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Crystal and Molecular Structure of Bis(3,3′-(thiopropionatopropionic acid) diaquocopper(II)

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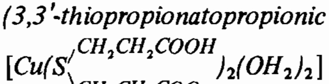
The crystal and molecular structure of bis-(3,3′-thiopropionatopropionic acid)diaquocopper(II),  $[Cu(S\genfrac{}{}{0pt}{}{/CH_2CH_2COOH}{\backslash CH_2CH_2COO})_2(OH_2)_2]$, *was determined from single-crystal three-dimensional X-ray data collected by counter methods. The compound crystallizes as blue plates in the space group* Pbca. *The unit cell parameters are* a = *8.366(2),* b = *9.262(2),* c = *23.221(4)* Å, Z = *4 formula units/cell. The structure was solved by direct methods, and the least-squares refinement of 1079 reflections gave the final value of* R = *0.048. There are no discrete molecules in the crystal. The structure consists of centrosymmetric complex units in which the central Cu(II) is in a tetragonal planar arrangement of two* trans-*coordinated water molecules (Cu–O 1.912* Å*) and the carboxylate groups of two organic ligands (Cu–O 1.946* Å*). Additional interaction with the –OH of the carboxylic acid groups of two neighbouring molecules leads to two weak apical Cu–O bonds (Cu–O 2.731* Å*) and links the planar complex units to form a carboxylic acid-bridged polymeric structure. There exists an effective hydrogen bonding system between the water molecules, carboxylate and carboxylic acid groups of the ligands.*

Introduction

Thiopolycarboxylic acids are a class of ligands containing, in addition to carboxyl groups, sulphur atoms which are known to have a distinct affinity towards certain soft metals. Stability constant measurements on dicarboxylic acid–metal systems have been made by several workers [1–5]. A few solid complexes of both 1:1 and 1:2 metal-to-thiodicarboxylic acid ratios have been isolated, and their structures have been determined by spectroscopic and magnetic studies [6–8]. The crystal structure investigations on the Zn(II) [9], Cd(II) [10] and Nd(III) [11] complexes of thiodiacetic acid revealed that the ligand is bonded to the metal atom through the sulphur atom in addition to the carboxylic groups. Our interest primarily is to find out the bonding ability of the sulphur atom in thiodipropionic acid, the higher homologue of thiodiacetic acid, in its metal complexes. We report here the crystal structure of bis(3,3′-thiopropionatopropionic acid) diaquocopper(II) dihydrate.

Experimental

The title compound $[Cu(OOCCH_2CH_2SCH_2CH_2\cdot COOH)_2(OH_2)_2]$ was prepared by the reaction of basic copper(II) carbonate with a hot saturated solution of thiodipropionic acid. The reaction mixture was stirred at 70 °C for several hours and filtered. The filtrate was concentrated on a water bath and was kept at room temperature for slow evaporation. After several days fairly good column-shaped crystals of the complex separated out, which were collected and washed with acetone and ether. *Analysis*: Found, C, 32.22; H, 5.16; S, 14.86; Cu, 13.77; Calcd. for $C_{12}H_{22}S_2O_{10}Cu$: C, 31.74; H, 4.89; S, 14.12; Cu, 14.00%.

X-ray Data

Preliminary Weissenberg and precession photographs indicated orthorhombic symmetry. The systematic absences as read from the photographs are $hk0$, $h = 2n + 1$, $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$ which suggested that the space group being *Pbca* (D_{2h}^{15}, No. 61). A crystal of approximate dimensions 0.08 × 0.11 × 0.31 mm^3 was used for intensity data collection. The unit cell parameters of the crystal, after least-squares refinement from diffractometer coordinates of 15 high-order reflections are a = 8.366(2), b = 9.262(2) and c = 23.221(4) Å. The measured density of 1.67(2) $g\cdot cm^{-3}$ is in agreement with the calculated density of 1.676 $g\cdot cm^{-3}$ for four formula units of the complex in the unit cell. The X-ray intensity data were collected at 22 °C using a Syntex $P2_1$ four-circle diffractometer and graphite

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TABLE I. Bis(3,3′-thiopropionatopropionic acid)diaquocopper(II): Coordinates of the Atoms and Coefficients of the Anisotropic Temperature Factors with Standard Deviations.[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.5	0.5	0.5	2.13(4)	1.59(3)	2.25(4)	0.07(6)	0.00(6)	−0.47(5)
S	0.37721(24)	0.06600(18)	0.28755(7)	7.12(13)	2.82(8)	1.53(6)	0.12(9)	−0.48(8)	−0.08(7)
O1	0.28355(48)	0.52300(47)	0.52484(18)	2.1(2)	3.1(3)	4.2(2)	−0.5(2)	0.6(2)	−2.1(2)
O2	0.53646(72)	0.19265(49)	0.08804(21)	4.6(3)	2.9(2)	3.1(3)	0.9(2)	0.2(2)	1.4(2)
O3	0.30571(48)	0.29491(42)	0.11109(16)	4.0(3)	2.8(2)	3.2(2)	1.2(2)	0.2(2)	1.1(2)
O4	0.42813(46)	0.35204(40)	0.44646(15)	3.5(3)	1.7(2)	2.4(2)	0.4(2)	−0.5(2)	−0.7(2)
O5	0.55013(40)	0.17108(36)	0.49182(16)	3.0(2)	2.2(2)	2.0(2)	0.5(1)	−0.6(2)	−0.6(2)
C1	0.41049(81)	0.21195(69)	0.12075(24)	3.4(4)	2.4(3)	1.7(3)	0.0(3)	0.4(3)	0.4(2)
C2	0.41363(98)	0.11435(98)	0.17182(38)	5.5(6)	5.4(5)	3.2(4)	2.4(5)	1.3(4)	1.7(4)
C3	0.36282(148)	0.18301(109)	0.22587(36)	12.1(9)	5.3(5)	2.4(3)	5.4(5)	2.1(4)	1.0(3)
C4	0.40609(82)	0.19945(65)	0.34286(28)	3.8(4)	1.9(3)	2.5(3)	0.1(3)	0.4(3)	−0.1(3)
C5	0.43561(79)	0.12420(62)	0.39926(28)	3.2(4)	1.8(3)	2.1(3)	0.4(3)	0.2(3)	−0.2(2)
C6	0.47640(70)	0.22246(62)	0.44932(22)	1.7(3)	2.3(3)	1.5(2)	−0.1(3)	0.2(2)	−0.5(2)

[a] Definition of the anisotropic temperature factors: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE II. Interatomic Distances and Bond Angles in the Structure of Bis(3,3′-thiopropionatopropionic acid)diaquocopper(II).

Bond Distances (A)			Bond Angles (°)	
*Cu-Coordination**				
Cu–O1	(–O1^{I})**	1.912(4)	O1–Cu–O4	88.8(2)
Cu–O4	(–O4^{II})	1.946(4)	O1–Cu–O4^{I}	91.2(2)
Cu–O2^{II}	(–O2^{III})	2.731(5)	O1–Cu–O2^{II}	92.7(2)
			O1–Cu–O2^{III}	87.3(2)
			O2^{II}–Cu–O4	87.0(2)
			O2^{III}–Cu–O4	93.0(2)
Thiodipropionate Ion				
C1–O2	1.311(9)		Cu–O2–C1	115.7(4)
C1–O3	1.187(8)		O2–C1–O3	124.9(6)
C1–C2	1.491(12)		O2–C1–C2	111.3(6)
C2–C3	1.470(14)		O3–C1–C2	123.7(7)
C3–S	1.800(10)		C1–C2–C3	114.3(8)
S–C4	1.799(7)		C2–C3–S	113.6(8)
C4–C5	1.504(9)		C3–S–C4	99.4(4)
C5–C6	1.515(9)		S–C4–C5	109.0(5)
C6–O4	1.268(7)		C4–C5–C6	115.3(5)
C6–O5	1.257(7)		O4–C6–O5	123.7(5)
			O4–C6–C5	117.2(5)
			O5–C6–C5	119.0(5)
			Cu–O4–C6	122.3(4)

*O1: water oxygen, O2: hydroxyl oxygen.

**Symmetry code: I: 1 – x, 1 – y, 1 – z; II: 1 – x, ½ + y, ½ – z; III: x, ½ – y, ½ + z.

monochromated MoK$_\alpha$ radiation, (K$_{\alpha_1}$ 0.70926, K$_{\alpha_2}$ 0.71354 Å, θ–2θ scan, scintillation counter, take-off angle 6°). The sampling interval in 2θ for each reflection was 2.1–2.3°. The rate of scanning varied from 2–15°/min, depending on the intensity. The background measurements at both sides of the scan were made with the total time for background counts being equal to the scan time. A standard reflection was measured for every 50 reflections. A complete set of 1973 unique reflections was measured up to $(\sin\theta)/\lambda = 0.64$ Å^{-1} out of which 1079 reflections were accepted as statistically above the background on the basis of $I > 1.96\sigma(I)$. The data reduction was done by applying Lorentz and polariza-

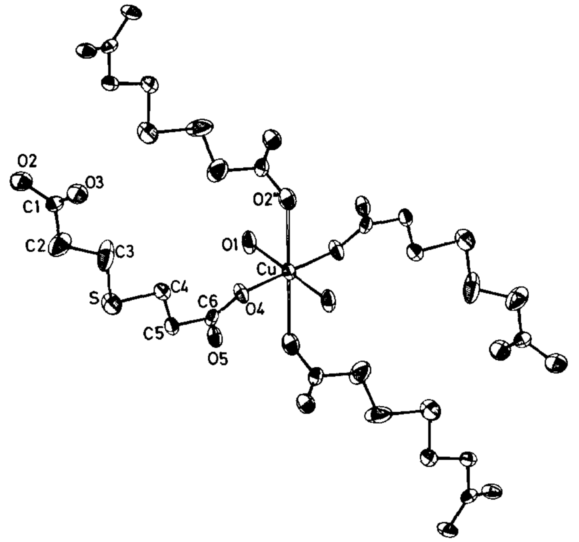


Fig. 1. Bis(3,3'-thiopropionatopropionic acid)diaquocopper(II): Structural unit (fragment of the polymeric network) with atomic designations and thermal ellipsoids (50% probability).

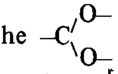
tion corrections. No absorption correction was applied ($\mu = 15.3\ cm^{-1}$).

Solution and Refinement of the Structure

The structure was solved by direct methods using the MULTAN programme system [12]. Most of the non-hydrogen atoms were located from the first E map obtained using the phases for the set of the best figures of merit. The other non-hydrogen atoms were located from subsequent Fourier and difference Fourier syntheses. All hydrogen positions were obtained from the difference Fourier maps after the anisotropic refinement of the non-hydrogen atoms. The atomic scattering factors for Cu, S, O, C and H were taken from the International Tables [13]. Full-matrix least-squares refinement with anisotropic temperature factors for all the nonhydrogen atoms and fixed isotropic temperature factors of 4.0 Å^2 for the hydrogen atoms converged to residuals $R_1 = 0.048$, $R_2 = 0.043$, where $R_1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. The weighting scheme was based on the counting statistics of the intensities. The shifts in the final cycle were below 0.02σ. The final difference Fourier map had no significant features. The final coordinates and thermal parameters are tabulated in Table I. A table of calculated and observed structure factors and a table of all H atom coordinates are available from the Editor.

Results and Discussion

The structure consists of centrosymmetric $Cu(OOCH_2CH_2SCH_2CH_2COOH)_2(OH_2)_2$ complex units containing tetragonally coordinated Cu(II). Two water molecules and a carboxylate group each from two ligand molecules form a planar *trans* configuration with an equatorial set of four oxygen atoms around copper. There are, however, no discrete molecules in the crystal. Additional interaction to the two hydroxyl oxygen atoms of carboxylic acid groups from neighbouring 3,3'-thiodipropionic acid molecules gives rise to two additional axial bonds which connect the planar Cu(II) complexes into a carboxylic acid-bridged polymeric structure. The six-fold coordination around copper(II) can be regarded as a tetragonally Jahn–Teller-distorted octahedron. An ORTEP plot of a segment of the structure is reproduced in Fig. 1.

The bond lengths and the bond angles are given in Table II. In several aquo complexes of copper(II) the Cu–O(water) bond distance is found to be between 1.92–2.04 Å with a mean value of 1.98 Å [14]. The value of 1.912(4) observed in the present complex suggests strong interaction of water with copper. The carboxylate group can coordinate to metal atoms in several ways with different structural variations [15]. The notable modes of bonding are unidentate, unsymmetric bidentate and bridging either through the  $-C\genfrac{}{}{0pt}{}{\diagup O-}{\diagdown O-}$ group or through a single carboxyl oxygen atom [16]. Among the typical copper(II) carboxylates where structures are crystallographically established, the Cu–O bond distances fall in the range 1.85 to 2.09 Å [17–28] with an average value of 1.96 Å [14]. In the title compound the observed bond distance of 1.946 Å (Cu–O4) falls within this range. However, it is to be pointed out that the Cu–O(water) distance is significantly shorter than the Cu–O(carboxylate) distance. The axial bond distances, in many of the known tetragonally distorted octahedral copper(II) carboxylates, show a large variation in their values, from 2.29–2.75 Å [14, 23–30]. In the present complex the Cu–O2 distance of 2.731(5) Å definitely indicates bonding of the –OH group of the carboxylic acid to copper, though the interaction is presumably quite weak. It is interesting to note that the apical interaction to the tetragonal plane of copper is through the hydroxyl oxygen and not through the carboxyl oxygen of the carboxylic acid group (C1–O3 1.187, C1–O2 1.311, O2–Cu 2.731, O2–H3 0.77 Å). It is one of the exceptional cases that a carboxylic acid group is bonded to a metal through the –OH group in preference to the carboxyl group. This may be due to the weak acidity [31] of this carboxylic group.

The bond distances and bond angles of 3,3'-thiodipropionic acid are normal. The carboxylate groups are effectively planar. In Table III the hydrogen bond distances and bond angles are tabulated. The water molecules are hydrogen-bonded to the

TABLE III. Hydrogen Bond System: Interatomic Distances (Å) and Bond Angles (°).

	O–H	O···O	H···O	O–H···O
O1–H1···O5	0.78(6)	2.682(6)	1.90(6)	173(6)
O1–H2···O3	0.82(5)	2.723(6)	1.90(5)	173(6)
O2–H3···O5	0.77(7)	2.569(6)	1.84(7)	159(8)

Coordinates: H1 0.213(7), 0.470(6), 0.5175(21); H2 0.250(8), 0.574(6), 0.5510(18); H3 0.525(9), 0.251(7), 0.0651(27).

non-coordinated carboxyl oxygen atoms of the carboxyl groups (O1···O3 2.72, O1···O5 2.68 Å). Further, the carboxylic acid groups are strongly hydrogen bonded to the non-coordinated carboxylic oxygen atoms of neighbouring carboxylate groups (O2···O5 2.57 Å).

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References

1 R. M. Tichane and W. E. Bennett, *J. Am. Chem. Soc., 79,* 1293 (1957).
2 K. Suzuki and K. Yamasaki, *J. Inorg. Nucl. Chem., 28,* 473 (1966).
3 J. Podlaha and J. Podlahovà, *Inorg. Chim. Acta, 4,* 521 (1970).
4 O. Prochazkova, J. Podlahovà and J. Podlaha, *Collect. Czech. Comm., 38,* 1128 (1973), and references therein.
5 D. K. Laing and L.D. Pettit, *J. Chem. Soc. Dalton,* 2297 (1975).
6 J. T. Morrison and W. A. Baker Jr., *Inorg. Chim. Acta, 3,* 463 (1969).
7 J. Podlahovà, *Inorg. Chim. Acta, 4,* 549 (1970).
8 G. K. Ramachandra, *Ph.D. Thesis, Indian Institute of Technology, Madras* (1979).
9 M. G. B. Drew, D. A. Rice and C. W. Timewell, *J. Chem. Soc. Dalton,* 144 (1975).
10 S. H. Whitlow, *Acta Cryst., B31,* 2531 (1975).
11 T. Malmborg and A. Oskarsson, *Acta Chem. Scand., 27,* 2923 (1973).
12 The calculations were carried out on a Data General Eclipse computer, using, besides, own programmes, the programmes of the Syntex EXTL System, and on an IBM 360/50, using C. Johnson's ORTEP programme.
13 'International Tables for X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham (1974). pp. 99 ff; R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42,* 3175 (1965).
14 K. W. Muir, 'Molecular Structure by Diffraction Methods', Vol. 1, p. 631, The Chemical Society, London (1973).
15 M. A. Porai-Koshits, *Soviet Phys. Cryst., 16,* 1047 (1971).
16 J. N. Brown, H. R. Eichelberger, E. Schaeffer, M. L. Good, and L. M. Trefonas, *J. Am. Chem. Soc., 93,* 6290 (1971).
17 R. S. Mc Ewen, *J. Chem. Soc. Chem. Comm.,* 68 (1973).
18 M. B. Ferrari, L. C. Capacchi, G. G. Fava and M. Nardelli, *J. Cryst. Mol. Struct., 2,* 291 (1972).
19 D. van der Helm and C. E. Tatsch, *Acta Cryst., B28,* 2307 (1972).
20 G. G. Aleksandrov, Yu. T. Struchkov, A. A. Kurganov, S. V. Rogozhin and V. A. Davankov, *J. Chem. Soc. Chem. Comm.,* 1328 (1972).
21 G. G. Aleksandrov, Yu. T. Struchkov, A. A. kurganov, S. V. Rogozhin and V. A. Davankov, *Zh. Strukt. Khim., 13,* 671 (1972).
22 J. R. Brush, R. J. Magee, M. J. O'Connor, S. B. Teo, R. J. Geue and M. R. Snow, *J. Am. Chem. Soc., 95,* 2034 (1973).
23 A. Dijkstra, *Acta Cryst., 20,* 588 (1966).
24 D. van der Helm, M. B. Lawson and E. L. Enwall, *Acta Cryst., B27,* 2411 (1971).
25 F. S. Stephens, R. S. Vagg and P. A. Williams, *Acta Cryst., B31,* 841 (1975).
26 C.-C. Ou, D. A. Powers, J. A. Thich, T. R. Felthouse, D. N. Hendrickson, J. A. Potenza and H. J. Schugar, *Inorg. Chem., 17,* 34 (1978).
27 T. G. Fawcett, M. Ushay, J. P. Rose, R. A. Lalancette, J. A. Potenza and H. J. Schugar, *Inorg. Chem., 18,* 327 (1979).
28 G. Davey and F. S. Stephens, *J. Chem. Soc. A,* 2577 (1971).
29 G. Davey and F. S. Stephens, *J. Chem. Soc. A,* 1917 (1971).
30 M. R. Udupa and B. Krebs, *Inorg. Chim. Acta, 31,* 251 (1978).
31 J. H. MacGregor and C. Pugh, *J. Chem. Soc.,* 736 (1950).