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Bis(2,2′-bipyridyl)-*catena*-μ-tetrathionato-copper(II)

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Abstract. $C_{20}H_{16}N_4O_6S_4Cu$, M_r = 599·54, orthorhombic, *Pbcn*, a = 11·260 (10), b = 12·839 (10), c = 16·170 (11) Å, Z = 4, D_x = 1·733 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, R = 0·0379 for 1139 diffractometer data. The Cu^{II} ion lies on a twofold axis and involves a regular elongated-tetragonal octahedral stereochemistry with the two 2,2′-bipyridyl (bpy) ligands coordinating in the equatorial plane (Cu—N, 1·99 Å) but with a significant tetrahedral twist to the planes of the two ligands (56·3°). The tetrathionate ion lies on a twofold axis which bisects the central S—S bond, and bridges separate Cu^{II} atoms through semi-coordinating oxygen atoms at 2·63 Å.

Introduction. As part of a programme to examine the ability of coordinated thionate ions, $S_nO_6^{2-}$, to determine the local molecular stereochemistry of the copper(II) ion in the $(Cubpy_2)^{2+}$ cation the crystal structure of Cu(2,2′-dipyridyl)$_2S_4O_6$ has been determined.

An aqueous solution of $Na_2S_4O_6$ was prepared by adding an aqueous iodine solution to aqueous $Na_2S_2O_3$; the stoichiometric amount of a solution of $Cubpy_2Cl_2$ was added and royal-blue crystals were deposited overnight [found: C, 39·97; H, 2·74; N, 9·37; Cu, 10·43%; calculated for $Cu(C_{20}H_{16}N_4)S_4O_6$: C, 40·02; H, 2·68; N, 9·37; Cu, 10·58%]. Intensity data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. A θ–2θ scan mode was used and reflections with $3·0 < \theta < 32°$ in one quadrant were examined. A constant scan speed of 0·05° s^{-1} and a variable scan width of $(0·7 + 0·1 \tan \theta)°$ were used. With the acceptance criterion $I > 2·5\sigma(I)$, 1139 unique reflections were retained; Lorentz and polarization corrections were applied, but no correction was made for absorption [μ(Mo $K\alpha$) = 12·71 cm^{-1}]. The structure was solved using Patterson and Fourier techniques and refined by full-matrix least-squares analysis with isotropic temperature factors to R = 0·10. Anisotropic temperature factors were then refined for all non-hydrogen atoms. The positions of the H atoms were calculated geometrically and 'floated' on the adjacent carbon atoms assuming C—H 1·08 Å and a fixed temperature factor of 0·07 Å^2. The data converged when the maximum shift/e.s.d. was <0·003 with a

Table 1. *Atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

Values for H are calculated (see text).

	x	*y*	*z*
Cu	0	1533 (1)	2500
N(1)	−125 (4)	2500 (3)	3454 (2)
N(2)	625 (4)	575 (3)	3368 (2)
C(1)	−647 (5)	3430 (4)	3452 (3)
C(2)	−811 (5)	4013 (4)	4156 (3)
C(3)	−402 (6)	3604 (5)	4887 (4)
C(4)	147 (6)	2642 (4)	4910 (3)
C(5)	252 (4)	2092 (4)	4180 (3)
C(6)	766 (5)	1039 (4)	4112 (3)
C(7)	1372 (5)	539 (5)	4741 (4)
C(8)	1830 (6)	−437 (5)	4609 (4)
C(9)	1710 (5)	−898 (5)	3854 (4)
C(10)	1097 (5)	−373 (4)	3234 (4)
S(1)	4214 (1)	887 (1)	2791 (1)
S(2)	3149 (1)	1900 (1)	2059 (1)
O(1)	2227 (3)	2108 (3)	2657 (2)
O(2)	2763 (4)	1286 (3)	1366 (3)
O(3)	3851 (4)	2793 (3)	1832 (2)
H(1)	−960 (5)	3735 (4)	2869 (3)
H(2)	−1238 (5)	4766 (4)	4135 (3)
H(3)	−513 (6)	4039 (5)	5453 (4)
H(4)	490 (6)	2325 (4)	5480 (3)
H(5)	1483 (5)	924 (5)	5329 (4)
H(6)	2278 (6)	−845 (5)	5103 (4)
H(7)	2089 (5)	−1656 (5)	3735 (4)
H(8)	992 (5)	−730 (4)	2634 (4)

refined weighting scheme, $w = k[\sigma^2(F_o) + g(F_o)^2]$ with $k = 1{\cdot}177$ and $g = 0{\cdot}0002$, $R = 0{\cdot}0379$, $R_w = 0{\cdot}0380$ and $R_g = 0{\cdot}0427$. The final ratio of the number of reflections to number of parameters was 7·0 and the maximum residual electron density was 0·33 e Å^{-3}. Complex atomic scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). All calculations were carried out using the program *SHELX* 76 by G. M. Sheldrick and *PLUTO* by S. Motherwell on an IBM 370/138 computer. Final atomic coordinates and their e.s.d.'s are given in Table 1, Table 2 lists final bond lengths and Table 3 the bond angles.* Table 4 reports some relevant mean planes. Fig. 1 illustrates the molecular structure and atom numbering scheme and Fig. 2 the molecular packing viewed along the *b* axis.

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

N(1)–Cu	1·985 (6)	C(6)–C(5)	1·474 (8)
N(2)–Cu	1·995 (6)	C(7)–C(6)	1·382 (8)
C(1)–N(1)	1·331 (7)	C(8)–C(7)	1·373 (9)
C(5)–N(1)	1·355 (7)	C(9)–C(8)	1·363 (9)
C(6)–N(2)	1·352 (7)	C(10)–C(9)	1·391 (8)
C(10)–N(2)	1·346 (7)	S(2)–S(1)	2·129 (4)
C(2)–C(1)	1·375 (8)	O(1)–S(2)	1·443 (5)
C(3)–C(2)	1·374 (9)	O(2)–S(2)	1·438 (5)
C(4)–C(3)	1·381 (9)	O(3)–S(2)	1·440 (5)
C(5)–C(4)	1·380 (8)	Cu–O(1)	2·627 (6)

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

N(2)–Cu–N(1)	82·2 (3)	C(5)–C(6)–N(2)	115·1 (5)
N(1′)–Cu–N(1)	102·5 (3)	C(7)–C(6)–N(2)	120·5 (6)
C(1)–N(1)–Cu	126·2 (4)	C(7)–C(6)–C(5)	124·4 (6)
C(5)–N(1)–Cu	114·1 (4)	C(8)–C(7)–C(6)	119·8 (7)
C(5)–N(1)–C(1)	119·2 (5)	C(9)–C(8)–C(7)	119·8 (7)
C(6)–N(2)–Cu	113·3 (4)	C(10)–C(9)–C(8)	119·0 (7)
C(10)–N(2)–Cu	125·7 (5)	C(9)–C(10)–N(2)	121·2 (6)
N(2′)–Cu–N(2)	103·9 (3)	C(10)–N(2)–C(6)	119·7 (6)
C(2)–C(1)–N(1)	123·1 (6)	O(1)–S(2)–S(1)	98·4 (3)
C(3)–C(2)–C(1)	117·3 (6)	O(2)–S(2)–S(1)	105·6 (3)
C(4)–C(3)–C(2)	121·0 (6)	O(2)–S(2)–O(1)	114·0 (4)
C(5)–C(4)–C(3)	118·3 (6)	O(3)–S(2)–S(1)	108·6 (3)
C(4)–C(5)–N(1)	121·0 (6)	O(3)–S(2)–O(1)	114·7 (3)
C(6)–C(5)–N(1)	114·5 (5)	O(3)–S(2)–O(2)	113·8 (4)
C(6)–C(5)–C(4)	124·5 (6)		

Table 4. *Some relevant mean planes given in the form* $lx + my + nz = p$; *deviations* (Å $\times 10^3$) *of the most relevant atoms from the planes given in square brackets*

Plane (1): N(1), N(2), C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10)
$0{\cdot}8816x + 0{\cdot}4117y - 0{\cdot}2307z = -0{\cdot}2161$
[N(1) 125; N(2) −116]

Plane (2): N(1), C(1), C(2), C(3), C(4), C(5)
$0{\cdot}8893x + 0{\cdot}4327y - 0{\cdot}1483z = 0{\cdot}4271$
[C(4) 10·1; C(5) −14·7]

Plane (3): N(2), C(6), C(7), C(8), C(9), C(10)
$0{\cdot}8550x + 0{\cdot}4169y - 0{\cdot}3086z = -0{\cdot}7627$
[C(8) 10·0]

Interplanar angle (°) (2)–(3) 9·45.

Discussion. The local molecular structure of the Cu^{II} ion involves an elongated rhombic octahedral CuN_4O_2 chromophore with Cu^{II} on a twofold axis. The 2,2′-bipyridyl ligands bond in the *xy* plane with Cu–N bond lengths of 1·985 and 1·995 Å, and a bite angle of 82·2°. The CuN_4 involves a very flattened tetrahedron with an angle of 56·3° between the two 2,2′-bipyridyl mean planes. An oxygen atom, O(1), from the tetrathionate anion occupies the tetragonal positions above and below the Cu ion at a distance of 2·627 Å with a non-linear O(1)–Cu–O(2′) angle of 147·4°. The tetrathionate anion lies on a twofold axis which bisects the central S(1)–S(1′) bond; the anions are involved in a bridging role between two distinct Cu^{II} ions in a direction approximately parallel to *a*. All the bond lengths and angles of the anion are comparable with values reported for the free anion in $Na_2S_4O_6.2H_2O$ (Foss & Hendrik, 1958) with all S–O bonds being equivalent and yielding no significant crystallographic evidence for the semi-coordinating role (Proctor, Hathaway & Nicholls, 1968) of the O(1) oxygens to the Cu^{II} ion. In view of the high accuracy of this structure this result is disappointing. The pyridine rings of the 2,2′-bipyridyl ligands are essentially planar and

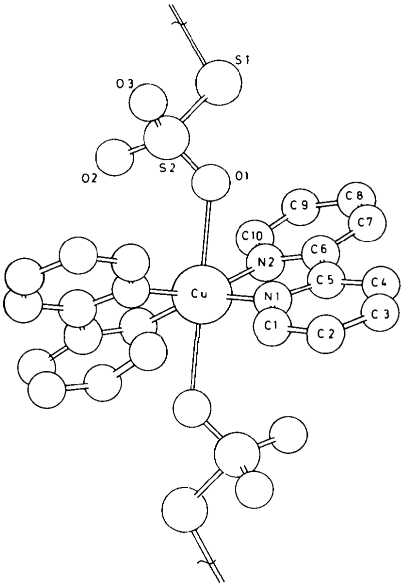

Fig. 1. The molecular structure of Cu(2,2′-bipyridyl)$_2S_4O_6$ and the atom numbering system used.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33596 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

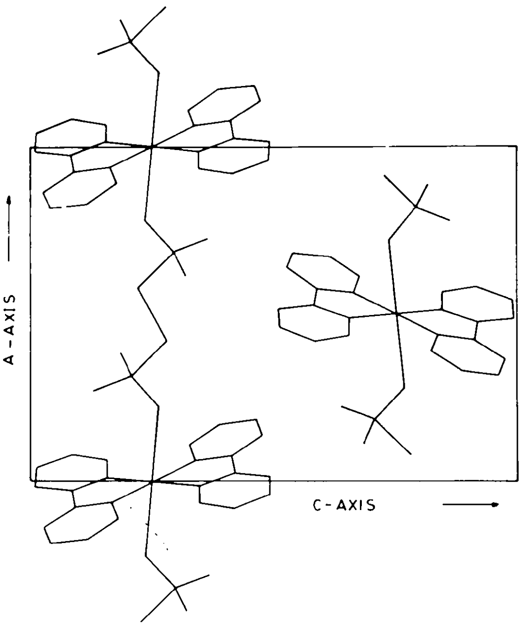

Fig. 2. The projection of the crystal structure of Cu(2,2′-bipyridyl)$_2$S$_4$O$_6$ along the *b* axis.

orientated at angle of 9·45° with respect to each other; there are no unusual bond lengths or angles in the 2,2′-bipyridyl ligands (Tables 2 and 3). Cubpy$_2$S$_4$O$_6$ is nearly isomorphous with the corresponding Cubpy$_2$S$_3$O$_6$ complex [a = 10·29 (2), b = 13·05 (2), c = 16·38 (2) Å, *Pbcn*, Cu–N = 1·98, Cu–O(2) = 2·82 Å; Ferrari, Fava & Pelizzi, 1977] crystallizing in the same space group and only differing significantly in the *a* axis length, reflecting the presence of an additional sulphur atom in the anion. Both complexes involve comparable stereochemistries for the CuN$_4$O$_2$ chromophores, but there is a significant difference in the Cu–O(1) bond lengths of 2·627 and 2·82 Å respectively, which yielded tetragonalities ($T = R_S/R_L$) of 0·76 and 0·71 respectively. This difference in the observed tetragonalities is surprising in view of the similarity of the electronic reflectance spectra which involve a single broad peak at 14 700 and 14 930 cm^{-1} for the trithionate and tetrathionate complexes respectively. It is of interest that the elongated rhombic octahedral chromophore is regular in both thionates, which contrasts with the irregular CuN$_4$O$_2$ chromophore in Cubpy$_2$(ClO$_4$)$_2$ (Nakai, 1971) with two clearly different out-of-plane Cu–O bonds of 2·45 and 2·73 Å respectively, despite the fact that the dihedral angles between the 2,2′-bipyridyl ligands are comparable (37°) and the corresponding O(1)–Cu–O(2) angles are similar (156·2°). The thionate structures also contrast with the stereochemistry in (Cubpy$_2$ONO$_2$)NO$_3$.H$_2$O (Nakai, Ooi & Kuroya, 1970) which involves a very distorted five-coordinate CuN$_4$O chromophore.

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Thallium(III) Triacetate

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Abstract. Tl(O$_2$CCH$_3$)$_3$, monoclinic, $C2/c$, a = 15·540 (10), b = 8·630 (7), c = 7·848 (6) Å, β = 113·92 (5)°, Z = 4, D_x = 2·57 g cm^{-3}. The structure determined by X-ray diffraction (R_w = 0·057) shows that the Tl atom is chelated by the three acetate groups (Tl–O distances between 2·26 and 2·34 Å) and forms two further bonds (2·57 Å) to adjacent molecules along the *c* axis.