Syntheses and Properties of Copper(II), Nickel(II), and Cobalt(II) Complexes of Alkylthioglycolic Acids

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Copper(II), nickel(II), and cobalt(II) complexes of alkylthioglycolic acids, $R\cdot S\cdot CH_2COOH$ (where R=ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and *s*-butyl), were synthesized. Except for some copper complexes, these are new compounds. The attempt to synthesize the solid zinc complexes by the same method has not yet been successful. The relative stabilities of these complexes in the solid state seem to be Zn(II)<Co(II), Ni(II)<Cu(II), considering the yield of the syntheses of the products as well as the solvolizing tendency of the complexes. The nickel and cobalt complexes are expected to be in an octahedral form from the magnetic moments as well as from their electronic spectra. The relation between Taft's substitution constants and the wave numbers of the maxima of the absorption spectra of these complexes in the solid state is not clear.

As a step in the studies of the metal complexes containing sulfur compounds as the ligands, alkylthioglycolato complexes,[1] especially their copper complexes, have been synthesized and studied.[2] As it seems that the structure of the alkylthioglycolato complexes would be more clarified by studying the properties of the complexes of other metals, nickel(II) and cobalt(II) complexes other than the copper(II) complexes were also synthesized. Although the complexes of these metals resemble each other and the solid hydrates are very stable, the nickel and cobalt complexes were a little more difficult to synthesize. The syntheses of zinc(II) complexes were also attempted, but as the complexes were unstable, hardly any solid products were obtained. This fact is understandable referring to the fact that the general stability order of complexes of these metals is: Zn(II)<Co(II), Ni(II)<Cu(II), as has been shown by Mellor and others.[3,4]

As the ligands, ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, isobutyl-, and secondary butyl- thioglycolic acids were used to investigate the substitution effect of the alkyl groups. Hereafter, they will be abbreviated in this paper as follows: H EtS_1, H *n*-PrS_1, H *i*-PrS_1, H *n*-BuS_1, H *i*-BuS_1, H *s*-BuS_1.

Experimental

Instruments. The infrared spectra were obtained by the Nujol or hexachloro-1,3-butadiene mull procedure, using a 403G-type infrared spectrophotometer of the Japan Spectroscopic Co., Ltd. The electronic spectra were obtained with Hitachi EPS-2-type automatic recording spectrophotometer. The magnetic moments were measured with a Gouy balance at room temperature (20°C).

Syntheses of the Materials. *The syntheses of the Ligands*: H EtS_1, H *n*-PrS_1, H *i*-PrS_1, H *n*-BuS_1, H *i*-BuS_1, and H *s*-BuS_1 were synthesized by Pettit's[5] or Larsson's[6] method from the alkyl halide and thioglycolic acid.

The Syntheses of n-*Propylthioglycolato Cobalt(II) Dihydrate*: An aqueous solution of 1.2 g (5.0 mM) of cobalt(II) chloride hexahydrate was treated with sodium hydroxide, and the cobalt(II) hydroxide thus obtained was washed well with water (by the centrifuge technique). The hydroxide, 5 m*l* of water, 5 m*l* of formalin (37%), and 1.35 g (10 mM) of H *n*-PrS_1 were mixed and stirred. After several minutes, the residue was filtered off and the filtrate was kept overnight in a refrigerator. The product was washed with ice cold water, a little cold ethyl alcohol, and ethyl ether, in that order. The yield was 0.4 g (1.1 mM). If the formalin was not used, a brown by-product, probably the thioglycolate, precipitated when the metal salt was mixed with the ligand and the yield was much lowered.

The other complexes were synthesized by almost the same method. In the case of the copper and nickel complexes, formalin was not used. As was reported previously, in the case of isopropylthioglycolatocopper(II) dihydrate blue and violet isomers were obtained.[2] However, until now this kind of isomerism has not been observed in the cases either of nickel and cobalt complexes or of copper complexes of other alkylthioglycolic acids.

Results and Discussion

The elemental analyses, the chemical formulae of the complexes thus obtained, and the approximate yields of the products are shown in Table 1. From the results, all of these compounds can be said to have the formulae of $ML_2\cdot 2H_2O$, where HL is an alkylthioglycolic acid.

The magnetic moments of these complexes, as measured by Gouy's balance, are shown in Table 2. Generally, the cobalt and nickel complexes have much higher magnetic moments than the spin-only values. Cobalt complexes have the magnetic moments of about 4.7—5.2 B.M. when they are in the octahedral form and 4.4—4.8 B.M. when in tetrahedral ones.[7] The magnetic moments of nickel complexes are 2.9—3.4 B.M. in the cases of octahedral complexes and 3.5—4.2 B.M. in the cases of tetrahedral complexes.[7] The observed magnetic moments of these products are about 2.9—3.1 B.M. in the cases of nickel complexes and 4.6—5.1 B.M. in the cases of cobalt complexes. Therefore, all of these com-

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Table 1. The analyses of complexes (Figures are given in %)

		Metal	C	H	S	Yield
$Cu(EtS_1)_2\cdot 2H_2O$	Calcd	18.81	28.44	5.37	18.98	
	Found	18.16	28.76	5.41	18.40	65
$Ni(EtS_1)_2\cdot 2H_2O$	Calcd	17.63	28.85	5.45	19.25	
	Found	17.91	29.14	5.02	18.75	57
$Co(EtS_1)_2\cdot 2H_2O$	Calcd	17.68	28.83	5.44	19.24	
	Found	17.80	29.09	5.64	18.75	57
$Cu(n\text{-}PrS_1)_2\cdot 2H_2O$	Calcd	17.36	32.82	6.06	17.52	
	Found	17.56	32.95	5.88	17.04	59
$Ni(n\text{-}PrS_1)_2\cdot 2H_2O$	Calcd	16.26	33.26	6.14	17.76	
	Found	16.45	33.40	6.05	17.50	57
$Co(n\text{-}PrS_1)_2\cdot 2H_2O$	Calcd	16.31	33.24	6.14	17.75	
	Found	16.11	33.60	6.29	17.04	52
$Cu(i\text{-}PrS_1)_2\cdot 2H_2O$[a]	Calcd	17.36	32.82	6.06	17.52	
	Found	17.29	33.07	5.96	17.05	42[b]
$Ni(i\text{-}PrS_1)_2\cdot 2H_2O$	Calcd	16.26	33.26	6.14	17.76	
	Found	16.20	33.26	6.07	18.05	42
$Co(i\text{-}PrS_1)_2\cdot 2H_2O$	Calcd	16.31	33.24	6.14	17.75	
	Found	16.75	33.26	5.89	17.51	42
$Cu(n\text{-}BuS_1)_2\cdot 2H_2O$	Calcd	16.13	36.58	6.65	16.27	
	Found	16.27	37.01	6.53	16.80	90
$Ni(n\text{-}BuS_1)_2\cdot 2H_2O$	Calcd	15.08	37.03	6.73	16.48	
	Found	15.23	37.74	6.23	16.53	68
$Co(n\text{-}BuS_1)_2\cdot 2H_2O$	Calcd	15.13	37.01	6.73	16.47	
	Found	14.70	37.28	6.56	16.13	58
$Cu(i\text{-}BuS_1)_2\cdot 2H_2O$	Calcd	16.13	36.58	6.65	16.27	
	Found	16.54	36.74	6.52	15.98	82
$Ni(i\text{-}BuS_1)_2\cdot 2H_2O$	Calcd	15.08	37.03	6.73	16.48	
	Found	14.78	38.07	6.30	16.74	39
$Co(i\text{-}BuS_1)_2\cdot 2H_2O$	Calcd	15.13	37.01	6.73	16.47	
	Found	15.63	36.53	6.26	16.66	39
$Cu(s\text{-}BuS_1)_2\cdot 2H_2O$	Calcd	16.13	36.58	6.65	16.27	
	Found	15.70	36.93	5.95	15.99	76
$Ni(s\text{-}BuS_1)_2\cdot 2H_2O$	Calcd	15.08	37.03	6.73	16.48	
	Found	15.34	37.52	6.89	16.85	58
$Co(s\text{-}BuS_1)_2\cdot 2H_2O$	Calcd	15.13	37.01	6.73	16.47	
	Found	15.65	36.28	6.49	16.32	49

H EtS_1 =ethylthioglycolic acid, H $n\text{-}PrS_1$=n-propylthioglycolic aicd,
H $i\text{-}PrS_1$=isopropylthioglycolic acid, H $n\text{-}BuS_1$=n-butylthioglycolic acid,
H $i\text{-}BuS_1$=isobutylthioglycolic acid, H $s\text{-}BuS_1$=secondary butylthioglycolic acid.

a) blue isomer.

b) optimum yield of the blue isomer (in the run the sum of the blue and the violet complexes was 57%).

Table 2. Magnetic moments (B.M.) of the metal complexes (dihydrate) at 25°C.

Metal	Cu	Ni	Co
H EtS_1	1.73	3.13	4.79
H $n\text{-}PrS_1$	1.85	3.13	4.77
H $i\text{-}PrS_1$	1.84	2.97	4.66
H $n\text{-}BuS_1$	1.83	3.29	4.62
H $i\text{-}BuS_1$	1.95	3.39	5.06
H $s\text{-}BuS_1$	1.64	2.95	4.86

pounds seem to be octahedral complexes.

The water molecules in these products are relatively hard to remove and remain even after overnight drying at room temperature (on silica gel) in a vacuum desiccator. Therefore, the water molecules are probably coordinated with the metal ion, although the linking structure by water molecules is also possible; in any way they occupy two coordination bonds of the metal ion. There are two possibilities of how the alkylthioglycolic acid works as a bidentate ligand; i) two oxygen atoms of a carboxyl group bond to separate two metal ions, and the bridge structure is formed, or ii) one oxygen atom of a carboxyl group and a sulfur atom bond to the metal ion. The thioether-type sulfur does not coordinate to transition-metal ions strongly, and in the cases of some methionine complexes, the sulfur does not coordinate to metal ions.[8] However, at least the copper complexes seem to be S,O-coordinated complexes.[2] The order of the stabilities of various metal complexes of each alkylthioglycolic acid, as expected from the

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TABLE 3. THE MAXIMUM WAVE NUMBERS AND THE ABSORPTION COEFFICIENTS OF THE ELECTRONIC SPECTRA OF SOME METAL COMPLEXES

Figures are given in kK for wave numbers and log ε for intensities (in parentheses).

$\mathrm{Cu}(n\text{-}\mathrm{PrS}_1)_2\cdot 2\mathrm{H_2O}$	35 90 (3.48)	28.20 (3.45)	15.15 (2.48)
$\mathrm{Cu}(i\text{-}\mathrm{BuS}_1)_2\cdot 2\mathrm{H_2O}$	35.70 (3.52)	28.00 (3.52)	14.95 (2.35)
$\mathrm{Ni}(n\text{-}\mathrm{PrS}_1)_2\cdot 2\mathrm{H_2O}$	39.50 (3.31)	25.15 (1.63)	14.71 (1.35)
$\mathrm{Ni}(i\text{-}\mathrm{BuS}_1)_2\cdot 2\mathrm{H_2O}$	39.25 (3.28)	25.25 (1.58)	14.93 (1.62)
$\mathrm{Co}(n\text{-}\mathrm{PrS}_1)_2\cdot 2\mathrm{H_2O}$	33.30sh(2.94)	20.20sh(1.62)	
$\mathrm{Co}(i\text{-}\mathrm{BuS}_1)_2\cdot 2\mathrm{H_2O}$	33.30sh(2.95)	20.20sh(1.73)	

yields, the facility of their syntheses, and the resistivity to solvolysis in solution is: Cu>Ni, Co>Zn. Recently the stability constants of ethyl thioglycolates of copper, nickel, and zinc in aqueous solutions were studied; the order of their stabilities was Cu>Ni>Zn.[9] This order is similar to that of a series of complexes where the neutral sulfur atom of the ligand bonds with these metals to form a chelate ring.[10] Consequently, in the nickel and cobalt complexes, the sulfur atom bonds to the central metal less strongly and they are expected to be less stable than the copper complex. Moreover, as the zinc-sulfur bond is weaker, zinc complexes are more unstable and are hard to obtain by this method. As will be shown later, the infrared bands presumably identified as ν(M–S) bands seem to appear in the spectra of these complexes. Therefore, considering also the spectral data, although the possibility of the i) case cannot be completely rejected, the ii) case is more likely, even though the metal-sulfur bonds in these solid complexes are not very strong.

The absorption electronic spectra of ethanolic solutions of several complexes are given in Table 3.

As is shown in the table, when the central metal ion is the same, almost the same patterns of the spectra were obtained, even if different alkylthioglycolic acids are used as the ligands; the wave numbers and the log ε of the complexes of the same metals almost coincide with each other, within the limits of experimental error. The bands at about 15 and 25 kK of the nickel complexes are likely to be ${}^3A_{2g}\rightarrow{}^3T_{1g}$(F) and ${}^3A_{2g}\rightarrow{}^3T_{2g}$ (P)re-

TABLE 4. THE WAVE NUMBERS OF THE STRETCHING BANDS OF THE CARBOXYL GROUP AND THE METAL-CHALCOGEN BOND (cm^{-1})

Ligand	Metal	$\nu(\mathrm{COO})_{\mathrm{asym}}$	$\nu(\mathrm{COO})_{\mathrm{sym}}$	ν(M–O)	ν(M–S)
	H	1710s	1422s		
$\mathrm{H\ EtS_1}$	Cu	1614s	1443m	382s	238s
	Ni	1610s	1445w	363s	227s
	Co	1610s	1444m	365s	210m
	H	1708s	1420m		
$\mathrm{H}\ n\text{-}\mathrm{PrS_1}$	Cu	1590s	1460m	370s	245,224s
	Ni	1596s	1460m	365s	226s
	Co	1600s	1460s	365m	212s
	H	1710s	1424m		
$\mathrm{H}\ i\text{-}\mathrm{PrS_1}$	Cu	1588s	1460s	368s	242,223s
	Ni	1598s	1461,1442m	366s	236s
	Co	1575s	1457m	367s	228s
	H	1707s	1465,1420s		
$\mathrm{H}\ n\text{-}\mathrm{BuS_1}$	Cu	1590s	1463m	370s	225s
	Ni	1594s	1465m	362s	227s
	Co	1600s	1463m	360s	210s
	H	1706s	1460s		
$\mathrm{H}\ i\text{-}\mathrm{BuS_1}$	Cu	1566s	1460m	360s	223s
	Ni	1565s	1460sh	355s	223s
	Co	1575s	1460m	360s	209m
	H	1707s	1456m		
$\mathrm{H}\ s\text{-}\mathrm{BuS_1}$	Cu	1583s	1460,1452m	370s	238s
	Ni	1596s	1460,1452m	363s	227s
	Co	1600s	1460,1452m	365s	210m

s : strong, m: medium, w:weak.

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spectively.[11] The cobalt complexes seem to be solvolized in an ethyl alcohol solution; the solution is brown in color, and the maxima did not appear clearly, only some shoulders being observed. The shoulder near 20 kK is probably the $^4T_{1g}(\mathrm{F}) \rightarrow {}^4T_{1g}(\mathrm{P})$ band.[12] Therefore, from the electronic spectra, at least the nickel species, and probably also the cobalt complex species in the solution, which is possibly in a form similar to that of the original complexes, are likely to be in the octahedral form. The bands in the 33—39 kK region seem to be the absorption of the ligand.

The infrared spectra of these compounds were examined. The general feature of the spectra in the fingerprint region (1300—700 cm^{-1}) are almost the same as those of each ligand. The anti-symmetric and symmetric bands of ν (COO) as well as the ν (M–O) and ν (M–S) bands of the complexes are shown in Table 4. The assignments of the bands were obtained with reference to the spectra of the other carboxylato complexes as well as to those of metal complexes of thio compounds.[13–16] Therefore, these assignments are only tentative. The wave numbers of the ν (M–O) and ν (M–S) bands of these complexes are a little lower than those of thioketonato or usual carboxylato complexes.[5,6] This is probably due to the weakness of the bond between the central metal ions and the chalcogen atoms of the ligands; really, the ν (M–S) band of the thiourea complexes, for example, appears in a lower wave-number region.[17]

The effect of the substitution of the alkyl group of alkylthioglycolic acid on the strength of the M–O bond may not be serious, but as the alkyl group is adjacent to the sulfur atom, the M–S bond is likely to be more affected by the substitution. In the case of silver complexes of alkylthioglycolic acids, their stability constants in the solution state are related to the Taft's σ^* functions of the alkyl groups.[5] However, probably because of the restriction from the crystal structure, the wave numbers of the bands of these stretching modes of these solid complexes do not have any clear relation to the σ^* functions of the alkyl groups.

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