

3.5°). This slight, but significant, twist about the Ru—Ru bond fits in well with the pattern already described for [M₂(mhp)₄] complexes (Clegg, 1980). The mean torsion angle, mean Ru—N [2.089 (5) Å], mean Ru—O [2.044 (10) Å] and the difference between these two mean bond lengths [0.045 (12) Å] are all intermediate between the corresponding values for the Mo and Rh complexes; C(Me)···C(Me) distances [3.98 (1) and 4.03 (1) Å] are similar to those in the Rh complex, supporting the explanation of the twist in terms of steric interactions between methyl groups.

The Ru—Ru length appears to be the shortest yet determined between two Ru atoms. In complexes containing the [Ru₂(O₂CR)₄]⁺ structural unit, Ru—Ru varies between 2.248 (1) and 2.292 (7) Å, depending on the nature of R and of additional axial ligands (Bino, Cotton & Felthouse, 1979; Bennett, Caulton & Cotton, 1969). The Ru—Ru bond in these complexes has a formal bond order of 2.5 (Bennett, Caulton & Cotton, 1969; Norman & Kolari, 1978), compared with the value of 2 in [Ru₂(mhp)₄] (Berry, Garner, Hillier, MacDowell & Clegg, 1980a). This tendency of mhp and a variety of similar ligands to support very short M—M bonds is now well established for many

transition metals, and has both electronic and steric causes.

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References

- BENNETT, M. J., CAULTON, K. G. & COTTON, F. A. (1969). *Inorg. Chem.* **8**, 1–6.
 BERRY, M., GARNER, C. D., HILLIER, I. H., MACDOWELL, A. A. & CLEGG, W. (1980a). *Inorg. Chim. Acta*. In the press.
 BERRY, M., GARNER, C. D., HILLIER, I. H., MACDOWELL, A. A. & CLEGG, W. (1980b). *J. Chem. Soc. Chem. Commun.* pp. 494–495.
 BINO, A., COTTON, F. A. & FELTHOUSE, T. R. (1979). *Inorg. Chem.* **18**, 2599–2604.
 CLEGG, W. (1980). *Acta Cryst.* **B36**, 2437–2439.
 CLEGG, W. (1981). *Acta Cryst.* **A37**. In the press.
 COTTON, F. A., FANWICK, P. E., NISWANDER, R. H. & SEKUTOWSKI, J. C. (1978). *J. Am. Chem. Soc.* **100**, 4725–4732.
 NORMAN, J. G. JR & KOLARI, H. J. (1978). *J. Am. Chem. Soc.* **100**, 791–798.

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Structure of Bis[(isopropylthio)acetato]copper(II) Dihydrate

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Abstract. [Cu(C₅H₉O₂S)₂].2H₂O, *a* = 14.318 (2), *b* = 10.968 (2), *c* = 4.949 (1) Å, β = 93.74 (2)°, *Z* = 2, *D*_m = 1.57, *D*_x = 1.56 Mg m⁻³; *R* = 0.043 for 1802 independent reflexions. The space group is *P2*₁; however, the symmetry of the molecular arrangement is very close to *P2*₁/*a*, which was used to determine the average structure in this work. The (isopropylthio)acetato acts as a terdentate ligand, coordinating *via* one S, and one carboxylato O to a Cu atom, and *via* the other O to another Cu atom. The Cu atom has a deformed octahedral coordination, and the complexes are aligned to form a polymer chain parallel to *c*. The crystalline waters are in interstitial positions, forming hydrogen bonds with one O atom of a carboxyl group and with two other water molecules.

Introduction. (Alkylthio)acetic acid is an interesting ligand, as it is able to coordinate to metals using its S

atom, as well as both O atoms of its carboxyl group. For alkoxyacetato complexes of metals, a number of interesting modes of coordination have been found (Forrest, Prout & Rossotti, 1966; Prout, Carruthers & Rossotti, 1971; Carruthers, Prout & Rossotti, 1975). Accordingly, various structures for alkylthioacetato complexes of metals are expected; for example, bis[(propylthio)acetato]cobalt(II) consists of hexameric units (Shimoi, Ebina, Ouchi, Yoshino & Takeuchi, 1979). In the case of bis[(isopropylthio)acetato]copper(II) dihydrate, two kinds of crystals were obtained: a pale-blue complex, which has spectral properties similar to those of other Cu^{II} (alkylthio)acetates, and a black-violet isomer. The latter seems to be more stable than the former, but as yet black-violet isomers have not been obtained for other (alkylthio)acetate complexes. The surface reflectance spectra of a crystalline powder of the black-violet isomer shows

broad absorption, with a maximum at 567 nm, and a shoulder at about 680 nm. Dissolution in water, acetonitrile, acetone, or ethanol shifts the maximum to about 680 nm, and the colour turns to blue. On the other hand, the blue complex, in the solid state as well as in solution, shows an absorption maximum at 680 nm. Between the blue and the black-violet isomers, almost no differences were recognized in the wave-numbers of the $\nu_s(\text{COO})$ and $\nu_{as}(\text{COO})$ bands of their infrared spectra; their magnetic moments were also very similar (Ohashi, Takeuchi, Ouchi & Yoshino, 1970).

The black-violet crystals were obtained according to Ohashi *et al.*'s (1970) method, and were recrystallized from water. Intensities and cell dimensions were measured on a Philips PW 1100 automated four-circle diffractometer with a crystal of dimensions $0.26 \times 0.24 \times 0.20$ mm. Data were collected by the θ - 2θ scan technique with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Of 2353 reflexions measured in the range $2\theta < 60^\circ$, 1802 independent reflexions with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination and refinement. Data were corrected for Lorentz and polarization factors, but not for absorption [$\mu(\text{Mo K}\alpha) = 0.868 \text{ mm}^{-1}$].

Systematic extinctions occur only for $0k0$ with k odd. In addition, it was observed that all $h0l$ reflexions with h odd are very weak, and contribute only 0.7% of the total intensity of all $h0l$ reflexions (of 105 measured reflexions, only 25 could be observed, and most were also recognized in the long-exposure Weissenberg photographs). This indicates that the symmetry is very near to, but not exactly, that of space group $P2_1/a$, which was used throughout this investigation.

The structure was solved by the heavy-atom method, and refined by the block-diagonal least-squares method. The atomic scattering factors and corrections for anomalous scattering for Cu and S were taken from *International Tables for X-ray Crystallography* (1974). The weighting scheme $w = 1/[\sigma^2 + (0.03F_o)^2]$ was used. All atoms except for two H atoms were found. The coordinates of one H atom of a methyl group, H(43), were calculated. The final R value was 0.043 with anisotropic temperature factors for all non-hydrogen atoms.*

Attempts at refinement in $P2_1$ by a full-matrix least-squares method without any restriction on the parameters led to some bond lengths, such as C—C and C—O, being abnormal. We have also made many trials to explain the $h0l$ (h odd) reflexions, but have not succeeded. Consequently, the structure described below

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35619 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is the average one; however, it does not contradict any property of the complex.

The final atomic coordinates, and interatomic distances and bond angles, with their estimated standard deviations, are listed in Tables 1 and 2.

Table 1. Final atomic coordinates ($\times 10^4$ for non-hydrogen atoms, and $\times 10^3$ for hydrogen atoms) and isotropic temperature factors (\AA^2) with estimated standard deviations in parentheses

Parameters are referred to the space group $P2_1/a$.

	x	y	z	B_{eq}^* or B_{iso}
Cu	0	0	0	2.4
S	-1280 (0)	-1326 (1)	403 (1)	2.2
O(1)	415 (2)	-1931 (2)	6760 (4)	3.1
O(2)	568 (1)	-753 (2)	3164 (4)	2.7
O(W)	94 (3)	-4460 (3)	7534 (6)	5.5
C(1)	164 (2)	-1604 (2)	4418 (5)	2.1
C(2)	-654 (2)	-2252 (3)	2933 (6)	2.8
C(3)	-2135 (2)	-540 (3)	2382 (6)	2.9
C(4)	-2531 (3)	518 (4)	682 (10)	4.7
C(5)	-2905 (3)	-1433 (4)	3094 (8)	4.4
H(W1)	16 (2)	-377 (3)	735 (6)	3.1 (7)
H(21)	-44 (3)	-300 (5)	201 (10)	7.2 (13)
H(22)	-109 (3)	-258 (4)	444 (8)	5.0 (9)
H(3)	-172 (3)	-35 (4)	406 (9)	5.3 (10)
H(41)	-298 (3)	95 (4)	161 (8)	4.9 (9)
H(42)	-203 (4)	99 (6)	57 (10)	8.3 (11)
H(43)	-286	23	-123	14.0
H(51)	-335 (3)	-103 (4)	411 (9)	6.3 (11)
H(52)	-263 (3)	-200 (4)	416 (8)	4.8 (9)
H(53)	-319 (5)	-177 (6)	67 (14)	13.0 (23)

$$* B_{\text{eq}} = \frac{1}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac \cos \beta).$$

Table 2. Interatomic distances (\AA) and bond angles ($^\circ$) with estimated standard deviations in parentheses

Cu—S	2.358 (1)	C(1)—C(2)	1.519 (4)
Cu—O(1 ⁱ)	2.745 (2)	C(3)—C(4)	1.521 (5)
Cu—O(2)	1.905 (2)	C(3)—C(5)	1.533 (5)
S—C(2)	1.804 (3)	O(W) \cdots O(1)	2.843 (4)
S—C(3)	1.833 (3)	O(W) \cdots O(W ⁱⁱⁱ)	2.742 (6)
O(1)—C(1)	1.244 (3)	O(W) \cdots O(W ^{iv})	2.771 (6)
O(2)—C(1)	1.280 (3)		
S—Cu—O(1 ⁱ)	76.86 (5)	O(2)—C(1)—C(2)	117.7 (2)
S—Cu—O(2)	87.46 (6)	O(1)—C(1)—C(2)	118.9 (2)
O(1 ⁱ)—Cu—O(2)	92.78 (8)	C(1)—C(2)—S	113.9 (2)
Cu—S—C(2)	93.0 (1)	C(2)—S—C(3)	102.3 (1)
Cu—O(1 ⁱ)—C(1)	105.2 (2)	S—C(3)—C(4)	107.5 (3)
Cu—O(2)—C(1)	122.2 (2)	S—C(3)—C(5)	109.7 (2)
O(2)—C(1)—O(1)	123.4 (3)	C(4)—C(3)—C(5)	111.5 (3)
		O(W) \cdots O(1)—C(1)	111.6 (2)
		O(1) \cdots O(W) \cdots O(W ⁱⁱⁱ)	124.6 (1)
		O(1) \cdots O(W) \cdots O(W ^{iv})	107.6 (1)
		O(W ^{iv}) \cdots O(W) \cdots O(W ⁱⁱⁱ)	127.8 (2)

Symmetry code: (i) $x, y, z - 1.0$; (ii) $x, y, z + 1.0$; (iii) $-x, -y - 1.0, 2.0 - z$; (iv) $-x, -y - 1.0, 1.0 - z$.

Discussion. A perspective drawing of the complex, including the numbering scheme, is shown in Fig. 1. The complex has a centre of symmetry at the Cu atom. An (isopropylthio)acetato ligand forms a five-membered chelate ring, bonding to a Cu atom through S and O(2), and further coordinating to another Cu through O(1). Thus, the complexes form one-dimensional polymers along *c*, as shown in Fig. 2. The bridges between the complexes are not strong, as Cu—O(1') is longer than Cu—O(2) by 0.84 Å. No interaction between the Cu atoms exists, as the magnetic moment of the complex is $17.2 \times 10^{-24} \text{ JT}^{-1}$ at ambient temperature (Ohashi *et al.*, 1970). The angle between the Cu—O(1') axis and the plane consisting of Cu, S, and O(2) is $76.4(1)^\circ$. Therefore, the coordination geometry of the Cu atom is deformed octahedrally. The bond lengths and angles in the ligand are all normal.

The crystalline water forms hydrogen bonds with a carboxyl oxygen atom O(1), and with two other crystalline water molecules. As shown in Fig. 2, crystalline waters are aligned along the *c* axis; the O atom of the water deviates from the (100) plane by

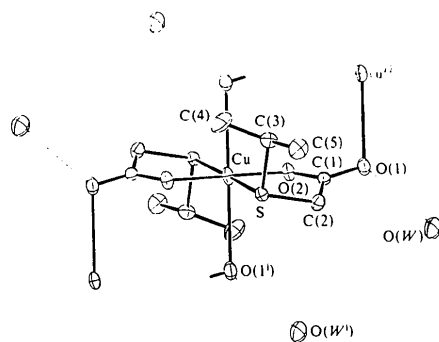


Fig. 1. A perspective drawing of the title compound, with the numbering scheme.

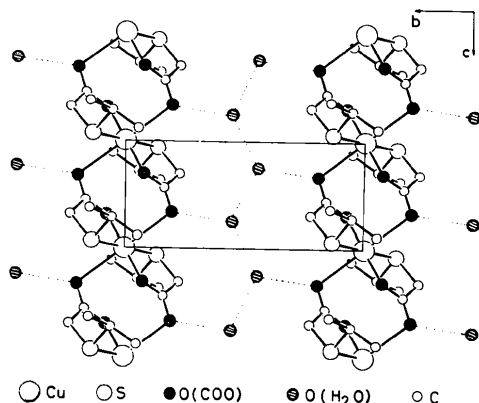


Fig. 2. A crystal packing diagram projected along a^* .

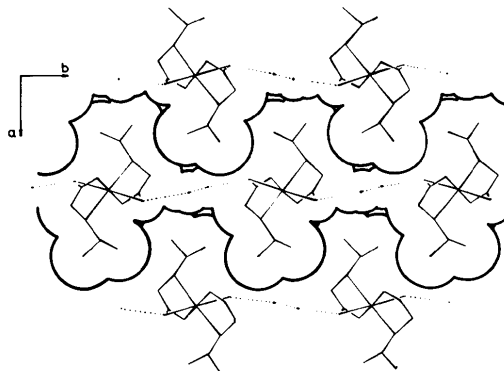


Fig. 3. A crystal packing diagram projected along c^* . Thick lines show the domain of the complex molecules, calculated from the van der Waals radii of the component atoms.

0.134 (4) Å. The layers are packed as shown in Fig. 3. The chains of the complex polymers in the second layer are parallel to those in the first layer, but are just above the chains of crystalline waters. Superimposed layers are only held together by van der Waals forces, and the cleavage of the crystal was found along the (100) plane. The arrangement of the complex and water molecules is very similar to that in bis(picolinato)copper(II) dihydrate (Takenaka, Utsumi, Yamamoto, Furusaki & Nitta, 1970; Faure, Loiseleur & Thomas-David, 1973).

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References

- CARRUTHERS, J. R., PROUT, C. K. & ROSSOTTI, F. J. C. (1975). *Acta Cryst.* B31, 2044–2046.
 FAURE, P. R., LOISELEUR, H. & THOMAS-DAVID, G. (1973). *Acta Cryst.* B29, 1890–1893.
 FORREST, J. G., PROUT, C. K. & ROSSOTTI, F. J. C. (1966). *Chem. Commun.* pp. 658–659.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 OHASHI, Y., TAKEUCHI, T., OUCHI, A. & YOSHINO, Y. (1970). *Bull. Chem. Soc. Jpn.* 43, 2845–2850.
 PROUT, C. K., CARRUTHERS, J. R. & ROSSOTTI, F. J. C. (1971). *J. Chem. Soc. A*, pp. 554–556.
 SHIMOI, M., EBINA, F., OUCHI, A., YOSHINO, Y. & TAKEUCHI, T. (1979). *J. Chem. Soc. Chem. Commun.* pp. 1132–1133.
 TAKENAKA, A., UTSUMI, H., YAMAMOTO, T., FURUSAKI, A. & NITTA, I. (1970). *Nippon Kagaku Zasshi*, 91, 928–935.