Crystal Structure of the Copper(I) Complex of 2,5-Dithiahexane-1,6-dicarboxylic Acid

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Crystals of the title compound are monoclinic, space group $P2/n$, with $Z = 2$ in a unit cell of dimensions: $a = 9{\cdot}937$, $b = 7{\cdot}708$, $c = 11{\cdot}660$ Å (all $\pm 0{\cdot}001$ Å) and $\beta = 94{\cdot}95 \pm 0{\cdot}01°$. The structure was determined from three-dimensional diffractometer data by Patterson and minimum function methods and refined by least-squares methods to R 0·081 for 1339 reflections. The copper atoms, tetrahedrally surrounded by the sulphur atoms of two complexing molecules, are on special positions on diad axes.

BELLAART and Verbeek [1] prepared a number of complexes by the reaction of Cu_2O and Ag_2O with acids of the type $CO_2H{\cdot}[CH_2]_n{\cdot}SCH_2{\cdot}CH_2S{\cdot}[CH_2]_n{\cdot}CO_2H$. They suggest for these complexes a structure in which the metal atom is surrounded by four sulphur atoms and two oxygen atoms in CO_2^--groups. However, the indications for this suggestion are few.

The determination of the crystal structure of the copper(I) complex of 2,5-dithiahexane-1,6-dicarboxylic acid was undertaken in order to reveal unequivocally the environment of the copper atom. Two acid molecules and one metal atom form a complex of formula $Cu^+[O_2C{\cdot}CH_2{\cdot}SCH_2{\cdot}CH_2{\cdot}SCH_2{\cdot}CO_2H]_2H^+$.

EXPERIMENTAL

The compound crystallizes in a monoclinic space group, and systematic absences showed the presence of an n-glide plane. By means of a Wilson scaling the intensities were converted to normalized structure factors and the statistical data obtained revealed a centrosymmetric intensity distribution. The structure was therefore assigned the space group $P2/n$, which was confirmed by the subsequent analysis.

Cell constants were determined from Weissenberg photographs calibrated with Al-powder lines.

Crystal Data.—$C_{12}H_{18}CuO_8S_4$, $M = 483$, Monoclinic, $a = 9{\cdot}937$, $b = 7{\cdot}708$, $c = 11{\cdot}660$ Å (all $\pm 0{\cdot}001$ Å), $\beta = 94{\cdot}95 \pm 0{\cdot}01°$, $U = 889{\cdot}8$ Å^3, $D_m = 1{\cdot}7$, $Z = 2$, $D_c = 1{\cdot}80$, $F(000) = 496$. Space group $P2/n$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 63·1 cm^{-1}.

With an automatic Nonius single-crystal diffractometer a total of 1342 non-zero reflections were observed up to θ 68·5° by use of Ni-filtered Cu-K_α radiation; the θ—2θ scan-mode was used. A few reflections, suspected to suffer from extinction, were removed in the course of the refinement. No absorption correction was applied.

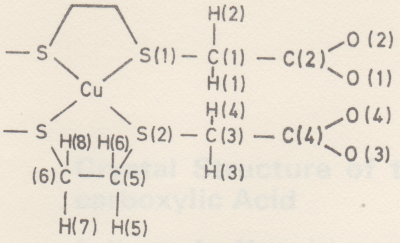
Structure Analysis.—The positions of the copper and sulphur atoms were readily found from the pattern of their Harker and non-Harker vectors. Light atoms were located by the minimum function technique.[2] Since the copper atoms lie on special positions on diad axes, their use for the construction of a minimum function would have introduced false symmetry, and a sulphur atom was therefore used. Although the sulphur–light-atom peaks are at about the same level as the noise, all but two of the light atoms could be found in the minimum function. These operations were all performed by use of one computer program.[3] The missing atoms were located in a Fourier synthesis after a few preliminary cycles of least-squares refinement. Finally the atom positions were refined by a block-diagonal least-squares program with atomic scattering factors in analytic form given by Moore [4] and the weighting scheme of Cruickshank.[5] Copper and sulphur atoms were refined anisotropically and the light atoms with isotropic temperature factors. The refinement was terminated at R 0·081, when all co-ordinate shifts had fallen below their corresponding standard deviations. Most of the hydrogen atoms were located in a difference-Fourier synthesis; however, the hydrogen atoms of the carboxy-groups could not be found. In view of the objective of the

[1] A. C. Bellaart and J. L. Verbeek, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 1005.
[2] M. J. Buerger, ' Vector Space,' Wiley, New York, 1959.
[3] H. van der Meer, *Diss. Amsterdam*, 1971.
[4] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.
[5] D. W. J. Cruickshank, ' Computing Methods and the Phase problem in *X*-Ray Crystal Analysis,' Pergamon, Oxford, 1961.

structure determination no further refinement was attempted.*

DISCUSSION

Description of the Structure.—Table 1 lists the positional and thermal parameters; the estimated standard deviations are those given by the block-diagonal least-squares procedure. The Figure shows a projection of the structure along [010] together with atomic distances and bond angles. Table 2 lists the hydrogen atom co-ordinates, from the difference-Fourier synthesis, together with bond distances involving them.



Numbering scheme

TABLE 1

Fractional co-ordinates and temperature parameters, with estimated standard deviations in parentheses

Atom	x	y	z	B_{iso}
Cu	0·2500(0)	0·2283(2)	0·2500(0)	*
S(1)	0·1012(2)	0·3888(2)	0·3532(2)	*
S(2)	0·4239(2)	0·0970(2)	0·3599(2)	*
O(1)	0·2621(7)	0·4110(9)	0·5718(6)	3·4(1)
O(2)	0·1662(6)	0·2028(9)	0·6658(5)	3·2(1)
O(3)	0·3812(7)	0·6074(8)	0·4280(6)	3·3(1)
O(4)	0·2485(7)	0·8355(10)	0·4550(6)	3·7(1)
C(1)	0·0779(8)	0·2542(10)	0·4769(7)	2·2(1)
C(2)	0·1779(8)	0·2964(10)	0·5778(7)	2·1(1)
C(3)	0·4347(8)	0·8648(11)	0·3389(7)	2·7(1)
C(4)	0·3431(8)	0·7707(10)	0·4146(7)	2·2(1)
C(5)	0·5657(8)	0·1580(11)	0·2796(7)	2·5(1)
C(6)	0·5539(8)	0·3420(11)	0·2356(7)	2·4(1)

* Anisotropic parameters in the expression $\beta_{ij} = 2\pi^2 a^*_i a^*_j U_{ij}$.

	β_{11}	β_{22}	β_{33}
Cu	0·0064(2)	0·0136(3)	0·0053(1)
S(1)	0·0053(2)	0·0073(3)	0·0029(1)
S(2)	0·0060(2)	0·0087(3)	0·0031(1)
	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{13}$
Cu	0·0000(0)	0·0000(0)	0·0005(2)
S(1)	−0·0004(4)	−0·0013(3)	−0·0002(2)
S(2)	0·0013(4)	0·0025(3)	−0·0002(2)

The cation is tetrahedrally surrounded by the four sulphur atoms of two ligand molecules. The Cu–S distances of 2·30 and 2·34 Å are the same as encountered in other compounds.[6-8] The sulphur tetrahedron itself has the approximate symmetry D_2 (222); the S · · · S distances within a ligand molecule are shorter than those between sulphur atoms belonging to two different ligands. The whole complex has a two-fold axis running through the Cu atoms. The two tails

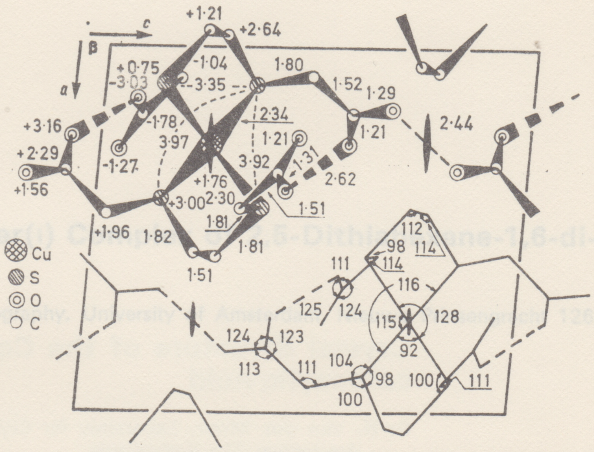


FIGURE Projection of the structure along [010], atomic distances and bond angles; for clarity the tapering bonds are drawn only in the upper half of the Figure

$-SCH_2{\cdot}CO_2H$ of each ligand have a different shape; one stretches out to form a hydrogen bond with a neighbouring complex over a two-fold axis, while the other bends back and forms a hydrogen bridge with a molecule in the next cell along the b axis (see Figure). The first of these hydrogen bonds is a short symmetric hydrogen bond with a length of 2·44 Å, also found in other acid salts.[9]

TABLE 2

Co-ordinates and distances involving hydrogen atoms found from the difference-Fourier synthesis

(*a*) Co-ordinates

Atom	x	y	z
H(1)	0·086	0·152	0·468
H(2)	−0·014	0·280	0·499
H(3)	0·527	0·835	0·363
H(4)	0·396	0·837	0·280
H(5)	0·650	0·128	0·326
H(6)	0·568	0·088	0·226
H(7)	0·540	0·402	0·282
H(8)	0·632	0·372	0·193

(*b*) Bond lengths (Å)

C(1)–H(1)	0·81	C(5)–H(5)	0·99
C(1)–H(2)	0·98	C(5)–H(6)	0·82
C(3)–H(3)	0·97	C(6)–H(7)	0·73
C(3)–H(4)	0·79	C(6)–H(8)	0·98

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* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20541 (7 pp., 1 microfiche). For details see *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[6] C. I. Brändén, *Acta Chem. Scand.*, 1967, **21**, 1000.
[7] A. Domenicano, R. Spagna, and A. Vaciago, *Chem. Comm.*, 1968, 1291.
[8] M. R. Truter and R. W. Rutherford, *J. Chem. Soc.*, 1962, 1748.
[9] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonds in Solids,' Benjamin, New York, 1968.