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Syntheses and Properties of Metal Chelates of Ethanediylidenetetrathiotetraacetic Acid (ETTA) and Some Other Thioglycolic Acid Derivatives

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Some new metal chelate compounds of ethanediylidenetetrathiotetraacetic acid (H_4ETTA), $Co_2L \cdot 5H_2O$, $Cu_2L \cdot 4H_2O$, $Zn_2L \cdot 3H_2O$, $Ni_2L \cdot 6H_2O$, and $FeHL \cdot 3.5H_2O$, where H_4L is H_4ETTA, were obtained. The infrared spectra and other properties of these compounds were compared with those of the metal complexes of other thioglycolic acid derivatives, some of which are also new compounds. Judging from the wave numbers of the stretching bands, the carboxyl group of these complexes can be said to be rather ionic. Though the bond is not very strong, thioglycolic acid derivatives seem to bond with the central metal ion with both the sulfur atom and the carboxyl group.

Many kinds of chelate compounds of various metals with ethylenediaminetetraacetic acid (H_4EDTA) and its analogous ligand have already been synthesized and their properties investigated.[1] Recently many ligands which bond with the central metal ion by one or more sulfur atoms, or by one sulfur atom and some others, such as nitrogen or oxygen atoms, have been investigated very actively.[2,3] Therefore, it seemed that it would be interesting to study multidentate sulfur containing ligands and their metal complexes. The ethanediylidenetetrathiotetraacetic acid (H_4ETTA) is one of the ligands in this line of the research; moreover, as the structure of ETTA resembles that of EDTA, it led us to study the synthetic method and the properties of the metal chelates of this ligand. Only a few reports have been published about ETTA metal chelates. Longo and others have, though, prepared H_4ETTA and its chelate compounds of silver(I), iron(III), and mercury(II).[4] Saini and others have reported that the mole ratio of copper to ETTA in the chelate is 1 : 1 in the solution.[5]

Therefore, we have newly synthesized solid ETTA chelates of other metals; nickel(II), cobalt(II), copper(II), zinc(II) and cadmium(II). The iron(III) complex was also synthesized. The mole ratio of ETTA to iron was 1 : 1, unlike Longo's product, which had the mole ratio of 1 : 2.

In order to study the structure of the ETTA complexes and of the several thioglycolic acid derivatives shown below, their metal complexes were synthesized and investigated; they were benzylidenebisthioglycolic acid $C_6H_5CH(SCH_2CO_2H)_2$ (H_2BzS_2), ethylidenebisthioglycolic acid $CH_3CH(SCH_2CO_2H)_2$ (H_2EtS_2), methylenebisthioglycolic acid $CH_2(SCH_2CO_2H)_2$ (H_2MeS_2), benzylthioglycolic acid $C_6H_5CH_2SCH_2CO_2H$ (H_1BzS_1), and ethylthioglycolic acid $C_2H_5SCH_2CO_2H$ (H_1EtS_1). Their structure are shown in Fig. 1. The metal chelates of some of these compounds were studied by the solution-chemistry method. Ethylthioglycolic acid,

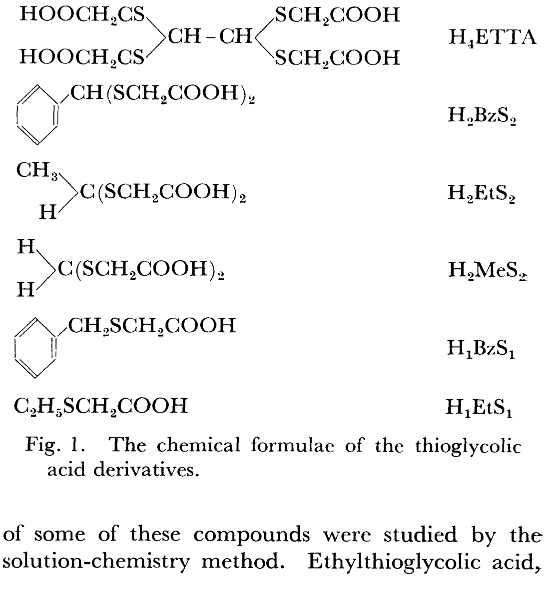

Fig. 1. The chemical formulae of the thioglycolic acid derivatives.

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[1] F. P. Dwyer and D. P. Meller, "Chelating Agents and Metal Chelates," Academic Press, New York (1964), p. 283.

[2] S. E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965).

[3] C. K. Jϕrgensen, "Inorganic Complexes," Academic Press, New York (1963), p. 131.

[4] F. R. Longo, A. Ventresca, Jr., J. E. Drach, J. McBride and R. F. Sauers, *Chemist-Analyst*, **54**, 101 (1965).

[5] G. Saini, G. Ostocoli, E. Compi and N. Cibrario, *Gazz. Chim. Ital.*, **91**, 904 (1961).

for example, has been studied by several authors;[6,7] according to their results, the ligand bonds to the central metal ion not only by its carboxyl group, but also by its sulfur atom. Although Yamasaki and Suzuki[8] have reported that the sulfur atom of phenylthioacetic acid seems not to be bonded with the metal ion in their metal complexes, the same authors wrote that ethylenedithiodiacetic acid seems to coordinate to a metal ion by means of sulfur atoms. The behavior of the former may be partly due to some steric interference with the chelate formation.

The chemical properties and the infrared spectra of the metal chelates of H_4ETTA and these thioglycolic acid derivatives resemble each other; accordingly, the structure of all of these chelates seem to be similar. The results obtained below seem to show that these ligands bond to the central metal ion as a multidentate, using both the sulfur atom and the carboxyl group, though the sulfur-metal bond is not very strong.

Experimental

Instruments. The infrared spectra were obtained by the Nujol or hexachloro-1,3-butadiene mull procedure, using a DS 301-type infrared spectrophotometer of the Japan Spectroscopic Co., Ltd. The electronic spectra were obtained with a Hitachi EPS-2-type automatic recording spectrophotometer. The reflectance spectra were obtained by using a reflectance attachment and a magnesium oxide standard. The magnetic moments were measured with a Gouy balance at room temperature (25°C).

Materials. The H_4ETTA was synthesized by Longo's method[4] by means of a condensation reaction between glyoxal and thioglycolic acid. The bisthioglycolic acid derivatives, H_2BzS_2, H_2EtS_2, and H_2MeS_2, were synthesized by Bongartz's method[9] and by Mattisson's method.[10] The monothioglycolic acid derivatives, $HBzS_1$ and $HEtS_1$, were synthesized by Larsson's method.[11]

The Syntheses of the Metal Chelates of ETTA. *(i) Cobalt(II), Copper(II), Nickel(II), Zinc(II) and Cadmium(II) Complexes.* The metal hydroxide of these metals was made from their nitrate and sodium hydroxide. It was suspended in water, about one fourth (mol/mol) of H_4ETTA was added, and the mixture was stirred for about 10 to 30 min at room temperature. The residue was then filtered off, and to the filtrate an equivolume of ethanol was added. The precipitate thus obtained was filtered off and washed by ethanol and acetone, in that order, before being dried in a vacuum desiccator at room temperature.

(ii) Iron(III) Complex. 1.3 g (1/300 mol) of H_4ETTA and 0.53 g (4/300 mol) of sodium hydroxide were dissolved in water. In a separate vessel, an aqueous solution of 2.7 g (1/100 mol) of iron(III) chloride hexahydrate was prepared; the pH of this solution was kept lower than 1 by perchloric acid. The two solutions were then mixed and stirred. The pH of the supernatant fluid was kept at 0.8 by adding perchloric acid. A precipitate thus appeared. It was filtered off, washed by acetone and ether, and dried in a vacuum desiccator at room temperature.

The Syntheses of Metal Complexes of Other Thioglycolic Acid Derivatives. The method of synthesizing the ETTA chelates can be used with slight modifications. Some examples are shown as follows.

(i) Copper(II) Complex of H_1BzS_1. Copper(II) hydroxide was obtained from 1 g of copper(II) chloride dihydrate. After suspending it in water, 2 g of H_1BzS_1 were added; the mixture was stirred well and boiled, and the insoluble residue was filtered off while hot. When the filtrate was cooled in an ice bath, pale blue $Cu(BzS_1)_2 \cdot 2H_2O$ deposited. The $Cu(BzS_1)_2 \cdot 2H_2O$, when boiled with an equivolume mixture of absolute ethanol and benzene, produced a green precipitate, $Cu(BzS_1)_2$. This was washed repeatedly with benzene and dried in a vacuum desiccator at room temperature.

(ii) Nickel(II) Complex of H_2EtS_2. Newly-made wet nickel(II) hydroxide obtained from 0.5 g of nickel(II) chloride hexahydrate and alkali was mixed with 0.7 g of H_2EtS_2(liquid). Ethanol was added to the mixture, after which the mixture was stirred, warmed, and filtered. The solid product thus obtained was washed well with ethanol and ethyl ether successively and then dried in a vacuum desiccator at room temperature.

Results and Discussion

The elemental analyses and the chemical formulae of the complexes thus obtained are shown in Table 1. Judging from these analytical results, many of these complexes can be said to contain water molecules and some of them seem to be coordinated complexes though the coordination number of the metals of these complexes cannot be determined from only these data.

The magnetic moments of these complexes, as measured by Gouy's balance at 25°C, are shown in Table 2. The cobalt complexes show magnetic moments of 4.5—4.9 B.M. per mole of metal. As these complexes are pink in color and have the oxidation number of +2, these cobalt(II) complexes can be said to be in a d^7 high spin configuration. Because of the orbital contribution, the observed magnetic moments are always higher than the spin-only values; they are 4.7—5.2 B.M. for octahedral- and 4.4—4.8 B.M. for tetrahedral-configuration complexes.[12] Consequently, the cobalt(II) complexes of ETTA and thioglycolic acid derivatives probably have an octahedral configuration.

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[6] R. J. Irving and W. C. Fernelius, *J. Phys. Chem.*, **60**, 1427 (1956).

[7] A. Sandell, *Acta, Chem. Scand.*, **15**, 190 (1961).

[8] K. Suzuki and K. Yamasaki, *J. Inorg. Nucl. Chem.*, **24**, 1093 (1962).

[9] J. Bongartz, *Ber.*, **21**, 478 (1888).

[10] B. Holmberg and K. Mattisson, *Ann. Chem.*, **353**, 123 (1907).

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

[12] A. Earnshaw, "Introduction to Magnetochemistry," Academic Press, New York (1968), p. 34.

TABLE 1. THE ANALYSES OF COMPLEXES (Figures are given in %)

		Metal	C	H	S
H_4ETTA	Calcd		30.80	3.59	
	Found		30.85	3.69	
$Co_2(ETTA)\cdot 5H_2O$	Calcd	19.85	20.25	3.38	21.45
	Found	20.10	20.21	3.70	21.38
$Cu_2(ETTA)\cdot 4H_2O$	Calcd	21.70	20.51	3.10	21.90
	Found	20.50	21.84	3.33	22.46
$Zn_2(ETTA)\cdot 3H_2O$	Calcd	22.90	21.02	2.81	22.43
	Found	23.00	21.14	3.05	22.47
$Ni_2(ETTA)\cdot 6H_2O$	Calcd	19.20	19.45	3.61	20.90
	Found	19.10	19.26	4.03	20.71
$Cd_2(ETTA)\cdot 4H_2O$	Calcd	32.98	17.60	2.64	18.73
	Found	33.16	17.51	2.77	18.62
$Fe(HETTA)\cdot 3.5H_2O$	Calcd	11.05	23.73	3.57	25.37
	Found	11.17	23.31	3.19	25.26
$Ni(BzS_2)\cdot 2H_2O$	Calcd	16.08	36.19	3.87	17.57
	Found	16.82	34.84	3.67	18.10
$Co(BzS_2)$	Calcd	17.90	40.13	3.06	19.48
	Found	18.05	36.53	3.08	19.60
$Cu(EtS_2)\cdot H_2O$	Calcd	21.93	24.88	3.45	22.07
	Found	22.25	24.72	3.47	22.93
$Ni(EtS_2)\cdot H_2O$	Calcd	20.72	25.26	3.51	22.46
	Found	21.01	25.39	3.18	22.92
$Co(EtS_2)$	Calcd	22.09	26.98	3.00	23.98
	Found	21.93	26.91	3.18	24.13
$Cu(MeS_2)\cdot H_2O$	Calcd	23.00	21.77	2.90	23.22
	Found	22.62	21.74	3.00	22.97
$Ni(MeS_2)\cdot H_2O$	Calcd	21.72	22.15	2.95	23.61
	Found	20.65	22.45	2.84	22.80
$Co(MeS_2)$	Calcd	23.14	22.59	2.69	24.96
	Found	22.90	23.27	2.69	24.64
$Cu(BzS_1)_2\cdot 2H_2O$	Calcd	13.77	46.78	4.76	13.85
	Found	13.67	46.97	4.86	13.70
$Cu(BzS_1)_2$	Calcd	14.91	50.78	4.23	15.04
	Found	14.98	50.07	4.46	14.43
$Co(BzS_1)_2\cdot 2H_2O$	Calcd	12.91	47.30	4.82	14.00
	Found	13.38	47.05	4.71	14.36
$Ni(BzS_1)\cdot H_2O$	Calcd	13.42	49.20	4.56	14.58
	Found	13.51	49.90	4.49	14.11
$Cu(EtS_1)_2\cdot 2H_2O$	Calcd	18.84	28.43	5.33	18.97
	Found	18.80	28.69	5.33	18.40
$Co(EtS_1)_2\cdot 2H_2O$	Calcd	17.71	28.85	5.41	19.23
	Found	17.68	28.84	5.32	18.50
$Ni(EtS_1)_2\cdot 2H_2O$	Calcd	17.71	28.85	5.41	19.23
	Found	17.40	28.95	5.34	18.78

In the case of nickel complexes, the observed magnetic moment values are in the range of 3.0—3.7 B.M. The nickel(II) complexes in an octahedral configuration show magnetic moments of 2.9—3.4 B.M., whereas the tetrahedral-configuration complexes show 3.5—4.2 B.M.[12] Therefore, these complexes are possibly in an octahedral configuration too, not in the planar or tetrahedral configurations. Although this method cannot be used with the complexes of other metals, they are probably in a hexacoordinated octahedral form, too, for the properties of all of these complexes resemble each other. Therefore, in order to make a hexacoordinate configuration not only the carboxyl group, but also the sulfur atoms and water should be coordinated to the central metal ion.

In the case of copper(II) complexes, the magnetic moments are about 1.7—1.9; therefore, the metal-metal bond of copper(II) acetate-type compounds does not exist. In the case of the copper(II)

Table 2. Magnetic moments (B.M.) of the metal complexes at 25°C
(The numbers of the crystalline water are shown in parentheses)

Metal	Cu	Co	Ni	Zn	Cd	Fe
Ligand						
H_4ETTA	1.71(4)	4.94(5)	3.04(6)	dia(3)	dia(4)	4.01(3.5)
H_2BzS_2		4.55(0)	3.13(2)			
H_2EtS_2	1.87(1)	4.85(0)	3.54(1)			
H_2MeS_2	1.95(1)	4.85(0)	3.71(1)			
H_1BzS_1	1.72(0) 1.82(2)	4.68(2)	3.30(1)			
H_1EtS_1	1.73(2)	4.79(2)	3.13(2)			

Table 3. The maximum wave numders and the absorption coefficients of the visible spectra of some metal complexes

Figures are given kK for wave numbers and log ε for intensities (in parentheses)
abs: the absorption spectra of aqueous solutions.
ref: the reflection spectra of solid samples.

$Ni_2(ETTA) \cdot 6H_2O$	abs.	9.10(1.39)	14.7(1.09)	25.4(1.42)	37.7(3.72)sh
	ref.		14.9	25.0sh	
$Co_2(ETTA) \cdot 5H_2O$	abs.	8.1 (1.01)	8.9(1.02)	21.0(1.70)	26.9(1.78)sh
	ref.		16.7sh	20.0	
$Cu_2(ETTA) \cdot 4H_2O$	ref.		14.6		
$Fe(HETTA) \cdot 3.5H_2O$	ref.	12.8sh	18.5sh	24.4sh	
$Ni(EtS_1)_2 \cdot 2H_2O$	abs.	8.8(0.79)	14.3(0.65)	25.3(1.02)	
	ref.		15.6	26.3	
$Co(EtS_1)_2 \cdot 2H_2O$	abs.	7.5(0.60)	18.9(0.87)		
	ref.		17.1	20.2	22.9
$Cu(EtS_1)_2 \cdot 2H_2O$	ref.	13.5sh	13.9sh 15.6	22.2sh	26.3

complex of benzylthioacetic acid, both $Cu(BzS_1)_2 \cdot 2H_2O$ and $Cu(BzS_1)_2$ were obtained. The extraordinarily low magnetic moment of the iron(III) ETTA complex seems to be due to the low spin-high spin equilibrium reported by Ewald and others.[13]

The visible spectral data, absorption as well as reflection spectra data, of colored complexes are shown in Table 3. Some of these complexes are not soluble in water or other organic solvents, and so it is difficult to study their absorption spectra. The spectra of soluble samples show relatively low absorption peaks in the visible region; the log ε is about 1, except for those in the ultra-violet region, which seem to be the absorptions of the ligands themselves. Consequently, from the visible spectral data, too, the complex species in the solution seem to be in a hexacoordinate octahedral configuration, although some solvolysis may change the configuration in the solution from that in the solid state. The solid complex salts are not deeply colored, either, and the tetrahedral configuration is less probable even in the solid state. The d-d bands of the cobalt(II) and nickel(II) complexes are observed at about 7.5—8.0 kK and about 9 kK respectively. Therefore, the coordination bond strength of the chelates is not very strong; possibly it is comparable to those of water or of usual amino acids in the spectrochemical series.

The infrared absorption bands of the carboxyl group are most useful for a study of the coordination structure of these complexes. The wave numbers of the antisymmetric and symmetric stretching bands of the carboxyl group of the metal complexes as well as of the free acids, H_4ETTA, and other thioglycolic acid derivatives are shown in Table 4. The antisymmetric stretching bands of the free acids appear at about 1700 cm^{-1}; they shift to about 1570 to 1600 cm^{-1} in the cases of metal chelates. In some cases, the band splits into two peaks. For example, the bands appear at 1715 cm^{-1} as well as at 1610 cm^{-1} in the case of the Fe(III) HETTA complex. Therefore, some carboxyl groups of the ligand bond to the central metal ion, while others are in a free –COOH form. As the wave numbers of the peaks of metal chelates make such a big shift to the lower-wave number side, the carboxyl group of the ligand must have an ionic character in these compounds. Therefore the group seems to bond with the central metal ion, but the bond seems not to be a purely

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[13] A. H. Ewald, R. L. Martin, I. G. Ross and A. H. White, *Proc. Roy. Soc., Ser. A*, **280**, 235 (1964).

TABLE 4. THE WAVE NUMBERS OF THE STRETCHING BAND OF THE CARBOXYL GROUP AND THEIR SEPARATION IN THE METAL COMPLEXES OF VARIOUS THIOGLYCOLIC ACID DERIVATIVES (cm^{-1})

(The numbers of the crystalline water of metal complexes are the same as Table 2.)

	H^+	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Fe^{3+}
$\tilde{\nu}(COO)_{asym}$						
ETTA	1703	1583	1583	1580	1590	1608
BzS_2	1693		1580	1580		
EtS_2	1697	1596	1578	1577		
MeS_2	1698	1590	1580	1579		
BzS_1	1692	1585	1598	1588		
EtS_1	1700	1632	1608	1605		
$\tilde{\nu}(-COO)_{sym}$						
ETTA	1397	1382	1375	1390	1383	1420
BzS_2	1390		1417	1400		
EtS_2	1408	1378	1387	1400		
MeS_2	1390	1384	1392	1384		
BzS_1	1449	1449	1452	1469		
EtS_1	1420	1441	1432	1443		
$\tilde{\nu}(-COO)_{asym}-(-COO)_{sym}$						
ETTA	306	201	208	190	207	188
BzS_2	303		163	180		
EtS_2	289	218	191	177		
MeS_2	308	206	188	195		
BzS_1	243	132	146	119		
EtS_1	280	191	176	162		

covalent one.[14,15] The symmetric stretching band of the carboxyl group of the free acids appeared at about 1400 cm^{-1}; the shift of the band of metal complexes should be another index of the bond type. According to Nakamoto,[16] the direction of the shift of the band depends on the symmetry of the carboxyl group in the metal complexes. If the carboxyl group in the complexes is not symmetric, antisymmetric and symmetric stretching bands shift to the higher- and lower-wave number sides respectively. On the other hand, if the coordination occurs symmetrically, both stretching bands shift in the same direction. Thus, the difference in the wave numbers of the antisymmetric and symmetric stretching bands of the carboxyl group of these compounds is useful for judging the structure of the chelate compounds.[17,18] Therefore, the observed values are also shown in Table 4. The values of carboxylic acid complexes increase in the following order of the central metals:

$$Ni(II) < Zn(II) < Cu(II) < Co(II).$$

The covalent character of the M–O bond also seems to increase in this order.[16]

In this case, however, the direction of the shift of the symmetric stretching band is not clear, and the values of the complexes of different metals are almost random; therefore, no meaningful conclusion could be drawn from the results. Two reasons for this are that the bonds between the metal-ligand bonds of all of these compounds are weak and that the bond strengths by different central metal ions are not very different. Moreover, if the sulfur atom bonds with the metal ion and forms a chelate ring, the order of the coordination bond strength of the simple carboxyl acid complexes should be modified. Whether or not sulfur is bonded to the central metal ion is not clear from the infrared spectral data in the 4000—600 cm^{-1} region, because the sulfur atoms in thio-ether-type compounds do not give strong bands in this region and so it is difficult to distinguish them from other bands. The weak band near 2550 cm^{-1} of the H_4ETTA seems to be due to dimerization by the hydrogen bond. It was not recognized in the spectra of its metal complexes.

Conclusions

From these data it may be concluded that the stabilities of the first-transition metal complexes of H_4ETTA and other thioglycolic acid derivatives are

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14) D. T. Sawyer and J. M. McKinnie, *J. Amer. Chem. Soc.*, **82**, 4191 (1960).

15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York (1963), pp. 201—210.

16) K. Nakamoto and P. J. McCarthy, "Spectroscopy and Structure of Metal Chelate Compounds," John Wiley & Sons, New York (1968), p. 269.

not high. Even ETTA acts at most as a tetradentate for each metal ion, and the chelate is not very stable. This is probably due to the weak coordination ability of the sulfur atoms of the thio-ether-type compounds. Moreover, the steric configuration of ETTA also shows that it finds difficult to act as a octadentate ligand for one metal atom with each four sulfur atoms and carboxyl groups. All of these metal complexes, however, are probably hexa-coordinated octahedral complexes, and the ligand bonds with the central metal ion by means of sulfur atoms and an ionized carboxyl group. Sometimes water molecules are also coordinated. In some cases, the polymerized form where a carboxyl group is coordinated with two metal ions is also possible.

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