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Structure and Properties of Diaquabis(ethylthioacetato)copper(II), $[Cu(C_4H_7SO_2)_2(H_2O)_2]$

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The crystal and molecular structure of the title complex has been determined by the X-ray diffraction method. The crystal was triclinic, space group $P\bar{1}$, $a=7.554(1)$, $b=9.001(1)$, $c=5.345(1)$ Å, $\alpha=104.83(1)$, $\beta=99.20(1)$, $\gamma=71.02(1)°$, $Z=1$, $D_x=1.684(1)$, $D_m=1.69(1)$ Mg m^{-3}, μ(Mo $K\alpha$)$=2.03$ mm^{-1}, and the final R value was 0.030 for 1818 reflections. The molecular arrangement has a center of symmetry and has a slightly distorted octahedral configuration around the central copper(II) atom; each ethylthioacetato ligand forms a chelate ring by coordinating through a sulfur atom and a carboxyl oxygen atom, and two water molecules are also coordinated to the central metal. The solid complex is deep green, different from the diaquabis(alkylthioacetato)copper(II) complexes of the higher alkyl groups (number of $C\geq3$), and it is likely due to the CT band caused by the strong copper–sulfur bond in the complex.

The coordination compounds of copper(II) with sulfur containing ligands are now studied very actively in relation to the model compounds of copper proteins. The (alkylthio)acetic acids** are coordinated to the central metal atom through a sulfide sulfur atom, however, their sulfur-metal bonding is not always stable. The authors have already reported the syntheses and properties[1–5] as well as the structures[6–8] of some metal alkylthioacetates. In the case of copper (II) complexes, the formation of the strong metal-sulfur bond is expected to be due to the relatively soft character of the copper(II) atom, and also to the observed relatively high stabilities of the complexes. Moreover, they are divided into three groups according to their colors; pale blue ones (the majority of them), deep green ones (the methylthio- and ethylthioacetates), and the violet isomer of the isopropylthioacetate. The complexes of each color seems to possess characteristic structures, and we had already begun to clarify their structure by the X-ray technique, and by spectroscopic methods. The structure of the violet isomer was already elucidated.[7] This paper presents the structure of a deep green complex. Although the X-ray diffraction technique was not yet applied to the pale blue complexes, due to the difficulty in obtaining the appropriate crystals, the comparison of the visible, infrared, and electron paramagnetic resonance spectroscopic data of these alkylthioacetate complexes, suggested some relations between their structures and their spectral properties.

Experimental

Synthesis of Diaquabis(ethylthioacetato)copper(II); $[Cu(C_2H_5SCH_2CO_2)_2(H_2O)_2]$. The ligand was obtained by the condensation reaction between ethyl iodide and mercaptoacetic acid in alkaline aqueous medium as shown by Larsson.[9] The copper(II) complex was obtained by reaction between the freshly obtained copper(II) hydroxide and the free acid ligand. The pure crystals were obtained when the concentrated aqueous solution of the complex was kept overnight at ambient temperature. Analyses of the complex: Found: Cu, 18.66; C, 28.66; H, 5.41%. Calcd for $CuC_8H_{18}S_2O_6$: Cu, 18.80; C, 28.44; H, 5.37%.

X-Ray Measurement. The crystals obtained were deep-green in color, and were stable in air. The crystal used for the X-ray diffraction study was reshaped into a sphere ($\phi=0.4$ mm). The crystallographic data are as follows: $CuC_8H_{18}S_2O_6$, F.W.$=337.89$, triclinic, space group $P\bar{1}$, $a=7.554(1)$, $b=9.001(1)$, $c=5.345(1)$ Å, $\alpha=104.83(1)$, $\beta=99.20(1)$, $\gamma=71.02(1)°$, $Z=1$, $D_x=1.684(1)$, $D_m=1.69(1)$ Mg m^{-3}, μ(Mo $K\alpha$)$=2.03$ mm^{-1}. The reflections within the range of $2\theta<60°$ were collected on a Philips 1100 automated four-circle diffractometer, using Mo $K\alpha$ radiation (0.7107 Å), applying the (ω-2θ) scan technique. The 1818 independent reflections with $|F_o|>3\sigma(|F_o|)$ were used for the structure refinement. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction.

All the calculations were carried out on a HITAC M-200H computer at the Computer Center of The University of Tokyo using the local version of UNICS program.[10] The atomic scattering factors were taken from the tables.[11]

Structure Determination. The structure was solved by the heavy-atom method. The position of the copper atom was fixed at the origin. The position of the sulfur atom was deduced from a three dimensional Patterson map, and the other non-hydrogen atoms were successively located by Fourier syntheses; their positions and their parameters were refined by a repeated block-diagonal least squares method. Then the positions of all hydrogen atoms were obtained from a difference Fourier synthesis, and were also refined. In the last cycle of the refinement with anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The final R value was 0.030.[12]

Other Measurements. The infrared spectra of the samples were obtained by means of a JASCO infrared spectrophotometer type 403G, using Nujol and hexachloro-1,3-butadiene mulls.

The visible absorption spectra of the samples were obtained on a Hitachi 124 spectrophotometer, and the reflectance spectra on the same instrument with the appropriate attachment, using magnesium oxide as the reference substance.

The electron paramagnetic resonance spectra of the solid sample were measured on a JEOL PE3X electron paramagnetic resonance spectrometer, at room temperature, using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as the standard for the determination of the g-values.

** For the simplicity, hereafter, the parentheses in the name of this type of compounds are neglected.

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

	x	y	z	B_{eq} a)
Cu	0	0	0	1.9
S	357(1)	2360.2(4)	3022(1)	2.0
O(1)	1826(1)	214(1)	−1885(2)	2.2
O(2)	3923(2)	1382(2)	−2184(3)	3.4
O(W)	−2492	1400(2)	−2885(2)	2.7
C(1)	2782(2)	1217(2)	−962(3)	2.1
C(2)	2513(2)	2192(2)	1795(3)	2.6
C(3)	−1300(2)	4006(2)	1712(3)	2.7
C(4)	−3209(3)	4323(3)	2679(4)	3.8
				B_{iso}
H(W1)	−326(4)	125(3)	−284(5)	4.7(6)
H(W2)	−218(4)	69(4)	−457(5)	5.7(7)
H(21)	348(2)	174(2)	300(4)	2.1(3)
H(22)	229(4)	344(3)	212(6)	4.9(6)
H(31)	−125(3)	358(3)	−9(4)	2.7(4)
H(32)	−79(4)	500(3)	257(6)	5.1(6)
H(41)	−376(3)	339(3)	192(5)	3.4(4)
H(42)	−315(4)	421(4)	444(6)	4.8(6)
H(43)	−398(4)	549(4)	234(6)	5.4(6)

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{\text{eq}} = \frac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab\cos\gamma + B_{13}ac\cos\beta + B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

Table 2. Interatomic distances (l/Å) and bond angles (ϕ/°) with estimated standard deviations in parentheses

Cu-S	2.381(1)	O(2)-C(1)	1.227(2)
Cu-O(1)	1.916(2)	C(1)-C(2)	1.517(2)
Cu-O(W)	2.457(1)	C(3)-C(4)	1.524(3)
S-C(2)	1.798(2)	O(W)···O(2$^{\text{i}}$)	2.798(2)
S-C(3)	1.815(2)	O(1)···O(W$^{\text{ii}}$)	2.841(2)
O(1)-C(1)	1.289(2)		
S-Cu-O(1)	86.49(4)	Cu-O(1)-C(1)	122.82(10)
S-Cu-O(W)	96.29(3)	O(1)-C(1)-O(2)	123.0(2)
O(1)-Cu-O(W)	88.97(5)	O(1)-C(1)-C(2)	117.9(2)
Cu-S-C(2)	92.63(6)	O(2)-C(1)-C(2)	119.1(2)
Cu-S-C(3)	104.27(5)	S-C(2)-C(1)	115.07(12)
C(2)-S-C(3)	102.13(8)	S-C(3)-C(4)	108.0(2)
O(W)···O(1$^{\text{ii}}$)-Cu$^{\text{ii}}$	124.34(5)		
O(W)···O(2$^{\text{i}}$)-C(1$^{\text{i}}$)	153.37(12)		
Cu-O(W)···O(1$^{\text{ii}}$)	108.71(4)		
O(2$^{\text{i}}$)···O(W)···O(1$^{\text{ii}}$)	106.22(5)		
Cu-O(W)···O(2$^{\text{i}}$)	113.28(6)		

Key to symmetry operations. i: $x-1.0$, y, z; ii: $-x$, $-y$, $-1.0-z$.

Results and Discussion

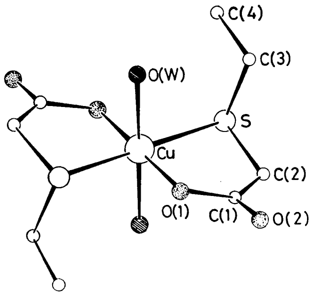

Fig. 1. A perspective drawing of the title compound with the numbering scheme of atoms.

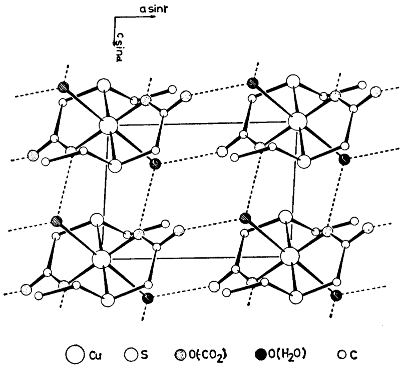

Fig. 2. Crystal packing diagram projected along b.

The final atomic parameters are listed in Table 1,[13] the interatomic distances and the bond angles in Table 2. A perspective drawing of the complex and the numbering scheme of atoms are shown in Fig. 1, and a projection of the structure along b in Fig. 2. The crystal consists of discrete molecules of $[\text{Cu}(\text{C}_2\text{H}_5\text{SCH}_2\text{CO}_2)_2(\text{H}_2\text{O})_2]$ except for weak hydrogen bondings. The molecule has a center of symmetry, occupied by a copper atom. As shown in Fig. 1, and in Table 2, the central metal in this complex is in a deformed octahedral environment, elongated to both of the oxygen atoms of the coordinated waters. The ethylthioacetato ligand forms a five-membered chelate ring, being coordinated through a sulfur atom and a carboxyl oxygen atom. As shown in the previous paper,[2] the value of the magnetic moment of this complex shows no interaction between copper atoms.

The Cu–S distance is 2.381(1) Å, which is a little longer than that in the violet isomer of bis(isopropylthioacetato)copper(II) dihydrate,[7] but shorter than that of the diaquabis(methylthioacetato)cobalt(II) (2.531(1) Å).[8] The structures of some copper(II) complexes of the aliphatic ligands containing sulfide sulfur, where the sulfur atom is coordinated with the central metal, were already clarified by X-ray method.[14–22] The observed Cu–S distances for them are about 2.3—2.4 Å, and the Cu–S distance of this complex seems to be a normal one; not weak, nor very strong.

The Cu–O(1) (where O(1) is the carboxyl oxygen) is 1.916(2) Å. On the other hand, the Cu–O(W) (where O(W) is the coordinated water oxygen) is 2.457(1) Å, which is much longer than the former one. Therefore, the octahedron around the copper (II) atom was elongated to the direction of this O(W)–Cu–O(W′) axis. As the C(1)–O(1), 1.289(2) Å, is

TABLE 3. INFRARED SPECTRA OF SOME METAL ALKYLTHIOACETATES (cm^{-1})

Complexes	ν(OH)	ν_{as}(COO)[a]	ν_s(COO) and others	Color
$Cu(MeSA)_2(H_2O)_2$	3300	1616	1441 1409 1370	dark green
$Cu(EtSA)_2(H_2O)_2$	3450 3370	1616	1409 1370	dark green
$Cu(nPrSA)_2(H_2O)_2$	3100	1593	1454 1399 1371	pale blue
$Cu(nBuSA)_2(H_2O)_2$	3100	1594	1463 1405 1376	pale blue
$Cu(iPrSA)_2 \cdot 2H_2O$	3380 3270	1592	1460 1387 1366	violet
$Co(MeSA)_2(H_2O)_2$	3180 3100	1615	1433 1391 1368	red

HMeSA: Methylthioacetic acid, HEtSA: ethylthioacetic acid, HnPrSA: propylthioacetic acid, HiPrSA: isopropylthioacetic acid, HnBuSA: butylthioacetic acid. a) Only the strongest peaks are shown.

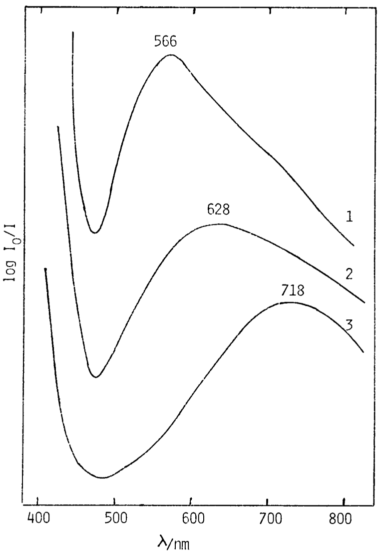

Fig. 3. Reflectance spectra of the complexes.
1: Bis(isopropylthioacetato)copper(II) dihydrate (violet isomer), 2: diaquabis(ethylthioacetato)copper(II), 3: diaquabis(propylthioacetato)copper(II).

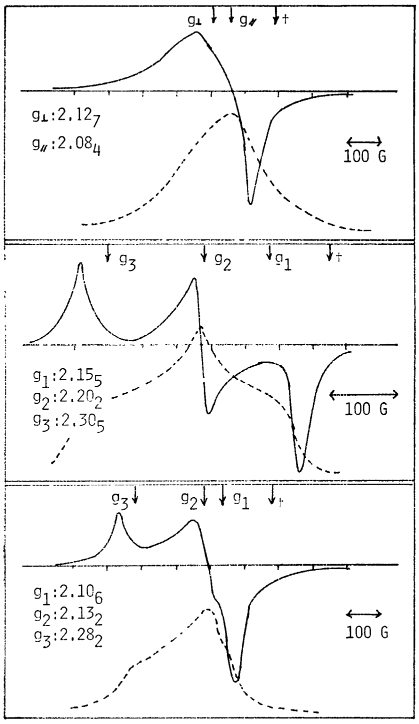

Fig. 4. Electron paramagnetic resonance spectra of the complexes.
1: Bis(isopropylthioacetato)copper(II) dihydrate (violet isomer), 2: diaquabis(ethylthioacetato)copper(II), 3: diaquabis(propylthioacetato)copper(II), †: DPPH standard. Broken lines show the integral curves of the spectra.
1 G$=1\times10^{-4}$ T.

longer than C(1)–O(2), 1.227(2) Å, the carboxyl group of the ligand seems to be the covalently bonded in the chelate.

The coordinated water molecule forms hydrogen bonds both with the O(1) atom of a complex adjacent in c-axis direction, and with the O(2) atom of the adjacent complex in a-axis direction.

Some infrared spectral data for the copper(II) ethylthioacetate together with some related complexes, are shown in Table 3.

The ν(O–H) band of methylthio- and ethylthioacetates appears at about 3300—3450 cm^{-1}, while the corresponding band of the hydrated copper(II) propylthio-, and butylthioacetates appears in the lower wave number region. (Although it is not shown in the table, the higher homolog of the alkylthioacetates also have the lower wave number ν(O–H) band.) The band of the violet isomer of the isopropylthioacetate appears in the intermediate region of them. Therefore, the grouping of the complexes in color, deep-green, pale-blue, and violet, corresponds with the grouping by the wave numbers of the ν(O–H) band. The lower wave number of the band was observed also in the spectra of diaquabis(methylthioacetato)cobalt(II), where the Co–O(W) (where O(W) is the oxygen atom of the coordinated water), is 2.066 (3) Å, and it is much shorter than that of Cu–O(W) in the present complex, even considering the difference of the radii of cobalt(II) and copper(II). On the other hand, there is no clear relation between the colors and the wave numbers of the ν_{as}(COO) and ν_s(COO) bands.

The reflectance spectra of the three types of complexes, ethylthio-, propylthio-, and isopropylthioacetates of copper(II) are shown in Fig. 3. As is shown in the figure, the pale blue complex, the propylthioacetate, has a d-d band at about 718 nm. On the other hand, the isopropylthioacetate (violet isomer), as well as the present ethylthioacetate show a broad band at 500—700 nm. Although the exact analysis of the absorption pattern has not yet been carried out, at least, it is likely that a band stronger than the common d-d one overlaps the latter one in these two cases. The ovelapping band seems to have the maximum in the 500—600 nm region, which is shorter than that of the pure d-d band. Probably this band is due to a pπ-pπ back donation from copper to sulfur, as the Cu–S bands of these complexes are short enough. On the other hand, this kind of charge transfer band does not exist in the spectra of the pale blue complexes, and therefore, their Cu–S bonds are expected to be longer than the deeper colored ones.

The electron paramagnetic resonance spectra of the complexes in the powdered solid state at room temperature are shown in Fig. 4, together with their integral curves. From these results, it can be seen that diaquabis(ethylthioacetato)copper(II) as well as diaquabis(propylthioacetato)copper(II) has three different axes like copper(II) chloride dihydrate.[23] Although the features of their spectral patterns are different from each other, their integral curves resemble each other. Therefore, the difference is likely to be a quantitative one concerning their *g*-values, only. On the other hand, bis(isopropylthioacetato)copper(II) dihydrate has only two kinds of axes, $g_{/\!/}$ and $g_{\perp}$, like copper(II) sulfate pentahydrate,[23] and the structure is expected to be different from the other copper(II) alkylthioacetates. Therefore, the pale-blue copper(II) alkylthioacetates are expected to have a coordination structure similar to that of the green ones.

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