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Strong and Symmetric Hydrogen Bonding in Coordination Compounds of Carboxylic Acid Derivatives; the Crystal Structure of (3,6-dithiaoctanedioato-S,S′–(3,6-dithiaoctanedioic acid-S,S′)-copper(I) Redetermined at 173 K

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3,6-dithianoctanedioic acid forms a Cu(I) compound in which electrical neutrality is achieved by elaborate hydrogen bonding and sharing of protons. The title compound crystallizes in the monoclinic space group P2/n with Z = 2. Unit-cell parameters are a = *11.625(2),* b = *7.664(1),* c = *9.874(2) Å, β = 95.16°,* D_m = *1.80(2),* D_c = *1.83 g cm^{-3}. The structure was solved by means of standard direct methods and refined with full-matrix least-squares techniques to an R-value of 0.026 (R_w = 0.042). The Cu(I) ion is tetrahedrally coordinated by four thioether S-atoms (Cu–S = 2.29–2.33 Å). The molecules are linked by very strong hydrogen bonds between non-coordinating carboxylate groups in such a way that the average number of acidic hydrogens per molecule is three. One of these hydrogens lies on a twofold axis and forms a short symmetrical hydrogen bond, with a O–O distance of 2.441(2) Å. Unusual features in the infrared spectrum of this compound can be interpreted on the basis of the observed crystal structure.*

Introduction

Many years ago, Ramberg and Tiberg [1] synthesized a compound with the unusual formula Cu^I-(LH)(L), where L = $^-OOC-CH_2-S-CH_2-CH_2-S-CH_2-COOH$. They suggested a structure in which one L anion is coordinated to Cu(I) and the other group is a non-coordinating acid residue, LH. A crystal structure determination of this compound [2] showed that the title compound contains Cu(I) coordinated tetrahedrally by four S-atoms of the two L(H) groups without coordination of the –COOH or –COO$^-$ group. Because in this latter work no study of the hydrogen-bond system was reported (although O···O interactions suggest such a hydrogen bonding) and because preliminary work in our laboratory showed some unusual absorptions in the infrared spectra, we decided to reinvestigate the crystal and molecular structure at low temperature and to compare the hydrogen-bond pattern with the infrared absorptions of the OH groups.

Copper(I) compounds with thioether groups as ligands are relatively rare [3, 4]. Also, coordination of carboxylate groups to Cu(I) has only been reported in a few compounds [5]. In coordination compounds, carboxylic acid residues are almost always coordinated to the metal ions, either *via* one or two oxygen atoms [5–7]. Only in a few cases have non-coordinating carboxylic acid residues been found, as in $[Ni(imH)_6](HCOO)_2$ (imH = imidazole) [8]. In such compounds the carboxylic group is strongly hydrogen-bonded to the ligand (in this case to the acidic N–H of the imidazole group, resulting in unusual low-frequency N–H vibrations) [8]. In view of the known [9] or proposed [10] presence of thioether and carboxylate ligands in copper enzymes, chelating ligands containing either or both of these groups are of interest from a coordination point of view. Carboxylate groups are also known to play an important role in salt bridges and hydrogen-bonding interactions, both in biological systems [11] and in low molecular weight compounds [12]. In simple salts and acid salts, carboxylate groups often form strongly hydrogen-bonded dimeric systems, similar to the dimers of acetic acid in the gas phase [12].

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TABLE I. Fractional Atomic Coordinates of Cu(L)(LH) at –100 °C. The first digit in the labels of the hydrogen atoms refers to the number of the carbon atom to which it is bonded. Estimated standard deviations in parentheses.

	10^4x	10^4y	10^4z	B_{iso}[a]
Cu	7500	2312.5(3)	2500	1.086(5)
S(1)	8536.1(3)	3918.5(4)	1013.3(3)	0.972(5)
S(2)	6391.9(3)	996.1(4)	753.0(3)	1.112(5)
O(1)	11659(1)	1984(2)	1666(1)	1.91(2)$_b$
O(2)	10729(1)	4097(2)	2651(1)	1.97(2)
O(3)	5440(1)	–1644(2)	2529(1)	2.22(3)
O(4)	5711(1)	–3926(1)	1169(1)	1.87(2)
C(1)	10774(1)	2944(2)	1790(1)	1.16(2)
C(2)	9762(1)	2522(2)	770(1)	1.30(2)
C(3)	7627(1)	3480(2)	–538(1)	1.33(2)
C(4)	7204(1)	1610(2)	–674(1)	1.29(2)
C(5)	6604(1)	–1336(2)	649(1)	1.43(2)
C(6)	5851(1)	–2295(2)	1562(1)	1.33(2)
	10^3x	10^3y	10^3z	B
H(21)	957(2)	131(4)	93(3)	3.1(6)
H(22)	1003(2)	265(3)	–5(3)	2.4(5)
H(31)	691(2)	433(4)	–59(2)	2.7(5)
H(32)	806(2)	383(3)	–131(2)	1.3(4)
H(41)	662(2)	149(3)	–142(2)	1.7(4)
H(42)	776(2)	80(3)	–71(2)	1.7(4)
H(51)	744(2)	–157(3)	95(2)	1.8(4)
H(52)	624(2)	–177(4)	–23(3)	2.6(5)
H(O1)	1250	208(8)	250	6.5(14)
H(O4)	523(2)	–440(3)	164(2)	1.8(4)

[a] $B_{iso} = 8/3\pi^2$ trace U. [b] O(2) shows high thermal anisotropy.

Experimental

Starting Materials

The ligand 3,6-dithiaoctanedioic acid was synthesized from thioglycolic acid and dibromoethane as described in the literature [1]. CuCl was prepared freshly by reduction of $CuCl_2$ with Na_2SO_3 by standard procedures.

Synthesis and Crystal Growth

Crystals of the title compound were prepared from 150 ml of a hot aqueous solution containing 1 mmol (2.1 g) of the ligand and an excess of CuCl in suspension. A few minutes after the reagents were mixed, the unreacted amount of CuCl was filtered off. When the filtrate was cooled under a nitrogen atmosphere colourless parallelopiped-shaped crystals of the Cu^I compound were formed. The crystals are insoluble and stable towards oxidation by air.

Crystal Data

$CuC_{12}H_{19}O_8S_4$; M = 483.1, monoclinic; a = 11.625(2), b = 7.664(2), c = 9.874(2) Å, β = 95.16(1)°, U = 876.2, D_m = 1.80(2) g cm^{-3}; Z = 2, D_c = 1.83 g cm^{-3}; F(000) = 496; space group P2/n, $\mu = 17.4$ cm^{-1} (MoKα).

Data Collection, Solution and Refinement

The intensities of 4005 independent reflections were measured on an Enraf-Nonius CAD-4 automatic diffractometer with MoKα radiation for $2° < \theta < 36°$, using a crystal of 0.5 × 0.3 × 0.25 mm. The space group followed from the systematic absences h + l = 2n + 1 for all h0l reflections. Accurate cell dimensions were determined from the angular settings of 24 reflections with $11° < \theta < 13°$. The 2993 reflections with $I > 2\sigma(I)$ were used for solution and refinement. Lorentz and polarization corrections were applied. No absorption correction was performed. Atomic scattering factors for neutral atoms were taken from International Tables [13], with corrections for anomalous dispersion. The structure was solved by direct methods.

Refinement was carried out using full-matrix least-squares techniques. The function minimized was $\Sigma w(|F_o| - s|F_c|)^2$ with $w = 1/\sigma^2$. All hydrogen

TABLE II. Bond Lengths (Å) and Angles (degrees) of Cu(L)(LH). Standard deviations in parentheses. The superscripts indicate the symmetry operations (i) 3/2 − *x*, *y*, ½ − *z*; (ii) 3/2 − *x*, 1 + *y*, ½ − *z*; (iii) 5/2 −*x*, *y*, ½ − *z*.

Cu–S(1)	2.3321(6)	C(3)–C(4)	1.518(2)	C(2)–H(22)	0.90(3)
Cu–S(2)	2.2920(6)	C(5)–C(6)	1.505(2)	C(3)–H(31)	1.06(3)
S(1)–C(2)	1.815(1)	C(1)–O(1)	1.279(2)	C(3)–H(32)	0.99(2)
S(1)–C(3)	1.812(1)	C(1)–O(2)	1.230(2)	C(4)–H(41)	0.96(2)
S(2)–C(4)	1.826(1)	C(6)–O(3)	1.213(2)	C(4)–H(42)	0.90(3)
S(2)–C(5)	1.808(2)	C(6)–O(4)	1.314(2)	C(5)–H(51)	1.00(3)
C(1)–C(2)	1.513(2)	C(2)–H(21)	0.97(3)	C(5)–H(52)	0.98(2)
				O(4)–H(04)	0.84(2)

S(1)–Cu–S(2)	92.62(1)	S(2)–C(5)–C(6)	111.1(1)
S(1)–Cu–S(1^{i})	116.29(2)	O(1)–C(1)–O(2)	124.3(1)
S(1)–Cu–S(2^{i})	114.77(1)	C(2)–C(1)–O(1)	113.4(1)
S(2)–Cu–S(2^{i})	127.77(2)	C(2)–C(1)–O(2)	122.3(1)
Cu–S(1)–C(2)	103.18(5)	O(3)–C(6)–O(4)	125.3(1)
Cu–S(1)–C(3)	98.00(5)	C(5)–C(6)–O(3)	124.2(1)
Cu–S(2)–C(4)	99.94(4)	C(5)–C(6)–O(4)	110.6(1)
Cu–S(2)–C(5)	114.06(5)	C(2)–S(1)–C(3)	100.59(6)
S(1)–C(2)–C(1)	110.99(9)	C(4)–S(2)–C(5)	97.36(7)
S(1)–C(3)–C(4)	114.17(9)	S(2)–C(4)–C(3)	111.17(9)
C(1)–O(1)–H(01)	120(2)	C(6)–O(4)–H(04)	109(2)

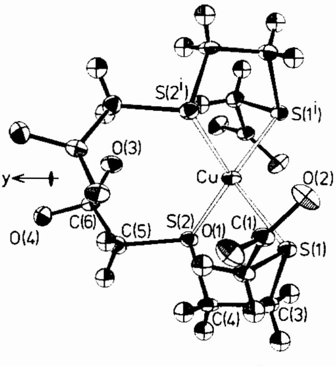

Fig. 1. Structure of the Cu^{I} compound of 3,6-dithiaoctanedioic acid, showing the thermal vibration ellipsoids (probability 30%) of the atoms and the atomic labelling. The carboxylate hydrogen atoms have been omitted for clarity.

atoms could be located, even those involved in hydrogen-bonding between carboxylate groups. Anisotropic refinement of all non-hydrogen atoms and refinement of the positions and isotropic temperature factors of all hydrogen atoms resulted in the final residuals $R = 0.0262$ and $R_w = 0.0418$.

The R and R_w values after a structure-factor calculation including all 4005 independent reflections were 0.044 and 0.046, respectively. A final difference Fourier synthesis showed no significant excursions above background, except one peak between C(3) and C(4). Atomic coordinates for all atoms are listed in Table I, together with isotropic B-values. Anisotropic thermal parameters for the non-hydrogen atoms are available as supplementary material, together with a Table of values for F_{obs} and F_{calc}.

Results and Discussion

Description of the Crystal Structure

The copper(I) atoms in the structure lie on twofold axes and are coordinated by four thioether S atoms in a distorted tetrahedral geometry (Fig. 1). The distortion results from the constraints imposed by the ligands. The five-membered chelate rings around Cu limit the S–Cu–S angles to approximately 90°. Bond lengths and angles are given in Table II. The carboxylate groups are not involved in metal binding. They lie at the surface of the molecule and play a role in intermolecular hydrogen bonding (Fig. 2 and Table III). Each molecule is hydrogen bonded to four neighbouring molecules by six hydrogen bonds.

Hydrogen bonds between O(2) and O(4) atoms of adjacent molecules result in infinite chains of hydrogen-bonded molecules in the *b* direction. The net sharing of protons between O(2) and O(4) accounts for two protons per molecule. There are additional strong hydrogen bonds between pairs of O(1) atoms in adjacent molecules related by an *a*-translation. This accounts for one proton per molecule. The hydrogen atom between these O(1) oxygen atoms is located on a twofold axis, apparently resulting in a symmetrical hydrogen bond (*vide infra*), as indicated in Table III. It should be noted, however, that a

TABLE III. Hydrogen Bond Formation on Cu(L)(LH).

Bond[a]	O•••O (Å)	O–H (Å)	O•••H (Å)	O–H•••O (°)
O(1)–H(01)–O(1^{iii})	2.441(2)	1.223(5)	1.223(5)	172.9(5)
O(4)–H(04)–O(2^{ii})	2.609(2)	0.84(2)	1.79(3)	165(1)

[a] Symmetry indicators ii and iii are as described in Table II.

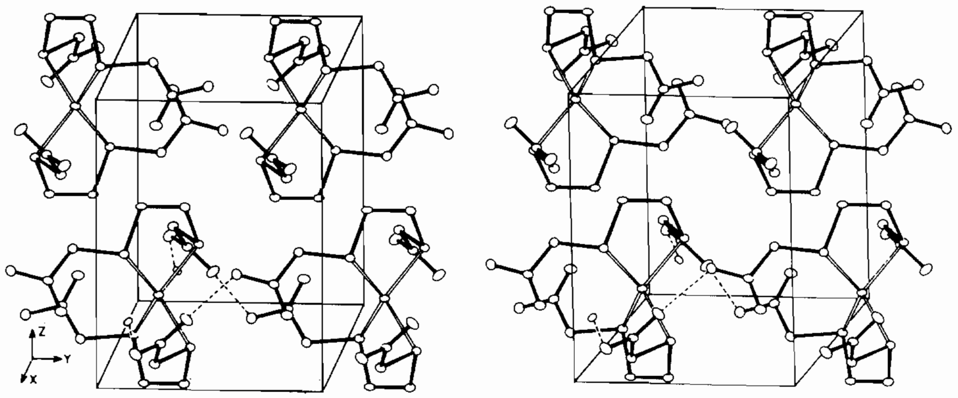

Fig. 2. The unit-cell packing of $CuC_{12}H_{19}O_8S_4$. Hydrogen bonds are indicated by dashed lines.

few positions nearby the twofold axis (with some disorder) cannot be excluded, because of the rather high B-value for H(01). The oxygen atom O(3) is not involved in hydrogen bonding and consequently the shortest C–O distance is C(6)–O(3). In total the hydrogen bonding system results in three protons per molecule, thus balancing the electrical neutrality.

The present structure is essentially the same as that found by Van der Meer [2], with only minor differences in bond lengths and bond angles, but in our present data all hydrogen atoms were found and could be refined. The relevant O•••O, O–H and O•••H distances and the O–H–O angles, listed in Table III, will be discussed below in relation with the infrared spectra.

A search in the Cambridge Crystallographic Data Base yielded only a few related structures with Cu^I coordinated by four thioether S atoms. In $Cu_2{}^ICu^{II}(CH_3SCH_2CH_2SCH_3)_6X_4$ ($X = BF_4$ or ClO_4) the Cu^I and Cu^{II} sites appeared to be randomly distributed, the inaccurate Cu^I–S bond lengths are 2.27(2) Å [14]. In $Cu^I(CH_3–S–CH_2–CH_2–S–CH_3)_2ClO_4$ the Cu^I–S bond length amounts to 2.263(6) Å [14], with S–Cu–S angles of 96.2(4) and 116.5(4)°. In $Cu^I(CH_3CH_2SCH_2CH_2SCH_2CH_3)_2(BF_4)$ the Cu^I–S bond lengths range from 2.280(4) to 2.318(5) Å [15]. The S–Cu–S (chelate) angles in this compound are 95.6(2)° and 94.0(2)°, whereas the other S–Cu–S angles are in the range of 110.4(2)–121.1(2)°. The coordination geometry in both compounds is similar to that of the title compound (Table II). Even the dihedral angles between the planes through the S–Cu–S triangles involving the different ligands are comparable, being about 85° in all compounds. Other thioether–Cu(I) bond lengths in the literature [16, 17] vary from 2.25–2.52 Å. The reported Cu(I)–S(methionine) distance of ≈2.5 Å in the copper enzyme plastocyanin falls within this range [18].

Infrared Spectrum

The IR spectrum of the title compound shows two unusual features. First, a broad band is observed with a maximum at about 2920 cm^{-1} with distinct shoulders at 2650, 2540 and 2450 cm^{-1}. Near the top of this band three sharp bands are observed, assigned to C–H stretchings. The other unusual feature is the very broad 'envelope' between 1400 and 300 cm^{-1}, with a maximum near 700 cm^{-1}. Superimposed on the envelope several other sharp bands are observed (often with apparently 'negative' peaks) [20], which are assigned to vibrations of the dithiaoctanedioate residues. Carboxylate vibrations occur at 1635 and 1705 cm^{-1}. A strong band at 395 cm^{-1} is assigned to a Cu–S stretching vibration. The spectra recorded in Nujol mull and KBr discs are identical.

Knowing the crystal structure and the hydrogen bonding pattern, we can now assign the broad band at 2920 cm^{-1} to the O–H stretching of the 'normal' assymetric hydrogen bond. Using the relationship developed by Bellamy and Owen [19] for weak and moderate hydrogen bonds, the O···O distance of 2.609 Å yields a ν_{OH} at 2870 cm^{-1} (assuming a free ν_{OH} to be at 3650 cm^{-1}) which compares very well with the observed value of 2920 cm^{-1}. The broad envelope-type band between 1400 and 300 cm^{-1} is typical for symmetrical O–H–O hydrogen bonds with O···O contacts of 2.40–2.45 cm^{-1}. Bands of this type have been reported by several authors [12, 20–22] in strongly hydrogen-bonded systems.

Concluding Remarks

The results described in the present paper have shown that Cu(I) preferentially binds to thioether groups when carboxylate groups are also present.

This observation is of interest in view of the biochemistry of copper and the observation that methionine is a ligand for copper(I) [18] and even – albeit weak – for copper(II) [9].

The observed intermediate and strong hydrogen bonds between oxygen atoms of carboxylate groups contribute to the stabilization of the crystal lattice to such an extent that the compound has an extremely low solubility. One of these hydrogen bonds belongs to the rare type of symmetrical hydrogen bonds; the proton could be clearly located on the twofold crystal axis.

Compounds of this type might be of great interest for molecular spectroscopy, since they are much simpler than the sodium, ammonium, potassium salts of carboxylic acids [21, 22]. The results of this study also indicate that in considering the coordination behaviour of a certain group or ligand, one should also consider possible competing hydrogen bonding.

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