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The Crystal Structures of Monoaquabis(2,2′-bipyridyl)copper(II) Disulphonatotrisulphane and Bis[bis(2,2′-bipyridyl)monochlorocopper(II)] Disulphonatotrisulphane Hexahydrate

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Abstract

The crystal structures of monoaquabis(2,2′-bipyridyl)copper(II) disulphonatotrisulphane, $C_{20}H_{18}CuN_4O^{2+}.O_6S_5^{2-}$, $[Cu(C_{10}H_8N_2)_2(H_2O)]S_5O_6$, (I) and bis[bis(2,2′-bipyridyl)monochlorocopper(II)] disulphonatotrisulphane hexahydrate, $2C_{20}H_{16}ClCuN_4^+.O_6S_5^{2-}.6H_2O$, $[Cu(C_{10}H_8N_2)_2Cl]_2S_5O_6.6H_2O$, (II) have been determined by X-ray analysis. (I) crystallizes in the monoclinic space group $P2_1/c$ with a = 7·651 (2), b = 12·980 (3), c = 26·140 (5) Å, β = 95·50 (5)°, Z = 4; (II) crystallizes in the triclinic space group $C\bar{1}$ with a = 20·577 (4), b = 14·177 (3), c = 8·726 (2) Å, α = 94·72 (5), β = 101·91 (5), γ = 92·03 (5)°, Z = 2. Both structures involve a distorted five-coordinate $[Cu(bpy)_2X]^{2+}$ cation and disulphonatotrisulphane anions. (I) involves the first structure reported in the solid state of a monoaquabis(2,2′-bipyridyl)copper(II) cation, while (II) involves the most distorted bis(2,2′-bipyridyl)monochlorocopper(II) cation. Both complexes involve the disulphonatotrisulphane anion with the previously unreported *trans* S_5 chain configuration.

Introduction

As part of a programme to investigate the stereochemistry of the polythionate anions $[S_nO_6]^{2-}$ and their ability to determine the stereochemistry of the $Cu(bpy)_2^{2+}$ cation (bpy = 2,2′-bipyridyl) (Ferrari, Fava & Pelizzi, 1977; Harrison & Hathaway, 1978) the crystal structures of $[Cu(bpy)_2(H_2O)]S_5O_6$ (I) and $[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$ (II) have been determined.

Experimental

Potassium disulphonatotrisulphane sesquihydrate ($K_2S_5O_6.1\frac{1}{2}H_2O$) was prepared by the method of Palmer (1970). The complexes (I) $[Cu(bpy)_2(H_2O)]S_5O_6$ and (II) $[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$ were prepared by addition of a stoichiometric amount of $K_2S_5O_6.1\frac{1}{2}H_2O$ to aqueous solutions of $Cu(bpy)_2(ClO_4)_2$ and $Cu(bpy)_2Cl_2.6H_2O$, respectively (McKenzie, 1962). In both preparations turquoise-blue crystals were deposited over a period of days and recrystallized from hot water. (I), found: C = 37·33, H = 3·21, N = 8·33, S = 24·15, Cu = 9·60%; calculated for $C_{20}H_{18}CuN_4O_7S_5$: C = 36·94, H = 2·79, N = 8·65, S = 24·65, Cu = 9·77%; (II), found: C = 40·44, H = 3·11, N = 9·44, S = 13·50, Cl = 6·09, Cu = 10·79%; calculated for $C_{40}H_{44}Cl_2Cu_2N_8O_{12}S_5$: C = 40·46, H = 3·73, N = 9·44, S = 13·50, Cl = 5·97, Cu = 10·70%.

The crystal and refinement data for (I) and (II) are summarized in Table 1. For both complexes the

Table 1. *Crystal and refinement data*

	(I)	(II)
Compound	$[Cu(bpy)_2H_2O]S_5O_6$	$[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$
M_r	650·25	1187·16
Stoichiometry	$C_{20}H_{18}CuN_4O_7S_5$	$C_{40}H_{32}Cl_2Cu_2N_8O_6$-$S_5.6H_2O$
Space group	$P2_1/c$ (monoclinic)	$C1$ (triclinic)
a (Å)	7·651 (2)	20·577 (4)
b (Å)	12·980 (3)	14·177 (3)
c (Å)	26·140 (5)	8·726 (2)
α (°)	–	94·72 (5)
β (°)	95·50 (5)	101·91 (5)
γ (°)	–	92·03 (5)
Z	4	2
U (Å^3)	2584·01	2478·78
D_m (Mg m^{-3})	1·70 (5)	1·57 (5)
D_c (Mg m^{-3})	1·67	1·59
Radiation (λ = 0·7107 Å)	Mo $K\alpha$	Mo $K\alpha$
F(000)	1323·96	1215·96
μ (mm^{-1})	1·233	1·185
Number of unique reflections	3341	3604
Number of varied parameters	119	175
$R = (\sum \Delta/\sum\lvert F_o\rvert)$	0·0491	0·0625
$R_w = (\sum \Delta w^{1/2}/\sum \lvert F_o\rvert w^{1/2})$	0·0536	0·0760
k	1·0037	1·3754
g	0·001394	0·001536
Maximum final shift/e.s.d.	0·031	0·063
Residual electron density (e Å^{-3})	0·52	0·54
Number of anisotropic atoms	37	35

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Table 2. *Fractional coordinates* (× 10^4) *for non-hydrogen atoms*

	(I) $[Cu(bpy)_2(H_2O)]S_5O_6$			(II) $[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$		
	x	*y*	*z*	*x*	*y*	*z*
Cu	1704 (1)	2902 (1)	6510 (1)	3784 (1)	1214 (1)	2250 (1)
*X**	−74 (4)	3568 (2)	6949 (1)	4027 (1)	313 (1)	157 (2)
N(1)	3701 (5)	3421 (3)	6979 (1)	3993 (2)	2415 (3)	1373 (4)
C(1)	4120 (6)	3037 (4)	7451 (2)	4545 (3)	2578 (4)	811 (7)
C(2)	5461 (6)	3441 (4)	7780 (2)	4657 (3)	3409 (3)	171 (7)
C(3)	6396 (6)	4254 (4)	7617 (2)	4198 (3)	4081 (4)	117 (8)
C(4)	5993 (6)	4649 (4)	7135 (2)	3632 (3)	3932 (4)	710 (7)
C(5)	4621 (5)	4206 (4)	6816 (2)	3538 (2)	3072 (3)	1324 (5)
C(6)	4056 (6)	4603 (4)	6295 (2)	2946 (2)	2825 (3)	1964 (5)
C(7)	4865 (8)	5376 (5)	6057 (2)	2436 (3)	3423 (4)	2035 (6)
C(8)	4188 (9)	5693 (6)	5578 (3)	1904 (3)	3120 (5)	2631 (6)
C(9)	2711 (9)	5218 (6)	5346 (2)	1890 (3)	2234 (5)	3149 (7)
C(10)	1961 (7)	4429 (5)	5595 (2)	2419 (2)	1654 (4)	3030 (6)
N(2)	2600 (5)	4128 (3)	6064 (2)	2939 (2)	1950 (3)	2454 (4)
N(3)	−273 (5)	2364 (3)	6046 (2)	3557 (2)	87 (3)	3289 (4)
C(11)	−1789 (6)	2880 (5)	5918 (2)	3104 (3)	−609 (4)	2596 (7)
C(12)	−3148 (6)	2456 (6)	5596 (2)	2962 (3)	−1387 (4)	3345 (7)
C(13)	−2944 (7)	1464 (5)	5418 (2)	3288 (3)	−1438 (4)	4870 (7)
C(14)	−1403 (7)	928 (5)	5546 (2)	3759 (3)	−730 (4)	5604 (6)
C(15)	−63 (6)	1410 (4)	5863 (2)	3891 (2)	24 (3)	4776 (5)
C(16)	1671 (6)	949 (3)	6013 (2)	4398 (2)	801 (3)	5424 (5)
C(17)	2183 (7)	−10 (4)	5843 (2)	4784 (2)	854 (4)	6937 (6)
C(18)	3881 (7)	−348 (4)	5994 (2)	5250 (3)	1607 (4)	7416 (6)
C(19)	4994 (7)	249 (4)	6314 (2)	5312 (2)	2284 (4)	6418 (6)
C(20)	4395 (6)	1199 (4)	6470 (2)	4915 (2)	2169 (3)	4927 (6)
N(4)	2770 (5)	1541 (3)	6325 (1)	4464 (2)	1454 (3)	4423 (4)
S(1)	1867 (2)	2616 (1)	9486 (1)	1293 (1)	−514 (1)	4169 (2)
S(2)	2042 (2)	2900 (1)	8695 (1)	685 (2)	581 (2)	4796 (5)
S(3)	−456 (2)	2751 (1)	8387 (1)	−243 (2)	−127 (4)	3892 (4)
S(4)	944 (2)	6234 (1)	6755 (1)			
S(5)	748 (2)	6101 (1)	7548 (1)			
O(1)	1451 (8)	1548 (4)	9494 (2)	1424 (3)	−391 (5)	2634 (8)
O(2)	3655 (6)	2813 (4)	9676 (2)	943 (5)	−1436 (6)	3864 (16)
O(3)	618 (7)	3298 (4)	9655 (2)	1809 (9)	−336 (19)	5353 (15)
O(4)	1317 (5)	5041 (3)	7633 (1)			
O(5)	1944 (4)	6852 (2)	7802 (1)			
O(6)	−1058 (4)	6292 (3)	7632 (2)			
O(2′)				1180 (6)	−1205 (12)	5054 (28)
O(3′)				1880 (5)	4 (9)	5095 (17)
S(2′)				498 (2)	418 (2)	3957 (4)
O(5H2)				1681 (3)	−3358 (4)	1276 (7)
O(6H2)				7872 (4)	980 (4)	1653 (7)
O(7H2)				1311 (3)	−1722 (4)	59 (7)

* *X* = O(7) in (I) and Cl in (II).

Table 3. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

	(I)	(II)		(I)	(II)		(I)	(II)
Cu—*X*	2·054 (5)	2·292 (4)	C(9)—C(8)	1·376 (11)	1·370 (10)	N(4)—C(20)	1·341 (7)	1·331 (7)
N(1)—Cu	1·983 (5)	1·992 (6)	C(10)—C(9)	1·370 (10)	1·402 (9)	O(1)—S(1)	1·422 (6)	1·442 (9)
N(2)—Cu	2·123 (6)	2·092 (6)	N(2)—C(10)	1·334 (7)	1·340 (8)	O(2)—S(1)	1·432 (6)	1·448 (10)
N(3)—Cu	1·973 (6)	1·988 (6)	C(11)—N(3)	1·353 (7)	1·346 (7)	O(3)—S(1)	1·405 (6)	1·321 (16)
N(4)—Cu	2·024 (6)	2·106 (5)	C(15)—N(3)	1·343 (7)	1·349 (6)	S(2)—S(1)	2·119 (4)	2·134 (6)
C(1)—N(1)	1·342 (7)	1·346 (8)	C(12)—C(11)	1·388 (8)	1·380 (9)	S(3)—S(2)	2·011 (4)	2·096 (7)
C(5)—N(1)	1·332 (7)	1·342 (7)	C(13)—C(12)	1·383 (11)	1·371 (9)	S(4)—S(3)	2·031 (5)	
C(2)—C(1)	1·377 (7)	1·377 (10)	C(14)—C(13)	1·382 (9)	1·387 (8)	S(5)—S(4)	2·099 (4)	
C(3)—C(2)	1·365 (8)	1·362 (10)	C(15)—C(14)	1·403 (8)	1·387 (8)	O(4)—S(5)	1·454 (5)	
C(4)—C(3)	1·368 (8)	1·385 (11)	C(16)—C(15)	1·474 (7)	1·482 (7)	O(5)—S(5)	1·454 (4)	
C(5)—C(4)	1·401 (7)	1·395 (8)	C(17)—C(16)	1·389 (8)	1·388 (7)	O(6)—S(5)	1·441 (4)	
C(6)—C(5)	1·482 (7)	1·482 (8)	N(4)—C(16)	1·354 (6)	1·346 (7)	O(2′)—S(1)		1·339 (22)
C(7)—C(6)	1·361 (9)	1·380 (8)	C(18)—C(17)	1·392 (9)	1·387 (8)	O(3′)—S(1)		1·445 (11)
N(2)—C(6)	1·362 (7)	1·346 (7)	C(19)—C(18)	1·375 (8)	1·367 (9)	S(2′)—S(1)		2·127 (6)
C(8)—C(7)	1·371 (10)	1·375 (10)	C(20)—C(19)	1·390 (8)	1·380 (8)	S(3)—S(2′)		1·674 (7)

preliminary cell dimensions and space group were determined from precession photographs and refined on a Phillips PW 1100 four-circle diffractometer. The intensities were collected on the diffractometer with graphite-monochromatized Mo *Kα* radiation. A θ–2θ scan mode was used and reflections with $3{\cdot}0 < \theta < 32°$ 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)° was used. With an acceptance criterion of $I > 2{\cdot}5\sigma(I)$, 3341 reflections for (I) and 3558 for (II) were retained. Lorentz and polarization corrections were applied, but none for absorption. The structures were solved by Patterson and Fourier techniques and refined by a full-matrix least-squares procedure with anisotropic temperature factors for all non-hydrogen atoms. The positions of the H atoms were calculated geometrically (except for those of the water molecules), and floated on the adjacent C atoms assuming C—H = 1·08 Å and a fixed temperature factor of 0·07 Å^2. The refinement converged when the maximum shift/e.s.d. was <0·05 with a weighting scheme $w = k/[\sigma^2(F_o) + g(F_o)^2]$ (Table 1). Complex atomic scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). All calculations were carried out with *SHELX* 76 (G. M. Sheldrick), and *PLUTO* (S. Motherwell), on an IBM 370/138 computer. The final non-hydrogen atomic coordinates and e.s.d.'s are given in Table 2; Table 3 gives the bond lengths, Table 4 the bond angles, and Table 5 details of some mean planes. Fig. 1 illustrates the structures and atom numbering.*

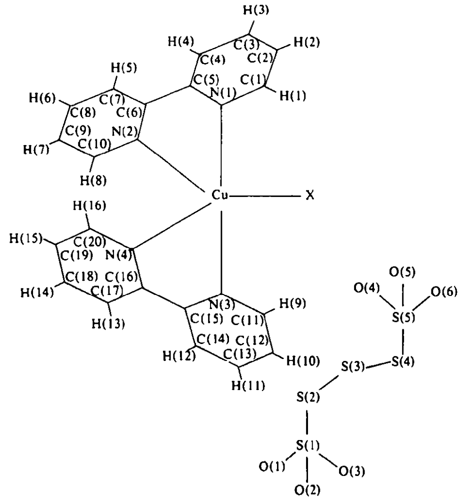

Fig. 1. The structure of the $Cu(bpy)_2X$ cation and $[S_5O_6]^{2-}$ ion and the atom numbering.

Table 4. *Bond angles* (°) *with e.s.d.'s in parentheses*

$[Cu(bpy)_2(H_2O)]S_5O_6$		$[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$	
N(1)–Cu–O(7)	91·4 (2)	N(1)–Cu–Cl	92·0 (2)
N(2)–Cu–O(7)	104·9 (2)	N(2)–Cu–Cl	130·7 (1)
N(2)–Cu–N(1)	79·3 (2)	N(2)–Cu–N(1)	79·9 (3)
N(3)–Cu–O(7)	89·0 (2)	N(3)–Cu–Cl	93·3 (2)
N(3)–Cu–N(1)	179·1 (2)	N(3)–Cu–N(1)	174·8 (2)
N(3)–Cu–N(2)	101·4 (3)	N(3)–Cu–N(2)	96·7 (3)
N(4)–Cu–O(7)	143·6 (1)	N(4)–Cu–Cl	122·0 (2)
N(4)–Cu–N(1)	98·0 (2)	N(4)–Cu–N(1)	97·5 (2)
N(4)–Cu–N(2)	111·4 (3)	N(4)–Cu–N(2)	107·3 (2)
N(4)–Cu–N(3)	81·2 (3)	N(4)–Cu–N(3)	79·7 (2)
C(1)–N(1)–Cu	123·0 (4)	C(1)–N(1)–Cu	123·8 (5)
C(5)–N(1)–Cu	117·5 (4)	C(5)–N(1)–Cu	116·2 (4)
C(5)–N(1)–C(1)	119·5 (5)	C(5)–N(1)–C(1)	120·0 (5)
C(2)–C(1)–N(1)	122·0 (5)	C(2)–C(1)–N(1)	121·6 (6)
C(3)–C(2)–C(1)	118·8 (6)	C(3)–C(2)–C(1)	118·8 (7)
C(4)–C(3)–C(2)	119·9 (5)	C(4)–C(3)–C(2)	120·4 (7)
C(5)–C(4)–C(3)	119·0 (5)	C(5)–C(4)–C(3)	118·5 (6)
C(4)–C(5)–N(1)	120·8 (5)	C(4)–C(5)–N(1)	120·6 (5)
C(6)–C(5)–N(1)	116·3 (5)	C(6)–C(5)–N(1)	116·0 (4)
C(6)–C(5)–C(4)	122·8 (5)	C(6)–C(5)–C(5)	123·3 (6)
C(7)–C(6)–C(5)	124·8 (5)	C(7)–C(6)–C(5)	123·8 (5)
N(2)–C(6)–C(5)	113·8 (5)	N(2)–C(6)–C(5)	114·2 (4)
N(2)–C(6)–C(7)	121·4 (5)	N(2)–C(6)–C(7)	122·0 (5)
C(8)–C(7)–C(6)	119·3 (7)	C(8)–C(7)–C(6)	119·2 (6)
C(9)–C(8)–C(7)	119·4 (8)	C(9)–C(8)–C(7)	119·7 (6)
C(10)–C(9)–C(8)	119·3 (7)	C(10)–C(9)–C(8)	118·6 (7)
N(2)–C(10)–C(9)	121·5 (6)	N(2)–C(10)–C(9)	121·8 (6)
C(6)–N(2)–Cu	113·0 (4)	C(6)–N(2)–Cu	113·7 (4)
C(10)–N(2)–Cu	127·9 (4)	C(10)–N(2)–Cu	127·5 (4)
C(10)–N(2)–C(6)	119·1 (5)	C(10)–N(2)–C(6)	118·8 (5)
C(11)–N(3)–Cu	124·4 (5)	C(11)–N(3)–Cu	124·2 (4)
C(15)–N(3)–Cu	115·7 (4)	C(15)–N(3)–Cu	116·8 (4)
C(15)–N(3)–C(11)	119·9 (5)	C(15)–N(3)–C(11)	119·0 (5)
C(12)–C(11)–N(3)	121·9 (6)	C(12)–C(-1)–N(3)	122·8 (6)
C(13)–C(12)–C(11)	118·1 (6)	C(13)–C(12)–C(11)	118·2 (6)
C(14)–C(13)–C(12)	120·6 (6)	C(14)–C(13)–C(12)	119·9 (6)
C(15)–C(14)–C(13)	118·4 (6)	C(15)–C(14)–C(13)	119·2 (6)
C(14)–C(15)–N(3)	121·1 (5)	C(14)–C(15)–N(3)	120·9 (5)
C(16)–C(15)–N(3)	114·6 (5)	C(16)–C(15)–N(3)	115·3 (5)
C(16)–C(15)–C(14)	124·3 (5)	C(16)–C(15)–C(14)	123·8 (5)
C(17)–C(16)–C(15)	123·6 (5)	C(17)–C(16)–C(15)	123·1 (5)
N(4)–C(16)–C(15)	114·9 (5)	N(4)–C(16)–C(15)	114·8 (4)
N(4)–C(16)–C(17)	121·5 (5)	N(4)–C(16)–C(17)	122·0 (5)
C(18)–C(17)–C(16)	118·4 (6)	C(18)–C(17)–C(16)	118·3 (6)
C(19)–C(18)–C(17)	120·1 (6)	C(19)–C(18)–C(17)	120·1 (5)
C(20)–C(19)–C(18)	118·5 (6)	C(20)–C(19)–C(18)	117·8 (6)
N(4)–C(20)–C(19)	122·2 (5)	N(4)–C(20)–C(19)	123·8 (6)
C(16)–N(4)–Cu	113·5 (4)	C(16)–N(4)–Cu	113·2 (3)
C(20)–N(4)–Cu	127·3 (4)	C(20)–N(4)–Cu	128·8 (4)
C(20)–N(4)–C(16)	119·2 (5)	C(20)–N(4)–C(16)	117·9 (5)
O(1)–S(1)–S(2)	102·7 (3)	S(2)–S(1)–O(1)	109·3 (4)
O(2)–S(1)–S(2)	99·1 (3)	S(2)–S(1)–O(2)	112·6 (6)
O(3)–S(1)–S(2)	107·8 (3)	S(2)–S(1)–O(3)	98·4 (11)
O(2)–S(1)–O(1)	112·1 (4)	O(2)–S(1)–O(1)	100·3 (7)
O(3)–S(1)–O(1)	116·7 (4)	O(3)–S(1)–O(1)	115·3 (9)
O(3)–S(1)–O(2)	115·8 (4)	O(3)–S(1)–O(2)	121·0 (13)
S(3)–S(2)–S(1)	103·2 (2)	S(3)–S(2)–S(1)	97·9 (3)
S(4)–S(3)–S(2)	103·5 (3)	O(2′)–S(1)–O(1)	140·2 (9)
O(4)–S(5)–S(4)	100·4 (3)	O(3′)–S(1)–O(1)	97·9 (7)
O(5)–S(5)–S(4)	107·2 (3)	O(3′)–S(1)–O(2′)	103·8 (10)
O(6)–S(5)–S(4)	107·2 (3)	S(2′)–S(1)–O(1)	94·8 (4)
O(5)–S(5)–O(4)	113·5 (3)	S(2′)–S(1)–O(2′)	109·5 (8)
O(6)–S(5)–O(4)	114·6 (3)	S(2′)–S(1)–O(3′)	107·5 (6)
O(6)–S(5)–O(5)	112·7 (3)	O(2)–S(1)–S(2′)	102·2 (5)
		O(3)–S(1)–S(2′)	118·7 (12)
		S(2)–S(1)–O(2′)	103·5 (9)
		S(2)–S(1)–O(3′)	90·5 (6)
		S(3)–S(2′)–S(1)	113·6 (3)

Discussion

Both compounds are made up of $[S_5O_6]^{2-}$ anions and discrete cations, $[Cu(bpy)_2(H_2O)]^{2+}$ and $[Cu(bpy)_2Cl]^+$

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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 34208 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Equations of least-squares planes in the form* $lX + mY + nZ = p$, *where* X, Y, Z *are orthogonal axes, with deviations* (Å) *of relevant atoms from the planes*

Plane	Atoms in the plane	r.m.s.d. (Å × 10^3)	l	m	n	p	Principal deviations from the plane (Å × 10^3)
$[Cu(bpy)_2(H_2O)]S_5O_6$							
1	N(1), C(1) to C(5)	6·0	−5·2241	8·2443	11·1055	8·2670	N(1) 9·9
2	C(6) to C(10), N(2)	12·7	−4·7213	8·6582	12·4077	9·8076	C(6) 13·0; C(10) 23·1
3	N(1), C(1) to C(10), N(2)	58·5	−5·0047	8·4456	11·6748	9·2404	N(1) 56·3; C(7) 67·5; C(9) 53·2; C(10) 47·3
4	N(3), C(11) to C(15)	19·7	−3·5717	−4·8577	22·0182	12·2635	C(12) −11·4; C(15) −15·3
5	C(16) to C(20), N(4)	14·6	−3·1359	−5·6773	21·8539	12·0853	N(4) −7·5
6	N(3), C(11) to C(20), N(4)	56·1	−3·3167	−5·2007	22·0887	12·1794	C(14) 53·7; C(15) 60·1; C(16) 55·3; N(4) 70·2
7	Cu, O(7), N(3), N(1)	6·3	0·5305	10·8032	−14·4840	−6·2126	Cu 10·2
8	Cu, O(7), N(2), N(4)	17·0	5·1947	2·0638	16·9486	12·4877	Cu 29·3; O(7) −11·0; N(4) −11·6
9	Cu, O(7), N(3), N(4)	259·3	3·1965	9·3007	−15·5809	−7·3184	Cu 420·2; O(7) −212·6; N(3) −217·0
10	S(1), S(2), S(3)	0	−1·2785	12·6531	4·2613	7·1130	
11	S(2), S(3), S(4)	0	−2·9759	−1·3578	24·7902	20·5531	
12	S(3), S(4), S(5)	0	7·3712	−2·5835	2·2551	0·8440	

Angles between normals to planes (°)

Plane 1–Plane 2	5·29
Plane 4–Plane 5	4·88
Plane 3–Plane 6	76·39
Plane 10–Plane 12	109·18

Plane	Atoms in the plane	r.m.s.d. (Å × 10^3)	l	m	n	p	Principal deviations from the plane (Å × 10^3)
$[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$							
1	N(1), C(1) to C(5)	5·4	5·8154	4·4675	6·9095	4·3508	C(4) 9·1
2	C(6) to C(10), N(2)	3·7	5·6970	3·9433	7·0707	4·1782	C(9) 6·2
3	N(1), C(1) to C(10), N(2)	20·1	5·7256	4·2013	6·9998	4·2334	N(1) 28·9; C(1) 19·8; C(3) −33·5; C(7) 24·0; C(10) −32·1
4	N(3), C(11) to C(15)	8·0	−16·8183	7·0558	3·9494	−4·6282	C(15) −11·8; C(12) −10·7
5	C(16) to C(20), N(4)	6·0	−16·3826	7·5309	3·8951	−4·4933	C(19) 10·0
6	N(3), C(11) to C(20), N(4)	22·3	−16·5118	7·3660	3·9377	−4·5525	N(3) 39·5; C(12) 42·7; C(15) 26·8
7	Cu, Cl, N(3), N(1)	0	17·9464	−1·2211	2·6062	7·2294	
8	Cu, Cl, N(2), N(4)	6·3	9·0617	11·7301	−4·0663	3·9491	
9	Cu, Cl, N(3), N(4)	419·5	15·2157	−9·4042	1·0048	5·5550	

Angles between normals to planes (°)

Plane 1–Plane 2	2·31
Plane 4–Plane 5	2·31
Plane 3–Plane 6	76·39

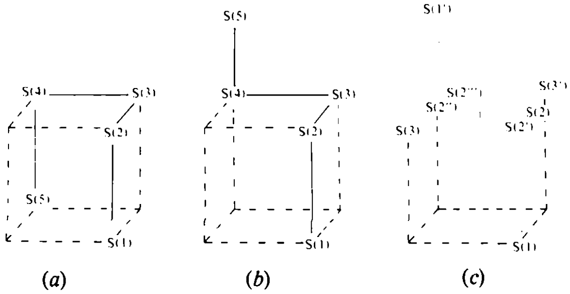

Fig. 2. Schematic representation of (*a*) the *cis* and (*b*) the *trans* configuration of the S_5 chain of the $[S_5O_6]^{2-}$ ions; (*c*) the type of disorder present in the $[S_5O_6]^{2-}$ anion of $[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$ [dihedral angles idealized at 90° (Wells, 1975)].

for (I) and (II), respectively. The latter also contains molecules of water. In neither structure is there any unusual feature in either the bond lengths or angles of the organic ligands (Stephens, 1969, 1972; Ray & Hathaway, 1978). Both Cu^{II} cations involve a distorted five-coordinate geometry with CuN_4O and CuN_4Cl chromophores in (I) and (II) respectively. There is no evidence for coordination or semicoordination of a sixth ligand or of the disulphonatotrisulphane anion in either structure; the shortest Cu···O distance is in (I) with Cu—O(6) 3·14 Å, a distance which is too long even for semicoordination (Tomlinson, Hathaway, Billing & Nichols, 1969). Thus both structures contrast with those of $Cu(bpy)_2S_3O_6$ (Ferrari, Fava & Pelizzi, 1971) and $Cu(bpy)_2S_4O_6$ (Harrison & Hathaway, 1978) which both involve the polythionate ion in a semicoordinating bridging role between two Cu^{II} atoms and contain an elongated-rhombic-octahedral CuN_4O_2 chromophore.

Both structures contain the disulphonatotrisulphane anion in the *trans* configuration. This contrasts with

Table 6. *Some* $[S_5O_6]^{2-}$ *anion bond length* (Å) *and angle* (°) *results*

	Configuration	S(1)–S(2)	S(2)–S(3)	S–O	S(1)–S(2)–S(3)	S(2)–S(3)–S(4)	S(1)–S(2)–S(3)/ S(3)–S(4)–S(5)
(I)	*trans*	2·11	2·02	1·45	103	103·5	109·2
(II)	*trans*	2·13	2·10	1·45 1·32	–	–	88·6
$BaS_5O_6.2H_2O$	*cis* Orthorhombic	2·14	2·04	1·43	103	106	110
	Triclinic	2·13	2·04	1·46	106	107	108

both the orthorhombic and triclinic forms of $BaS_5O_6.2H_2O$ (Foss & Zachariasen, 1954; Foss & Tjomsland, 1956), in which the $[S_5O_6]^{2-}$ ion is *cis* [Fig. 2(*a*) and (*b*)]. In the *cis* form the S-atom chain corresponds to an S_8 ring with three S atoms removed; in the *trans* form the chain is helical as in elemental Se and Te. As a result the *trans* form of the $[S_5O_6]^{2-}$ ion exhibits enantiomorphism, as a left- and right-handed helical S_5 chain, but due to the centrosymmetric space groups involved, $P2_1/c$ and $C\bar{1}$, both (+) and (–) forms of the $[S_5O_6]^{2-}$ ion are present in the unit cells of (I) and (II). Table 6 lists some bond lengths and angles for the $[S_5O_6]^{2-}$ ion in some known crystal structures. Both modifications of the Ba salt involve $[S_5O_6]^{2-}$ in a *cis* configuration (Foss & Zachariasen, 1954; Foss & Tjomsland, 1956) which has been suggested to arise as a result of the coordination of the O atoms of the $[S_5O_6]^{2-}$ ion to the Ba cation and the preference of Ba cations for high coordination numbers. It was also suggested that the configuration of the $[S_5O_6]^{2-}$ ion in its alkali-metal salts should involve a *trans* configuration. In support of this suggestion there is no evidence for even weak coordination of the O atoms of the $[S_5O_6]^{2-}$ ions in the present complexes. The $[S_5O_6]^{2-}$ ions in (I) and (II) display some differences. In (I) the $[S_5O_6]^{2-}$ ion occupies a general position; in (II) it is involved in a disordered structure about the centre of symmetry at $(0,0,\frac{1}{2})$; the sense of this disorder is illustrated in Fig. 2(*c*) for the S_5 chains, but also applies to some of the terminal O atoms; O(1) is not disordered but O(2) and O(3) are. The disorder of the S_5 chain suggests that these two disordered S_5 chains may be connected by a mirror-image relationship of enantiomorphic structures, but the significant displacements of the disordered O(2) and O(3) atoms completely remove this relationship. Despite the disordered solution proposed, some of the O atoms still retain very high anisotropic temperature factors and for this reason the geometry of the $[S_5O_6]^{2-}$ ion in (I) is considered to be the more accurate. In comparison with the results for $BaS_5O_6.2H_2O$ there appear to be no unexpected differences between the structures of the *cis* and *trans* forms of the $[S_5O_6]^{2-}$ ion. Even the angles between the S(1)S(2)S(3) and S(3)S(4)S(5) planes (Table 6) are closely comparable.

The structure of (I) is unique in being the first reported hydrated $Cu(bpy)_2^{2+}$ cation. The $[Cu(bpy)_2(H_2O)_2]^{2+}$ cation is said to exist in aqueous solution (Jörgenson, 1955) and is believed to have a *cis* configuration (Sigel, 1972). However, there is no X-ray crystallographic evidence for the existence of this cation in a solid complex. Previously reported hydrated $Cu(bpy)_2X_2$ complexes have not involved water in the Cu^{II} ion coordination sphere (Harris, Lockyer & Waterman, 1961; McKenzie, 1962; Hathaway, Proctor, Slade & Tomlinson, 1969). The stereochemistry of the $[Cu(bpy)_2H_2O]^{2+}$ cation is clearly five-coordinate in (I) and, despite the almost linear N(1)—Cu—N(3) angle of 179·1°, the three in-plane angles of a trigonal-bipyramidal stereochemistry are grossly distorted [Fig. 3(*a*)] from a regular 120°. In particular the O(7)—Cu—N(4) angle of 143·6° suggests a stereochemistry intermediate between trigonal-bipyramidal and square-pyramidal (Druhan & Hathaway, 1979; Ray & Hathaway, 1978; Ray, Hulett, Sheahan & Hathaway, 1978). Some evidence for this is the significantly longer Cu—N(2) distance of 2·123 Å [which lies opposite the N(4)—Cu—O(7) angle of 143·6°] relative to that of 2·024 Å for Cu—N(4), suggesting that the Cu—N(2) direction represents the out-of-plane bonding direction of a distorted square-pyramidal stereochemistry. The $[Cu(bpy)_2Cl]^+$ cation of (II) is shown in Fig. 3(*b*) to involve a distorted five-coordinate stereochemistry, but more nearly related to trigonal bipyramidal than to square pyramidal. The CuN_4Cl chromophore is significantly more distorted than that of $Cu(bpy)_2Cl_2.6H_2O$ (Stephens & Tucker, 1973), Table 7, which has an almost regular set of trigonal angles, a difference that is reflected in the electronic spectra of those two cation distortion isomers (Ray, Hulett, Sheahan & Hathaway, 1978); while the more regular $[Cu(bpy)_2Cl]_2Cl.6H_2O$ complex has a single peak at 1·28 μm^{-1}, that of the

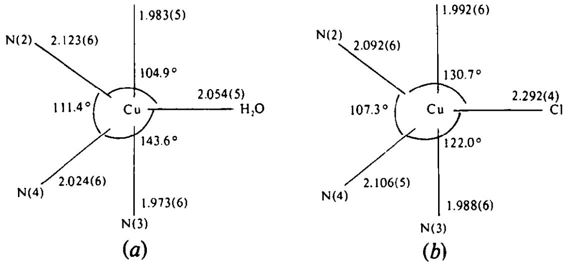

Fig. 3. The stereochemistries of the CuN_4X chromophores in (*a*) $[Cu(bpy)_2(H_2O)]S_5O_6$ and (*b*) $[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$.

Table 7. *Some ligand–copper bond angles* (°) *and electronic spectra of* $[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$ *and* $[Cu(bpy)_2Cl]Cl.6H_2O$

	$[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$	$[Cu(bpy)_2Cl]Cl.6H_2O$
Cl–Cu–N(2)	130·7	118·7
Cu–Cl–N(4)	122·0	118·6
N(2)–Cu–N(4)	107·3	122·7
Electronic reflectance (μm^{-1})	1·324, 1·047	1·28

more distorted $[Cu(bpy)_2Cl]_2S_5O_6.6H_2O$ involves two peaks with an energy difference of 0·277 μm^{-1}. The significance of this difference in the electronic energies of the Cu^{II} ion in these distorted trigonal-bipyramidal stereochemistries will be discussed elsewhere (Hathaway, Harrison & Kennedy, 1979).

The pyridine rings are reasonably planar in both (I) and (II); in (I) the pairs of pyridine rings in each 2,2′-bipyridyl ligand are inclined at angles of 5·29 and 4·88° and in (II) at angles of 2·31 and 2·31°, all of which are in reasonable agreement with previously reported values of 0·1–11° (Stephens, 1969, 1972).

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The Crystal and Molecular Structure of Hexacarbonyl-[μ-(2,4-dimethyl-4-sulfido-2-penten-3-olato)-μ-*O*,μ-*S*]-diiron(*Fe–Fe*)

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Abstract

A crystal structure analysis has been carried out for the title compound with data from a crystal cooled to *ca* 120 K. The space group is $P2_1/c$ with $Z = 4$, $a = 8{\cdot}492\,(1)$, $b = 15{\cdot}737\,(1)$, $c = 15{\cdot}499\,(1)$ Å, $\beta = 125{\cdot}129\,(5)°$. The structure was refined with 6546 data ($2\theta_{\max} = 70°$, Mo $K\alpha$) to $R = 0{\cdot}037$ and $R_w = 0{\cdot}055$. The crystalline complex displays a good approximation to the maximum allowed molecular symmetry,

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