METAL COMPLEXES OF THIOPOLYCARBOXYLIC ACIDS. VII.*
BIVALENT MERCURY

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Bivalent mercury forms complexes with the ratio metal : ligand = 1 : 1 and 1 : 2 with thio-diacetic, ethylenedithiodiacetic, and diethylenetrithiodiacetic acids, resp.; the complexes are very stable owing to a strong interaction mercury–sulfur. These substances were isolated in the solid state and their properties were studied. The molecular structure of the compounds prepared was suggested.

Our previous paper[1] has dealt with complexes of zinc and cadmium with thiopoly-carboxylic acids: thiodiacetic acid $HOOCCH_2SCH_2COOH = H_2G$, ethylene-dithiodiacetic acid $HOOCCH_2SCH_2CH_2SCH_2COOH = H_2Z$, and diethylenetri-thiodiacetic acid $S(CH_2CH_2SCH_2COOH)_2 = H_2T$. Mercury as the third element of the IIB subgroup of the periodic system exhibits a considerable affinity towards heavier donor atoms, particularly towards sulfur[2]. Therefore we studied compounds formed by mercury(II) cations with the three thio ligands mentioned.

Aqueous solutions of the systems Hg(II)–Z and Hg(II)–T were studied recently by Doležal and coworkers[3,4]. They proved polarographically the existence of the complexes HgZ_2^{2-} (log β_2 = 13·8) and HgT (log β_1 = 14·1). No other data about the systems mentioned are available.

EXPERIMENTAL

The commercially available chemicals were preparations of p.a. purity (Merck or Lachema). The preparation of the ligands has been described in the previous paper[1]. Mercury(II) bromide, iodide, and rhodanide, resp., were obtained by precipitating from a mercury(II) chloride or nitrate solution by the corresponding halides or by potassium rhodanide. The content of ligands was determined bromometrically[1]. In the presence of iodides or rhodanides, elemental analysis of carbon and hydrogen was carried out. The content of mercury was determined either complexo-metrically after the decomposition of the organic component by long-time boiling with concen-trated sulfuric acid, or by potentiometric titration by potassium iodide[5] yielding satisfactory results even in the presence of the ligands. Halides and rhodanides were determined gravimetrically

as AgX, sodium as $NaZn(UO_2)_3(CH_3COO)_9.6 H_2O$, and water from the difference. Acidic hydrogens were titrated potentiometrically by sodium hydroxide.

The instruments and measurement methods have been given previously[6,7]. The melting points were measured by means of the Boetius melting point microapparatus and are not corrected. The IR spectra in the range of $200-500 \text{ cm}^{-1}$ were scanned on the Perkin-Elmer 225 spectro-photometer by using the Nujol mull technique with cells with polyethylene windows.

RESULTS

Preparations

Low-soluble 1 : 1 compounds were obtained from an equimolar mixture of aqueous solutions of the mercury(II) salt and the disodium salt of the ligand at room temperature. Crystals of HgG.8 H_2O and HgZ.2 H_2O were obtained froms solution of the concentration $0.1-0.2M$, whereas HgT.5 H_2O was isolated in a wide concentration range only as an amorphous precipitate. After sucking off and washing with water, ethanol, and ether, the substances were dried at room temperature. The yields approached 80%. The 1 : 1 compounds are well soluble in an excess of solution of the disodium salt of the ligand in the cold. Complexes 1 : 2 were isolated from solutions thus formed. The compound $Na_2[HgZ_2].8 H_2O$ crystallizes slowly at 0°C from a 1M solution of Na_2Z saturated by solid HgZ.2 H_2O and mixed with an equal volume of ethanol; it was isolated in the yield of 60% by sucking off, washing with ethanol and ether, and drying at room temperature. Analogous complexes with G and T are oily substances; after unsuccessful attempts at crystallization, they were isolated as amorphous powders, $Na_2[HgG_2].3 H_2O$ and $Na_2[HgT_2].2 H_2O$ (yields 60 and 45%, resp.), by triturating with acetone. In nonaqueous solutions, mixed halo-complexes of the general formula H_2HgLX_2 were further prepared. For the
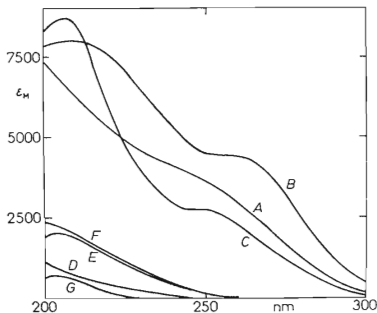

FIG. 1

Ultraviolet Absorption Spectra of 10^{-4}M Solutions

A $Hg(ClO_4)_2 + Na_2G$, B $Hg(ClO_4)_2 + Na_2Z$, C $Hg(ClO_4)_2 + Na_2T$, D Na_2G, E Na_2Z, F Na_2T, G $Hg(ClO_4)_2$. Cells 1 cm.

Table I

Analyses and Properties of the Compounds Prepared

Compound m. w.	Appearance	M.p. °C	Solubility in water g/100 g solution	%Na,H$^+$ calc. (found)	% Hg calc. (found)	% L calc. (found)	% X calc. (found)	% H$_2$O calc. (found)
HgG.8 H$_2$O (492·9)	white cryst. powder	b	0·015		40·70 (40·7)	30·06 (29·6)		29·24 (29·7)
Na$_2$HgG$_2$.3 H$_2$O (596·9)	white powder	b	58·9	7·70 (7·28)	33·61 (33·2)	49·64 (49·9)		9·05 (8·9)
HgZ.2 H$_2$O (444·9)	white cryst. powder	b	0·085		45·08 (44·9)	46·81 (46·8)		8·11 (8·3)
Na$_2$HgZ$_2$.8 H$_2$O (807·2)	white needles	b	54·6	5·70 (5·79)	24·85 (24·5)	51·60 (51·5)		17·85 (18·2)
HgT.5 H$_2$O (559·0)	white powder	b	0·001		35·88 (35·7)	48·00 (48·5)		16·11 (15·8)
Na$_2$HgT$_2$.2 H$_2$O (819·3)	white powder	b	59·2	5·61 (5·68)	24·48 (24·2)	65·51 (65·7)		4·40 (4·4)
H$_2$HgZCl$_2$ (481·7)	white crystals	117	a	0·42 (0·42)	41·64 (41·2)	43·22 (43·9)	14·72 (14·1)	
H$_2$HgZBr$_2$ (570·7)	white crystals	138	a	0·35 (0·34)	35·15 (34·8)	36·49 (36·9)	28·01 (27·8)	
H$_2$HgZI$_2$ (664·6)	yellowish crystals	136	a	0·30 (0·31)	30·18 (30·4)	31·33 (30·6)	38·19 (38·7)	
H$_2$HgZ(SCN)$_2$ (527·0)	white crystals	142	a	0·38 (0·39)	38·06 (37·8)	39·52 (39·9)	22·04 (21·7)	
H$_2$HgTCl$_2$ (541·8)	white powder	60—80	a	0·38 (0·40)	37·02 (36·9)	49·52 (49·1)	13·08 (13·2)	
H$_2$HgTI$_2$ (724·8)	yellowish crystals	114·5	a	0·27 (0·30)	27·68 (27·1)	37·03 (36·8)	35·02 (34·7)	

^{a} Incongruently soluble substance; ^{b} decomposes without melting.

synthesis of these substances, saturated acetone solution of the ligand was added to the solution or suspension of HgX_2 in refluxing acetone, in the equimolar ratio or in a slight excess, just necessary for the dissolving of the halide. Crystalline compounds H_2HgZX_2 (X = Cl, Br, I, CNS) and H_2HgTI_2 were obtained with high yields (up to 95%) by mixing the resulting solutions with equal volumes of chloroform and cooling; amorphous H_2HgTCl_2 was obtained from aquo-acetone solutions. For the other possible combinations, only one of the reaction component was isolated (usually HgX_2), even with a high excess of the other component and various combinations of solvents.
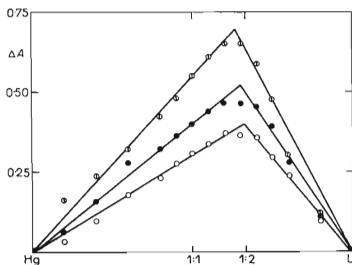

FIG. 2

Isomolar Series $Hg(ClO_4)_2$—Na_2L, Concentration $2 . 10^{-4}M$

○ G, 260 nm; ● Z, 270 nm; ⊙ T, 240 nm. Cells 1 cm.

Properties of the Substances Prepared

The appearance, analyses, solubilities, and melting points of the compounds obtained are given in Table I. The substances are diamagnetic, their electronic spectra in solutions as well as in the solid state exhibit intense bands in the ultraviolet region. Fig. 1 shows the changes of the electronic spectrum of an aqueous solution of mercury(II) perchlorate appearing on the addition of ligands. These changes made it possible to determine the composition of the complex formed by using the Job method. The results, given in Fig. 2, confirm the complex 1 : 2 to be the predominating particle in the solution. Analogous measurements in acetone solutions could not be carried out, owing to the high absorption of acetone in the ultraviolet region. The bands found in the diffuse reflectance spectra of the substances and their assignment to the electron transition types are given in Table II. Table III lists the powder diagrams of the samples. Selected band groups of their infrared spectra are given in Table IV. The thermal decomposition of the compounds is rather complicated and its various stages cannot be identified with certainty by the GTA method on air; the data are therefore not tabulated. The dehydration is usually accompanied by a starting oxidation-reduction reaction between bivalent mercury and the ligand. Combustion of the organic component follows; mercury(II) sulfide[1] remains as the residue, volatilizing on further heating. With sodium salts, sodium sulfate occurs as the final product. All the gaseous products of pyrolysis are very distasteful by their toxicity as well as their extremely bad smell.

Table II

Absorption Band Maxima in Diffuse Reflectance Spectra

A Integral band of the ligand; B charge transfer sulfur → mercury; C charge transfer mercury → halogen.

Compound	Wavenumber cm^{-1}	Assignment	Compound	Wavenumber cm^{-1}	Assignment
HgG.8 H$_2$O	44 500	A	H$_2$HgZCl$_2$	43 000	C
	36 300	B		37 000 sh	B
Na$_2$HgG$_2$.3 H$_2$O	44 500	A	H$_2$HgZBr$_2$	37 700	B
	38 500	B		32 300 sh	C
	36 300 sh	B			
HgZ.2 H$_2$O	45 500	A	H$_2$HgZI$_2$	38 500	B
	37 800	B		31 200	C
				27 000 sh	C
Na$_2$HgZ$_2$.8 H$_2$O	45 500	A	H$_2$HgZ(SCN)$_2$	37 700	B
	38 500	B		32 800	C
	36 300 sh	B			
HgT.5 H$_2$O	43 500	A	H$_2$HgTCl$_2$	43 500	C
	38 500	B		34 500	B
	35 700	B		32 300 sh	B
Na$_2$HgT$_2$.2 H$_2$O	43 500	A	H$_2$HgTI$_2$	34 500	B
	34 500	B		30 300	C

DISCUSSION

The complexes of thiopolycarboxylic acids with bivalent mercury differ by their properties considerably from those with transition metals, zinc, and cadmium, resp. This is obviously due to the high affinity of mercury towards sulfidic sulfur. The existence of strong coordination bonds S → Hg in all the substances studied is apparent particularly by the presence of new infrared spectral bands in the range of $225-295$ cm^{-1}. These bands were attributed to the Hg—S stretching vibrations, in agreement with published data[8]. As additional proofs of the presence of sulfur–mercury bonds, the shifts of the bands of the C—S stretching vibrations to lower wavenumbers as well as the appearance of isolated intense bands in the electronic spectra can be pointed out. These bands in the ultraviolet region (with energies lower than those of the integral bands of the ligands) correspond very probably to the charge transfer through the S→Hg bonds, similarly to, e.g., the complexes of nickel or copper[7,9,10].

For the consideration of the steric arrangement of the complexes, it is possible to assume the tetrahedral coordination, which is the most usual for bivalent mercury.

Table III

Interplane Distances and Line Intensities of Powder Diagrams
Radiation Cu K_{α}, λ 1·5405 Å, Ni-filter, photographic recording.

H₂HgTl₂		H₂HgZ(SCN)₂		H₂HgZI₂		H₂HgZBr₂		H₂HgZCl₂		Na₂HgZ₂.8 H₂O		HgZ.2 H₂O		HgG.8 H₂O	
d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I
4·86	1	6·91	4	8·66	2	6·65	4	7·02	3	6·51	4	5·82	4	7·02	3
4·28	4	6·00	3	6·86	4	5·60	3	6·41	2	6·06	2	4·45	1	4·87	2
3·62	1	5·15	4	5·78	2	4·53	3	5·27	3	5·40	1	4·12	2	4·39	4
3·39	2	4·39	3	4·64	1	4·28	2	4·62	4	4·48	1	3·77	2	4·15	2
3·27	1	4·12	2	4·02	2	3·97	2	4·15	2	4·00	1	3·42	2	3·16	1
2·96	1	3·74	4	3·74	4	3·69	4	3·89	2	3·59	2	3·03	2	2·60	2
2·65	2	3·52	2	3·48	2	3·42	1	3·53	3	3·33	1	2·81	2	2·35	4
2·43	2	3·06	3	3·17	4	3·16	4	3·25	1	2·96	3	2·68	2	2·07	1
2·22	1	2·85	3	2·89	2	2·86	3	3·14	4	2·78	3	2·64	1	2·01	1
1·84	1	2·62	1	2·72	2	2·65	3	2·85	2	2·55	1	2·49	2	1·88	1
		2·51	2	2·58	2	2·55	3	2·66	1	2·45	1	2·45	3	1·79	1
		2·38	2	2·21	2	2·45	2	2·56	4	2·35	1	2·43	3	1·70	1
		2·29	1	2·15	1	2·15	3	2·44	3	2·24	1	2·12	2	1·62	1
		2·19	1	2·08	1	1·99	2	2·28	3	2·15	1	2·06	2		
		2·12	1	2·04	1	1·93	2	2·04	4			2·01	1		
		2·06	1	1·97	1	1·86	2	1·92	3			1·94	1		
		1·84	1	1·84	1	1·72	1	1·86	2			1·90	1		
		1·82	2	1·76	1	1·70	2	1·78	1			1·85	1		
		1·77	2	1·67	1	1·64	2	1·67	2			1·81	1		
				1·62	1							1·73	1		
												1·67	1		
												1·63	1		
												1·59	1		
												1·57	1		
												1·50	1		
												1·38	1		

TABLE IV
Selected Bands of the Infrared Spectra

Compound	ν(Hg—S)	ν(C—S)	ν_s(COO)	ν_{as}(COO)	ν(H$_2$O)	ν(C≡N)
HgG.8 H$_2$O	293 s	705 m	1 380 s	1 628 vs	3 450 s,b	
Na$_2$HgG$_2$.3 H$_2$O	286 m	700 m	1 415 s	1 590 vs	3 440 s,b	
				1 620 vs		
HgZ.2 H$_2$O	272 m	702 m	1 401 m	1 631 vs	3 450 vs,b	
Na$_2$HgZ$_2$.8 H$_2$O	280 m	685 m	1 410 vs	1 590 s	3 450 s,b	
HgT.5 H$_2$O	275 w,b	685 w	1 380 s	1 625 vs	3 420 s,b	
		707 w				
Na$_2$HgT$_2$.2 H$_2$O	278 m	685 m	1 388 s	1 585 vs	3 425 s,b	
		711 w				
H$_2$HgZCl$_2$	282 m	680 w	1 230 m	1710 m		
H$_2$HgZBr$_2$	259 m	695 w	1 228 m	1 710 s		
H$_2$HgZI$_2$	227 w,b	692 w	1 230 m	1 700 s		
H$_2$HgZ(SCN)$_2$	275 w	660 w	1 225 m	1 720 s		2 080 m
		728 vw[a]				2 120 s
H$_2$HgTCl$_2$	270 m	705 w	1 229 m	1 715 s		
		715 sh				
H$_2$HgTI$_2$	235 s	685 w	1 225 m	1 700 s		
		702 sh				

[a] In the —SCN group.

Deviations from the tetrahedral arrangement are usually manifested by anomal properties, not observed in this case.

For the compounds 1 : 1, the coordination sphere is formed, besides the sulfur atoms, by carboxylic oxygens, as follows from the IR spectra. The position of the band of the antisymmetric stretching vibration of the carboxyl group, as well as the difference of the wavenumbers of the antisymmetric and symmetric vibrations, always higher than 220 cm^{-1}, indicate the covalent character of the carboxyl–metal bond[11,12]. The coordination number and the donating ability for HgZ is saturated by two carboxylic oxygens and two sulfur atoms; with HgG, coordination must be completed either by a molecule of water or by an intermolecular interaction, whereas for HgT one sulfur atom remains noncoordinated, as follows from the splitting of the C—S stretching vibration.

The properties of the compounds 1 : 2 show that the coordination around the mercury atom is realized only by the atoms of sulfur; carboxylic oxygens remain free. This is in accordance with the wavenumbers of the antisymmetric stretching vibrations, typical of the free —COO$^-$ group[11,12]. Only for the anions HgG$_2^{2-}$, where

the number of the sulfur atoms do not suffice for the saturation of the coordination number 4, the tetra-coordination must be completed by two of the four free carboxyl anions. This is proved by the distinct splitting of the $\nu_{as}(COO)$ band for the complex $Na_2[HgG_2] \cdot 3 H_2O$.

A very interesting group of compounds is represented by the mixed halo-complexes, formally similar to the complexes of palladium and platinum[13,14]. All their properties indicate that the coordination sphere of mercury is probably formed by two halides (rhodanides) and two sulfur atoms. The carboxyl groups are not coordinated and are protonated; the wavenumbers of the stretching vibrations of the —COOH group lie at 1230 and 1710 cm^{-1}, in accordance with ref.[11]. The coordination of halides and rhodanides is indicated by the charge-transfer bands in the electronic spectrum, shifted in the usual manner according to the optical electronegativity of the halogen in the sense of Jörgensen's definition[15]. The mercury–halogen stretching vibrations have not been identified in the infrared spectrum, but the two main stretching vibrations of the rhodanide anion (C—S and C≡N) belong unambiguously to the rhodanide group coordinated by the sulfur atom[16]. Coordination of halides and rhodanides to mercury is, in addition, reflected by the shift of the wavenumber of the Hg—S stretching vibration to lower values according to the decreasing electronegativity of the halogen. That shift reflects the decrease of the order of the Hg—S bond due to the changing polarizability of the halogen.

The optimum number of donor atoms for the formation of these mixed complexes occurs again in the case of H_2Z. The attempts at preparation of analogous compounds with H_2G failed. H_2T forms a chloro-complex, whose properties and way of preparation indicate its polymer character, and a iodo-complex, crystalline and obviously monomeric. It cannot be excluded that the excessive sulfur atom in H_2T causes the polymerization of the chloro-complex. The splitting of the C—S stretching vibration in the iodo-complex indicates that also one of the sulfur atoms remains noncoordinated, but the bulky iodide ions, bound strongly in the first coordination sphere of mercury, cause a steric hindrance of the formation of intermolecular bonds.

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