (Procter, Hathaway & Nicholls, 1968) at 2·367 Å. The S—O(1) bond in the elongated rhombic octahedral complex $[Cu(bpy)_2(S_4O_6)]$ showed no evidence for a longer S—O bond due to semi-coordination of O(1) to the Cu^{II} atom and must be associated with the significantly longer Cu—O(1) distance in the tetrathionate of 2·63 Å (Harrison & Hathaway, 1978). The S to terminal O atom angles are approximately tetrahedral, Table 3, but, due to the disorder, four O—S—O angles involving the peroxo O atom are much smaller, 88–90°. The S to peroxo O bond lengths, 1·68 and 1·66 Å, are significantly longer than the terminal S—O distances, due to their greater single-bond character (Wells, 1975). The peroxo O—O distance, 1·47 Å, compares with the 1·49 Å in H_2O_2 and 1·47 Å in $[B_2(O_2)_2(OH)_4]^{2-}$ (Wells, 1975). The angles at the peroxo O atoms are 106 ± 2° and contrast with the value of 125° in $Cs_2S_2O_8$ and $(NH_4)S_2O_8$ (Zachariasen & Mooney, 1934), but as this early structure also reports rather short O—O and S—O distances, 1·31 and 1·50 Å respectively, considerably shorter than the above, the angle may also be in doubt. The dihedral angles of the peroxo group, 124·6 and 131·0°, Table 4, are considerably larger than the 93·5° in H_2O_2 (Wells, 1975), a difference that may arise from repulsion between the bulky terminal SO_3 groups in (I).

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