METAL COMPLEXES OF THIOPOLYCARBOXYLIC ACIDS. VI.*
ZINC AND CADMIUM

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Complexes of zinc and cadmium with three homologous thiodicarboxylic acids, *viz.* thiodiacetic, ethylenedithiodiacetic, and diethylenetrithiodiacetic acid, resp., were studied in aqueous solutions and in the solid state. In solutions, the formation of compounds with the ratio metal : :ligand = 1 : 1 was proved in all cases; in addition, the ratio 1 : 2 was also found for the first ligand. The 1 : 1 compounds were isolated and studied in the crystalline state. Their properties are in agreement with the tetrahedral arrangement of the coordination sphere of the metal ion.

Thiopolycarboxylic acids as thio analogs of complexones have been subjected to relatively little study till now. Substances of that type exhibit a specific affinity towards chalcophilic cations of the type Cu(I) and Hg(II) for complex formation, whereas their ability to bind lighter cations of the transition elements is substantially lower. In our previous papers we have dealt with the study of interaction of the first row transition metals with some thio-complexons. These were above all

thiodiacetic acid[1,2] $HOOCCH_2SCH_2COOH = H_2G$

ethylenedithiodiacetic acid[3] $HOOCCH_2SCH_2CH_2SCH_2COOH = H_2Z$

diethylenetrithiodiacetic acid[4] $HOOCCH_2S(CH_2CH_2S)_2CH_2COOH = H_2T$.

With cations of the second subgroup of the periodic system, considerable differences in the interaction of these substances can be expected, owing to the substantial increase of the affinity towards sulfur in the order[5] Zn(II) < Cd(II) ≪ Hg(II). In this paper we present the results of the study of complexes of zinc and cadmium with the three thio-complexones mentioned.

The stability of complexes of zinc and cadmium with H_2G and H_2Z in diluted aqueous solutions has been determined by Tichane and Bennett[6] and by Yamasaki[7,8]. These authors ascer-

tained the formation of weak complexes MeG and MeZ. A low-soluble compound of zinc with thiodiacetic acid has been also proved qualitatively[9].

EXPERIMENTAL

Thiodiacetic acid was prepared by condensating mercaptoacetic acid with chloroacetic acid in a slightly alkaline medium[1]. After a two-fold recrystallization from a benzene–acetic acid mixture, the compound with the m.p. 127—128°C (ref.[10] 129°C) and alkalimetric equivalent 75·12 (calc. 75·08) was obtained. Ethylenedithiodiacetic acid is formed[3] on condensing 1,2-dibromoethane with sodium mercaptoacetate at pH 10—11. The substance, m.p. 108°C (ref.[11] 108—109°C) and alkalimetric equivalent 105·19 (calc. 105·14) was obtained on the recrystallization from ethyl acetate and hot water. Diethylenetrithiodiacetic acid was prepared by the reaction of β,β'-dimercaptodiethylsulfide with sodium chloroacetate[4], with the starting component prepared *in situ* by the alkaline hydrolysis of the bis-thiouronium salt obtained from thiodiglycol, thiourea, and hydrobromic acid[10]. The H_2T substance was purified by recrystallizing from ethyl acetate, until m.p. 109°C and alkalimetric equivalent 135·85 (calc. 135·20) were attained. Zinc and cadmium perchlorate hexahydrates were prepared by dissolving the oxides in the equivalent amounts of 30% $HClO_4$ and by repeated recrystallization from water. The other chemicals were commercial preparations (Merck and Lachema) of p.a. purity.
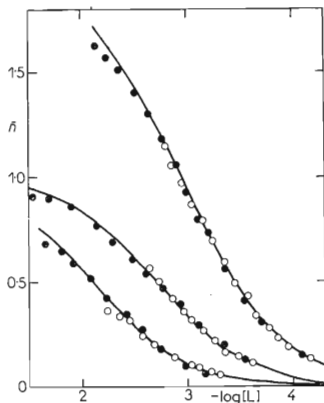

FIG. 1

Curves $\bar{n}$ *vs* — log [L] for Zinc Complexes

    Metal concentrations: ○ 0·002M, ● 0·005M. The curves are calculated from the data of Table I.
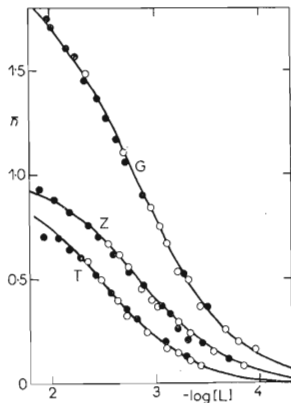
FIG. 2

Curves $\bar{n}$ *vs* — log [L] for Cadmium Complexes

    Metal concentrations: ○ 0·002M, ● 0·005M. The curves are calculated from the data of Table I.

The instruments and methods used are described in the previous papers[1,2]. The contents of the ligands were determined by titration by nascent bromine (solution of $KBrO_3$ containing an excess of KBr) in 2M-HCl, sulfidic sulfur being oxidized to sulfoxide. The excess of bromine was then retitrated iodometrically. Zinc and cadmium were determined by means of complexometry and polarography. The content of water was determined by weight loss on drying and from thermogravimetric curves. Computations were carried out by means of the computer IBM 7040.

RESULTS

Study of Aqueous Solutions

For the determination of the composition and stability of the complexes, pH-metric titrations of mixtures of the metal perchlorate (0·002 and 0·005M) with the ligand (0·005M) by NaOH were carried out at 25°C and ionic strength 0·1 (NaClO$_4$). The average pH values from several titrations, differing by at most 0·02 pH, were recalculated to $\bar{n}$ vs $-\log$ [L] curves by using programs given by Romary[12]. As apparent from Figs 1 and 2 those curves are independent of the metal concentration; only mononuclear complexes are therefore formed in the systems[13]. From the shape of the curves it is also obvious that for H$_2$G under the conditions given, two complexes with the ratios metal : ligand 1 : 1 and 1 : 2 are formed, whereas only the 1 : 1 complexes occur for H$_2$Z and H$_2$T. The calculation of the stability constants and their standard deviations was carried out by using the linear regression method after the transformation of the $\bar{n}$ vs $-\log$ [L] curves to the equation of straight line[13]. The resulting values of the constants are listed in Table I.

TABLE I

Stability Constants of Complexes of Zinc and Cadmium, resp., with Thiopolycarboxylic Acids 25°C, $I = 0·1$ (NaClO$_4$).

Ligand	$\log \beta_n$	This work		Literature	
		Zn	Cd	Zn	Cd
H$_2$G	β_1	3·30 ± 0·08	3·14 ± 0·08	3·0[6]; 2·9[7]	2·6[7]
	β_2	5·85 ± 0·11	5·57 ± 0·10		
H$_2$Z	β_1	2·68 ± 0·06	2·82 ± 0·07	2·7[8]	2·8[8]
H$_2$T	β_1	2·07 ± 0·07	2·43 ± 0·06		

Preparations

The 1 : 1 compounds are relatively low-soluble and are slowly deposited in the crystalline form from suitably concentrated solutions. In order to obtain pure crystalline samples, equal volumes of 0·4 to 0·6M solutions of the metal sulfate and of the disodium salt of the ligand[2−4] were mixed and left for crystallization at the room temperature for several days. The samples were then sucked off, washed with a little water, ethanol, and ether, and dried at room temperature.

The yields lay in the range of 80—90%. The compositions and analytical data of the compounds obtained are given in Table II. The attempts to prepare the complexes 1 : 2 (with H_2G) failed owing to the very low solubility of the compounds 1 : 1 in solutions of the ligand.

TABLE II

Analyses of the Compounds Prepared

Compound (m. w.)	% Me calc. (found)	% L calc. (found)	% H_2O calc. (found)
ZnG.4 H_2O (285·6)	22·89 (22·8)	51·87 (52·2)	25·24 (25·1)
CdG.H_2O (278·6)	40·35 (39·2)	53·18 (52·4)	6·47 (6·58)
ZnZ (273·6)	23·89 (23·9)	76·11 (75·9)	—
CdZ (320·6)	35·05 (34·7)	64·95 (64·9)	—
ZnT (333·7)	19·59 (18·8)	80·41 (80·3)	—
CdT.H_2O (398·8)	28·18 (27·5)	67·30 (68·4)	4·52 (4·30)

Properties of the Substances Prepared

The compounds obtained are white crystalline substances, low-soluble in water, stable on air. They are diamagnetic and their electronic spectra (diffuse reflectance in the UV region) are practically identical with those of the disodium salts of the corresponding ligands. The substances were characterized also by their powder diagrams (Table III), infrared spectra (for selected band groups see Table IV), and by the thermal decomposition. Pyrolysis on air starts by the contingent dehydration near 100°C and proceeds by the decomposition of the organic component in the range of 150—330°C, accompanied by the evolution of extremely bad-smelling gaseous products. A mixture of the metal oxide and sulfide appears as the final decomposition product, with the relative content of sulfide increasing in the order G—Z—T for the both metals. The overall scheme of the course of the thermal decomposition is represented by Table V. Table VI gives the solubility products of the 1 : 1 compounds, obtained by measuring the equilibrium concentrations of the metal in saturated solutions at 25°C and $I = 0·1$ (NaClO$_4$). During the dissolution,

as well as during the deposition from the solution of the components, the equilibrium established rather slowly. The solubility products were calculated considering the non-dissociated fraction of the compound, as follows from the corresponding stability constant.

TABLE III

Interplane Distance and Line Intensities of Powder Diagrams
Radiation $CuK_{\alpha 1}$, $\lambda = 1.5405$ Å, Ni-filter, photographic recording.

ZnG.4 H_2O		CdG		ZnZ		CdZ		ZnT		CdT.H_2O	
d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I
6·60	2	7·02	4	6·02	4	5·98	4	6·91	3	6·60	1
5·53	4	4·48	2	5·06	2	4·77	1	4·53	3	5·40	2
4·39	3	4·31	2	4·77	1	4·04	2	4·15	4	4·87	1
3·67	2	3·62	1	4·11	3	3·93	2	3·90	4	4·31	3
3·48	3	3·25	2	3·56	2	3·54	2	3·59	1	4·04	3
3·39	1	2·96	3	3·42	1	3·47	2	3·40	1	3·42	1
3·08	3	2·60	2	3·21	3	3·16	2	3·25	2	3·18	1
2·79	1	2·52	1	3·12	3	2·79	2	3·04	1	2·85	2
2·45	2	2·22	2	2·96	3	2·73	2	2·90	1	2·56	2
2·17	3	2·07	1	2·66	1	2·45	3	2·76	1	2·43	1
2·10	1	1·91	2	2·53	2	2·34	2	2·55	2	2·20	1
1·99	1	1·71	1	2·35	2	2·14	2	2·38	2	2·16	1
1·80	2			2·30	2	2·12	2	2·23	2	2·06	1
1·63	1			2·17	2	1·99	1	2·05	1	1·91	1
				2·08	2	1·92	2	1·95	2		
				2·00	2	1·80	1				
				1·86	1	1·75	1				
				1·81	1	1·69	2				
				1·74	1	1·66	1				
				1·69	2	1·62	1				
				1·61	1	1·59	1				
						1·53	2				
						1·42	1				
						1·41	1				
						1·39	1				
						1·29	2				

DISCUSSION

The properties of the compounds of zinc and cadmium with thiopolycarboxylic acids correspond to the generally low affinity of those metals towards sulfur. In solutions, weak complexes 1 : 1 are formed; their stability decreases in the order G—Z—T.

TABLE IV

Selected Bands of IR Spectra

Compound	ν(C—S)	ν_s(COO)	ν_{as}(COO)	δ(H$_2$O)	ν(H$_2$O)
ZnG.4 H$_2$O	715 w	1 400 m	1 590 vs	1 665 m	3 200 s,b
CdG.H$_2$O	717 w	1 380 vs	1 600 vs	1 660 sh	3 150 w,b
ZnZ	728 m	1 425 m	1 595 s		
CdZ	730 m	1 400 w	1 585 s		
ZnT	722 m	1 390 s	1 605 s		
CdT.H$_2$O	716 m	1 390 s	1 600 vs	1 660 sh	3 250 w,b

TABLE V

Course of Thermal Decomposition of the Compounds Prepared

Compound	Dehydration		Decomposition of the organic component	
	°C	product	°C	product (°C)
ZnG.4 H$_2$O	80	ZnG	160	ZnO
CdG.H$_2$O	110	CdG	200	CdO, CdS (450°) CdO (600°)
ZnZ	—	—	320	ZnO, ZnS (500°) ZnO (700°)
CdZ	—	—	330	CdO, CdS (450°) CdO (600°)
ZnT	—	—	240	ZnO, ZnS, C (400°) ZnO (700°)
CdT.H$_2$O	90	CdT	150	CdO, CdS, C (250°) CdO, CdS (500°) CdO (600°)

Steric hindrance, accounted for by the increasing length of the ligand chain, where the sulfur atoms are not coordinated, seems to be the main factor here. (A reverse trend of the stability constants has been observed with heavier transition metals[1,3,4], where sulfur coordinates.) Complexes with two ligands per one metal atom were found only for the relatively most stable thiodiacetates. The measurement conditions

TABLE VI
Negatives of Logarithms of Solubility Products
25°C, $I = 0.1$ (NaClO$_4$). — log $P = -$ log [Me] [L].

Metal	Ligand		
	G	Z	T
Zn	5·37	5·48	5·50
Cd	6·20	6·79	6·12

in solutions, limited especially by the low solubility of the complexes 1 : 1, did not allow to determine, if the complexes 1 : 2 are formed also in the other cases. Their existence cannot be, however, excluded on the grounds of the material collected. As apparent from Fig. 1 and 2, the data, obtained from measurements in solutions, are described by the calculated stability constants very well. In the systems studied, it showed therefore unnecessary to consider the presence of protonized complexes, whose existence was proved for transition metals. The stability constants agree also well with the data published for the complexes 1 : 1 under similar conditions.

The composition of the crystalline substances corresponds to simple salts of bivalent ligands and it is identical with the particles found in solutions. The properties of the substances indicate unambiguously that sulfur is not coordinated to the metal in the solid state either. In comparison with analogous compounds of bivalent elements of the transition first row[2−4], the main differences are apparent in the absence of S → Me charge-transfer bands in the electronic spectra, and in the agreement of the wavenumbers of the C—S stretching vibration in the infrared spectrum with respect to free ligands. Other characteristic band groups in the infrared spectra lead to the conclusion that hydrate water (if present) does not take part in the coordination and that the carboxyl–metal bond has essentially an ionic character[14].

It can be concluded that the behaviour of the compounds studied is typical of zinc and cadmium ions coordinated tetrahedrally by oxygen atoms as donors. In solutions, two carboxyls and two water molecules take probably part in the coordination, whereas in the solid state, the coordination sphere is formed alternately by bonding and nonbonding oxygen atoms of the carboxyl group. The low solubility in water seems to indicate that the nonbonding oxygen atoms are supplied by the neighbouring ligand molecules with the formation of a polymeric network.

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Note added in proof: Very recently, Ford, Pettit and Sherrington[15] have determined the 1 : 1 stability constants of zinc and cadmium complexes with H_2Z and H_2T. Their data are in a good agreement with our results and confirm a general decrease of β_1 with an increasing number of the sulfur atoms.