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The Hydrated and Anhydrous Copper(II) Complexes with Thioglycolic Acid Derivatives

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The dihydrates and anhydrous copper(II) complexes with methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and benzyl thioglycolic acids were synthesized, and their properties were investigated. The magnetic data show that the copper in the complexes is divalent and that the complexes do not have a copper(II) acetate structure. The spectroscopic data show that these ligands bond to the central metal ion as strongly as does amino acid or water. In the case of isopropyl thioglycolato copper(II) dihydrate, the blue and the violet isomers were obtained. The structures of the complexes in the solid state as well as in the solution were discussed.

In a previous paper,[1] solid metal complexes with ETTA(ethanediylidenetetrathiotetraacetic acid) and some alkyl di- or mono-thioglycolic acid derivatives were reported. The copper(II) complex of benzylthioglycolic acid was obtained in the dihydrate form as well as in the anhydrous form; their colors are quite different, the former being light blue, and the latter, dark green. On the other hand, McAuliffe recently studied the structural difference between hydrated and anhydrous nickel complexes of amino acids.[2] Therefore, in order to study the structural difference, hydrated and anhydrous copper complexes of methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl and benzyl thioglycolic acids were synthesized and investigated magnetically as well as spectroscopically. In the course of this study, two isomers of isopropyl thioglycolato copper(II) dihydrate were isolated.

Experimental

Instruments. The magnetic moments of the samples were measured with a Gouy balance at room temperature (15°C). The electronic absorption spectra were obtained by the use of a Hitachi EPS-2 automatic recording spectrophotometer. The reflectance spectra were measured with an Ito QU-3 spectrophotometer, using a reflectance spectra attachment. The infrared spectra were obtained by means of a nujol or hexachloro-1,3-butadiene mull procedure, using a Japan Spectroscopic Co. DS 403 G grating automatic recording infrared spectrophotometer.

The Syntheses of the Metal Complexes. The ligands were obtained by Larsson's method[3] from thioglycolic acid and alkyl halides. The metal complexes were synthesized from the ligands and copper(II) hydroxide. A typical pattern of the process is shown below.

The Synthesis of the Isopropyl Thioglycolato Copper(II). Copper(II) hydroxide, itself produced from one gram of copper(II) chloride dihydrate and sodium hydroxide, was mixed with 2 grams of isopropyl thioglycolic acid, and the mixture was stirred. After the copper(II) hydroxide had been dissolved, the residue was filtered off; the filtrate was kept overnight in a refrigerator. A pale blue dihydrate complex was thus precipitated. The product was filtered off and repeatedly washed with diethyl ether. It could be recrystallized with acetone, but the recrystallized product was found to be an anhydrous green complex and not the dihydrate. After the pale blue dihydrate had been filtered off and the filtrate had been kept several days more in a refrigerator, the violet dihydrate was deposited as black, needle-like crystals. The complex was filtered off and washed with diethyl ether. The yield of the blue complex was 0.6 g (26%), and that of violet one, 0.7 g (31%). The yield was calculated on the basis of copper chloride.

The other complexes in the dihydrate form were synthesized by almost the same procedure, but only those in the pale blue form have thus for been obtained. The isopropyl and the benzyl thioglycolato copper(II) dihydrate were dehydrated by refluxing them with acetone or benzene respectively (the violet and blue isomers of the former gave the same green anhydrous product). However, the anhydrous methyl, ethyl, *n*-propyl, and *n*-butyl complexes could not be obtained by refluxing their dihydrates with any organic solvents; some of them were decomposed. Therefore, their anhydrous complexes were obtained by heated their dihydrate to 40°C on phosphorus pentoxide in a vacuum for about 10 hours.

Results and Discussion

The elemental analysis, the expected chemical formulae, and the magnetic moments of the com-

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[1] A. Ouchi, Y. Ohashi, T. Takeuchi and Y. Yoshino, This Bulletin, **43**, 1088 (1970).

[2] C. A. McAuliffe and W. D. Perry, *J. Chem. Soc.*, *A*, **1969**, 634.

[3] E. Larsson, *Ber.*, **63**, 1347 (1930).

TABLE 1. ANALYSES AND THE MAGNETIC MOMENTS OF THE COMPLEXES

Chemical formula		Analysis (%)				Magnetic moment (B.M.)	Method of dehydration
		M	C	H	S		
$Cu(MeS_1)_2\cdot 2H_2O$	Calcd	20.51	23.26	4.55	20.70		
	Found	20.55	23.85	4.20	20.21	1.84	
$Cu(MeS_1)_2$	Calcd	23.21	26.32	3.68	23.42		*
	Found	23.48	25.26	4.20	22.75	1.82	
$Cu(EtS_1)_2\cdot 2H_2O$	Calcd	18.80	28.44	5.37	18.98		
	Found	18.16	28.76	5.41	17.40	1.73	
$Cu(EtS_1)_2$	Calcd	21.05	31.83	4.68	21.24		*
	Found	20.58	31.40	4.86	20.96	1.79	
$Cu(n\text{-}PrS_1)_2\cdot 2H_2O$	Calcd	17.36	32.82	6.06	17.52		
	Found	17.62	32.95	5.88	16.54	1.85	
$Cu(n\text{-}PrS_1)_2$	Calcd	19.26	36.41	5.50	19.44		*
	Found	18.57	36.60	4.87	18.50	1.71	
$Cu(i\text{-}PrS_1)_2\cdot 2H_2O$ (blue)	Calcd	17.36	32.82	6.06	17.32		
	Found	17.29	33.07	5.96	17.05	1.84	
$Cu(i\text{-}PrS_1)_2\cdot 2H_2O$ (violet)	Calcd	17.36	32.82	6.06	17.32		
	Found	17.52	32.17	6.05	16.30	1.88	
$Cu(i\text{-}PrS_1)_2$	Calcd	19.26	36.41	5.50	19.44		**(acetone)
	Found	19.59	36.25	5.70	19.44	1.87	
$Cu(n\text{-}BuS_1)_2\cdot 2H_2O$	Calcd	16.13	36.58	6.65	16.28		
	Found	16.27	37.01	6.53	17.40	1.83	
$Cu(n\text{-}BuS_1)_2$	Calcd	17.75	40.26	6.20	17.91		*
	Found	17.80	38.19	6.48	16.90	1.80	
$Cu(BzS_1)_2\cdot 2H_2O$	Calcd	13.75	46.79	4.80	13.88		
	Found	13.58	46.62	4.85	14.38	1.75	
$Cu(BzS_1)_2$	Calcd	14.92	50.75	4.26	15.05		
	Found	14.87	51.09	4.53	15.47	1.86	**(benzene)

* Dehydrized by Abderhalden exciccator on phosphorus pentoxide at 40°C under reduced pressure.

** Dehydrized by refluxing the hydrate in the written solvents.

MeS_1H = methyl thioglycolic acid, EtS_1H = ethyl thioglycolic acid, $n\text{-}PrS_1H$ = n-propyl thioglycolic acid, $i\text{-}PrS_1H$ = isopropyl thioglycolic acid, $n\text{-}BuS_1H$ = n-buthyl thioglycolic acid, BzS_1H = benzyl thioglycolic acid.

plexes obtained are shown in Table 1. The sulfur analyses sometimes gave values which were a little low, probably because of the experimental difficulties. However, as the contents of other elements coincided with calculated values well enough, the proposed chemical formulae seem to be supported.

The magnetic moments of these complexes are about 1.75—1.85 B.M. Although many copper(II) compounds show the magnetic moment of 1.9—2.1 B.M., some amine or amino acid complexes give values in the range of 1.8—1.88 B.M.[4-6]. Therefore, Cotton stated that usual copper(II) complexes show magnetic moments of 1.75—2.20 B.M.[7] Some copper(II) complexes show a subnornal magnetic moment (<1.74 B.M.).[8] Copper(II) acetate containing three atom bridges of the carboxyl group has a magnetic moment value of 1.43 B.M., while copper(II) bromide containing monoatomic bridges of halogen atom has a

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[4] W. E. Hatfield and R. Whyman, "Transition Metal Chemistry," Vol. 5, ed. by R. L. Carlin, Marcel Dekker, New York, N. Y. (1969), p. 84.

[5] C. A. McAuliffe, J. V. Quagliano and L. M. Vallarino, *Inorg. Chem.*, **5**, 1996 (1966).

[6] S. E. Livingstone and J. D. Nolan, *ibid.*, **7**, 1447 (1968).

[7] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd Ed., Interscience Publishers, New York, N. Y. (1966), p. 902.

[8] M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

TABLE 2. THE WAVE NUMBERS AND THE MOLAR EXTINCTION COEFFICIENTS OF THE ABSORPTION MAXIMA OF THE ELECTRONIC SPECTRA OF THE COMPLEXES (in kK for the wave numbers and log ε for the extinction coefficients (in parentheses))

Complex	Solvent	Absorption spectra				Reflection spectra	
$Cu(MeS_1)_2$	H_2O	13.9(1.79)	30.6(2.86)	38.5(2.84)		$2H_2O$	15.6 sh 15.9 16.4
	C_2H_5OH	14.7(2.23)	29.9(3.06)	36.4(3.20)		$0H_2O$	14.3 sh 14.9
$Cu(EtS_1)_2$	H_2O	14.3(1.94)	30.4(2.85)	38.5(2.87)		$2H_2O$	15.6
	C_2H_5OH	14.9(2.30)	28.9(3.36)	36.1(3.44)		$0H_2O$	14.5
$Cu(n\text{-}PrS_1)_2$	H_2O	14.5(1.97)	27.0(2.64)	30.3(2.87)	36.8(2.90)	$2H_2O$	15.3 sh 15.1 sh
	C_2H_5OH	14.9(2.17)	28.3(3.47)		36.1(3.35)	$0H_2O$	14.3 sh 14.9 16.4 sh
$Cu(i\text{-}PrS_1)_2$	H_2O	14.5(2.05)	27.0(2.70)	29.9(2.85)	38.5(3.11)	$2H_2O$	14.9 16.1 sh
(blue)	C_2H_5OH	14.5(2.41)	27.4(3.64)	34.9(3.51)		$0H_2O$	14.3 sh 15.9 sh
$Cu(i\text{-}PrS_1)_2$*	H_2O	14.5(2.02)	29.9(2.77)	38.0(2.89)		$2H_2O$	16.1 sh 17.2 18.5
(violet)	C_2H_5OH	14.9(2.38)	27.5(3.55)	35.1(3.49)	46.3(3.78)		
$Cu(n\text{-}BuS_1)_2$	H_2O	14.3(1.99)	27.0(2.70)	30.1(2.90)	38.4(2.91)	$2H_2O$	14.3
	C_2H_5OH	14.9(2.38)	27.6(3.25)	35.5(3.20)	46.1(3.49)	$0H_2O$	14.7 br
$Cu(BzS_1)_2$**	H_2O	13.1	30.7	37.7		$2H_2O$	13.7 sh 14.5
	C_2H_5OH	14.1	30.9	38.0		$0H_2O$	14.5 sh 15.3

The sample solutions for the absorption spectra were obtained by dissolving the anhydrous complexes unless the note is given.

* Solutions were made from the dihydrate.

** As hardly soluble in the solvents, log ε values could not be determined.

sh: shoulder br: broad. refer the other abbreviations in Table 1.

$2H_2O$: dihydrate, $0H_2O$: anhydrous complex.

value of 1.31 B.M. These phenomena are caused by the spin-spin interaction between copper(II) ions. However, the subnormally low magnetic moment is not found in all carboxyl group bridged polymers. Copper(II) benzoate trihydrate, for example, shows a magnetic moment of 1.87 B.M. in spite of its linear polymer structure.[9] These alkyl thioglycolato complexes surely do not have a strong spin-spin interaction between copper(II) ions. It is not probable that they have a structure like copper(II) acetate, but the possibility of some weakly-bonding linear polymer structure of the copper(II)-benzoate type, for example, can not be denied.

The reflectance spectra of the solid dihydrate and anhydrous complexes as well as the absorption spectra of ethanolic or aqueous solutions of the anhydrous complexes are shown in Table 2.[*1]

All of the complexes studied show one band in the visible region. It has been identified as the *d-d* band ($^2E_g \rightarrow ^2T_{2g}$) of the octahedral copper(II) ion.[10] As all octahedral copper(II) complexes are apt to be deformed by the Jahn-Teller effect, the band is broadened. These alkyl thioglycolates, do not seem to be in the pure square-planar form. The square-planar copper(II) complexes, bis-(acetylacetonato) copper(II), for example, show two bands of nearly equal intensities in the visible region, at about 15.0 and 18.0 kK; they are identified as the $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2E_g$ bands respectively.[11-13] Almost all of these alkyl thioglycolato copper(II) complexes show only one absorption maximum with a relatively low ν_{max} value, although in some cases they are broad or have a shoulder.

Two other bands in the ultraviolet region are probably charge-transfer or ligand-transition bands. By comparing the wave numbers of the *d-d* bands given in Table 2, it can be seen that, for

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[9] M. Inoue, T. Kishita and S. Kubo, *Nippon Kagaku Zasshi*, **84**, 759 (1963).

[*1] The absorption spectra of aqueous solutions of dihydrates are the same as those of the respective anhydrous salts. However, those of ethanolic solutions of both forms are slightly different from each other, although the general features of the spectra are the same and the difference in their maximum wave numbers (ν_{max}) is small. Probably a part of the coordinated water of the solid dihydrate is not removed completely even in the ethanolic solution.

[10] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw Hill, New York, N. Y. (1962), p. 269.

[11] F. A. Cotton and J. J. Wise, *J. Amer. Chem. Soc.*, **88**, 3451 (1966), *Inorg. Chem.*, **6**, 917 (1967).

[12] J. P. Fackler, Jr., F. A. Cotton and D. W. Barnum, *ibid.*, **2**, 97 (1963).

[13] B. N. Figgis, "Introduction to Ligand Field," Interscience Publishers (Wiley), New York, N. Y. (1966), p. 316.

each complex, the ν_{max} of the aqueous solution is the lowest, and that of the reflectance spectra of the solid dihydrate, which is a little higher, is next. The *d-d* band of the complex in the ethanolic solution always has higher ν_{max} and ε values than those of an aqueous solution. The *d-d* band of the reflectance spectra of the dihydrates shifts to the higher-wave number side in the cases of *n*-butyl and benzyl thioglycolato complexes when they are dehydrated. However, in the cases of methyl, ethyl and propyl thioglycolates, the band shifts to the opposite side.

It seems that these facts can be explained as follows. The alkyl thioglycolic acids generally have a little stronger ligand field effect than water, and the smaller the alkyl group is, the higher the affinity of the ligand is. In the aqueous solution, however, as the concentration of water is predominant, the complex species have four molecules of water and two molecules of ligand working as a monodentate and bonding with the copper ion by means of its carboxyl oxygen only. Therefore, the wave number as well as the intensity of the *d-d* band of the aqueous solution is low, although it is higher than that of $[Cu(H_2O)_6]^{2+}$.

In the cases of solid dihydrates, the complex is also in an octahedral form, but the ligand serves as a bidentate and bond with the central metal ion not only by means of the carboxyl group but also by means of the sulfur atom, although the metal-sulfur bond is probably not strong. The other two bonds of the octahedral copper ion may be linked with each other by means of the bridge of a water molecule, thus forming a linear polymer. The species in an ethanolic solution also seems to be in an octahedral form. Probably only two alcohol molecules bond weakly to the metal ion, and the ligand molecules work as the bidentate. In the case of a solid anhydrous complex, not a simple monomeric square-planar structure, where two molecules of the ligand coordinate to the metal, but a polymeric, distorted octahedral structure bridged with the carboxyl group of the ligand, as with the amino acid complexes of nickel proposed by McAulliffe,[2] is probable.

The violet isomer of isopropyl thioglycolato copper(II) dihydrate gives a different reflectance spectra as well as a different X-ray powder pattern of the solid from those of the blue isomer. Moreover, the violet color is very deep, although the exact measurement of the intensity of the bands is impossible. However, when the violet isomer is dissolved into solvents, its absorption spectra are just the same as those of the pale blue isomer, and when the violet or blue dihydrates were dehydrated by refluxing them with acetone, the same anhydrous complex was obtained. Therefore, the structural difference between them is probably caused only by the bond type of the ligand and the water in the complex. Probably the sulfur atom of the ligand bonds more tightly to the copper ion in the violet dihydrate than in the blue one.

TABLE 3. INFRARED SPECTRA OF THE ISOPROPYL THIOGLYCOLIC ACID AND ITS COPPER(II) COMPLEXES (1700—200 cm^{-1})

i-PrS$_1$-H	Cu(*i*-PrS$_1$)$_2$·2H$_2$O (blue)	Cu(*i*-PrS$_1$)$_2$·2H$_2$O (violet)	Cu(*i*-PrS$_1$)$_2$	Tentative assignment
1710 s	1588 s	1590 s	1583 s	$\nu_{antisym}$(COOH)
1460 sh 1420 s	1460m	1440 s	1460 1445 w	ν_{sym}(COOH)
	1380 s	1380 1360 s	1352 1342 m	$\delta(CH_3)$
1300 s				
1250w	1251m	1260 s	1243m	
1200w	1231m	1225w	1229m	δ(O-C=O)+others
1152m	1152m	1152m	1154m	
1044 s	1053m	1060m	1059 s	$\rho(CH_3)$
930w	941 s	925 s	930m	δ(O-C=O)+others
	896m	895 s	897 s	
790m	789 s		777 s	$\delta(COO^-)$
	710m	720m		
580m	638m	620 s	630m	
	538m	556m		
465 s	470m	467 s	467 s	δ(OCO) or others
		410 s		
348w	368 s	401 s	370 s 327 s	ν(M-O) or others
	242 s 226 sh	250 s 220m	260 s 192m	ν(M-S)

s: strong, m: medium, w: weak, sh: shoulder. Refer the other abbrevations in Table 1.

A nearly square planar form with two bidentate ligand molecules is probable in the former. The water molecules are only loosely bonded or are held in crystalline interstices.

The infrared spectra (1700—200 cm^{-1}) of the complexes were studied; their tentative assignments, obtained with reference to those of oxalato, acetylacetonato, and amino acid complexes,2,6,7,14—16) are shown in Table 3.

The antisymmetric COO stretching bands of the complexes appear at about 1580—1590 cm^{-1}. These values correspond to those of glycinato and other amino-acid complexes. The bridging carboxyl groups of metal carboxylato complexes also show the band in this region. Therefore, the low wave number of the band is not necessarily a proof of the ionized carboxyl group. The symmetric COO stretching bands appear at about 1440—1460 cm^{-1}. In the far infrared region, the ν(Cu–O) bands of pyridine-1-oxide complexes are found at about 400 and 450 cm^{-1};17) that of acetylacetonate, at about 480 cm^{-1},14) and those of oxalato complexes, at about 420 cm^{-1}. Therefore, the ν(Cu–O) bands of these alkyl thioglycolato complexes should appear near the 400—450 cm^{-1} region. The bands in 360—410 cm^{-1}, which appear only in the spectra of these metal complexes, not in those of the free ligands, are tentatively assigned as ν(Cu–O) bands, although their wave numbers are a little low.

The metal-sulfur stretching band of the first transition metals have been reported to occur over a wide range of wave numbers,7) the bands of monothio- or dithio-β-diketonates occur at about 350 cm^{-1}, while the bands occur in the range of 205—298 cm^{-1} in the cases of thiourea adducts.18) A broad band at 205 cm^{-1} was identified as the ν(Cu–S) one in the case of the ethylenethiourea complex of copper(I). Consequently, the bands at about 250 cm^{-1} can be tentatively assigned.

A strong band at about 450—470 cm^{-1} is also observed in the spectra of all metal complexes. However, the free ligands also have the band. Therefore, it is probable that this band is the δ(O-CO) one. As the alkyl thioglycolato complexes are less stable than β-diketonates and such complexes, the bond between the Cu–O and Cu–S of the former are probably weaker and, consequently, their stretching bands appear in the lower-wave number region.

TABLE 4. SOME INFRARED WAVE-NUMBERS OF THE ALKYL THIOGLYCOLIC ACIDS AND ITS COPPER(II) COMPLEXES

Refer the abbreviation in Table 1 and 3.

Chemical formula	Tentative assignments			
	ν_{antisym}(COOH)	ν_{sym}(CCOH)	ν(M–O)+others	ν(M–S)
MeS_1–H	1710 s	1420 s		
$Cu(MeS_1)_2 \cdot 2H_2O$	1600 s	1420w	387 s	248 s
$Cu(MeS_1)_2$	1600 s	1440w	398 s	262 s
EtS_1–H	1710 s	1420 s		
$Cu(EtS_1)_2 \cdot 2H_2O$	1665 s 1614 s	1455m 1443m	382 s	259 s
$Cu(EtS_1)_2$	1550 s	1453w	380 s	260w
n-PrS_1–H	1710 s	1420 s		
$Cu(n\text{-}PrS_1)_2 \cdot 2H_2O$	1590 s	1460m	375 s	245m
$Cu(n\text{-}PrS_1)_2$	1550 s	1438m	398 s	247m
i-PrS_1–H	1710 s	1420 s		
$Cu(i\text{-}PrS_1)_2 \cdot 2H_2O$ (blue)	1588 s	1460 s	368 s	242 s
$Cu(i\text{-}PrS_1)_2 \cdot 2H_2O$ (violet)	1590 s	1440 s	410 s 401 s	250 s
$Cu(i\text{-}PrS_1)_2$*	1583 s	1460 s 1443w	370 s	260 s
n-BuS_1–H	1710 s	1464 s		
$Cu(n\text{-}BuS_1)_2 \cdot 2H_2O$	1590 s	1463 s	370 s	262w 225 s
$Cu(n\text{-}BuS_1)_2$	1560 br	1463m	375 s	253w 249w 228m
BzS_1–H	1690 s	1490w		
$Cu(BzS_1)_2 \cdot 2H_2O$	1590 s	1494m	370 s	253 s 241 s
$Cu(BzS_1)_2$	1590 s	1494m	384 s	247m 231w

* Dehydrized the blue dihydrate.

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14) K. Nakamoto, "Infrated Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York, N. Y. (1963), pp. 197—225.

15) J. Fujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys.*, **36**, 324, 331 (1962).

16) K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 4528 (1961).

17) D. M. Adams and P. J. Lock, *J. Chem. Soc., A*, **1967**, 620.

18) D. M. Adams and J. B. Cornell, *ibid.*, **1967**, 884.

The characteristic difference in the infrared spectra between the blue and violet dihydrate isomers appears only in about the 200—400 cm^{-1} region. In the spectra of the violet isomer, the 368 cm^{-1} band of the blue isomer shifts to 401 and 410 cm^{-1} and the band near 242 cm^{-1}, to 250 cm^{-1}. In the case of the blue isomer, it is supposed that the sulfur atom of the ligand bonds to the central copper ion more weakly, and the water coordinates more strongly. On the other hand, in the violet form, the ligand works as a bidentate and water molecules bond weakly. Therefore, the shifts of the ν(Cu–O) as well as ν(Cu–S) of the violet isomer to the higher-wave number side are reasonable, and these results are consistent with those from the electronic spectra.

The wave numbers of several infrared bands, and the tentative assignments of other alkyl thioglycolic acids and their copper(II) complexes are summarized in Table 4.

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