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Metal Complexes of Thiopolycarboxylic Acids. IV. Diethylenetrithiodiacetic Acid*

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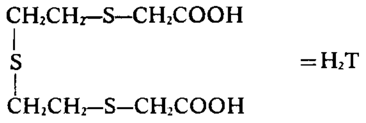
The complexes of diethylenetrithiodiacetic acid with the first transition row metal ions were studied in aqueous solution and in solid state. Only 1:1 complexes are formed with all ions studied. Nickel and copper complexes possess a remarkable stability attributable to the affinity of these metals towards sulphur. A number of solid complexes was prepared and from the study of their properties conclusions were drawn regarding their molecular structure.

Introduction

In the previous papers we have studied the complex-forming ability of simple thiodicarboxylic acids, namely thiodiacetic[1,2] and ethylenedithiodiacetic acid.[3] The next member of this homologous series is diethylenetrithiodiacetic acid



$$\begin{array}{ll} CH_2CH_2\text{—}S\text{—}CH_2COOH & \\ | & \\ S & =H_2T \\ | & \\ CH_2CH_2\text{—}S\text{—}CH_2COOH & \end{array}$$

It was the aim of the present work to study this hitherto unkown ligand.

Experimental Section

Materials. Diethylenetrithiodiacetic acid was prepared from β,β'—dimercaptodiethylsulphide and chloroacetic acid: 250 gr of thiourea (3.28 mole) and 170 ml of thiodiglycol (1.67 mole) were refluxed for 30 min. with 457 ml of 48% hydrobromic acid (4.10 mole). After cooling, a rapid stream of nitrogen was introduced and thiouronium salt was decomposed by a slow addition of 420 gr of sodium hydroxide (10.5 mole) dissolved in 600 ml of water. During the addition of alcali the mercaptan layer separated at first but dissolved almost completely at the end of addition. The mixture was then heated to 60-80° and a solution of 297 gr of chloroacetic acid (3.10 mole), neutralized previously with an equivalent amount of sodium hydrogen carbonate and diluted to 600 ml, was added gradually with constant stirring at such a rate as to keep the reaction mixture near to 90°. After 5 hours of additional refluxing the mixture was cooled, neutralized with concentrated HCl to pH=6 and filtered (charcoal). The clear colourless filtrate was then acidified with 10% HCl to pH=1 and allowed to stand overnight at 5°. The white precipitate was collected and recrystallized from four liters of boiling water by a quick cooling with vigorous stirring in order to prevent the formation of an oily product. The collected acid was dried at 50° and recrystallized from the hot ethyl acetate-petroleum ether (1:1) mixture. Yield, 251 gr (58%), white crystals of m.p. 109°.

For $C_8H_{14}O_4S_3$ (m.w. 270.39). Calcd C, 35.54; H, 5.22; S, 35.57, equiv. weight 135.20. Found C, 35.61; H, 5.37; S, 35.24, equiv. weight 135.85.

Other materials were obtained as described previously.[1,2]

Apparatus and Methods. These are described in the previous papers.[1-3]

Calculations. The computerized methods A and B as well as the Benesi-Hildebrand method C were used in this work in a manner analogous to that of previous papers.[1,3]

The stability of cupric complex, however, is too high to permit the stability constant to be calculated from the titration curve precisely. A method was then used based on a competitive reaction between Cu^{2+}, T^{2-}, and ethylenedithiodiacetate[3] ions. Since the molar extinction coefficients of both cupric complexes differ considerably at 365 nm, the competitive reaction can be followed spectrophotometrically, the stability constant being then calculated according to Irving and Mellor[4] (method D).

Results

Composition and Stability of Complexes in Solution. By measuring absorbancy at a proper wavelength in isomolar series, the formation of 1:1 complexes only was found to take place with all the cations studied. The manganous complex was not studied owing to its limited absorbancy, neither were the chromium complexes owing to their limited solubility.

(*) Dedicated to Professor S. Škramovský on the occasion of his 70th birthday.

(1) Podlaha J. and Podlahová J., *Inorg. Chim. Acta, 4,* 521 (1970).
(2) Podlaha J. and Podlahová J., *Inorg. Chim. Acta, 4,* 549 (1970).
(3) Podlaha J. and Podlahová J., *Inorg. Chim. Acta, 5,* 413 (1971).
(4) Irving H. and Mellor D.H., *J. Chem. Soc.,* 1955, 3457.

The shape of formation curves calculated from titration data confirmed the presence of 1:1 complexes only, as well as the mononuclear nature of the systems. As in the previous systems,[1,3] formation of mixed complexes $MeHT^+$ was taken into acocunt in order to explain the formation curves completely. Tervalent iron forms the $FeHT^{2+}$ complex only, an analogous complex of Cr^{III} being, however, too insoluble to allow a calculation of its stability constant.

The stability constants of complexes defined as (charges are omitted)

$$K_{MeHT}=\frac{[MeHT]}{[Me][HT]} \qquad K_1=\frac{[MeT]}{[Me][T]}$$

and the ligand dissociation constants

$$K_1^H=\frac{[H][HT]}{[H_2T]} \qquad K_2^H=\frac{[H][T]}{[HT]}$$

are summarized in Table I.

Preparation of Compounds. Sodium salts, Na_2T . $3H_2O$ and $NaHT$. H_2O, were prepared by the neutralization of a H_2T suspension with the equivalent amounts of $NaHCO_3$ followed by crystallization.

The complexes of general composition $Me^{II}T$ .nH_2O were obtained as sparingly soluble solids from equimolar amounts of metal sulphate and Na_2T solutions. The microcrystalline complexes MnT . $2H_2O$, FeT . $2H_2O$, CoT $2H_2O$, NiT . $3H_2O$, CuT . H_2O, and the amorphous CrT . $3H_2O$ were prepared. All attempts to prepare a vanadous complex, as well as a second form of the chromous complex (see ref. 3) were unsuccessful.

The tervalent metal complexes, $CrTOH$. $2H_2O$ and $FeTOH$. $2H_2O$, were prepared as insoluble amorphous precipitates from equimolar amounts of metal nitrate and Na_2T solutions at pH = 3 (chromium complex only after heating to 90°).

The preparation of ferrous and chromous complexes was carried out under nitrogen. All compounds were isolated by suction, washed with water, ethanol, and ether and dried at room temperature. The composition, appearance, and analytical data of compounds are given in Table II.

Table I. Dissociation constants of H_2T and stability constants of its complexes at 25° and I=0.1. Standard deviations are given in parentheses.

Constant	Method	H^+	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Fe^{3+}
pK_1^H	B	3.15 (0.01)								
pK_2^H	B	3.94 (0.02)								
log K_{MeHT}	A		*a*	*a*	0.6 (0.2)	0.7 (0.1)	1.58 (0.06)	2.42 (0.04)	3.36 (0.03)	
	C									(0.18) 5.26
log K_1	A		1.2 (0.1)	2.32 (0.07)	1.7 (0.1)	1.85 (0.08)	2.28 (0.05)	4.67 (0.03)		
	B		1.187	2.336	1.691	1.902	2.277	4.730		
	Average		1.2 (0.1)	2.33 (0.07)	1.7 (0.1)	1.88 (0.08)	2.28 (0.05)	4.70 (0.03)	5.90[b] (0.03)	

[a] too low to be calculated; [b] method D.

Table II. Analytical data of the compounds prepared.

Compound (m.w.)	Appearance	metal % calcd. (found)	T^{2-} % calcd. (found)	$H_2O(+OH)$ % calcd. (found)
$Na_2T.3H_2O$ (368.41)	white powder	12.48 (12.25)	72.85 (72.78)	14.67 (15.00)
$NaHT.H_2O$ (310.39)	white crystals	7.41 (7.36)	86.46 (86.73)	5.81 (5.79)
$CrT.3H_2O$ (374.43)	red powder	13.89 (13.96)	71.68 (70.82)	14.43 (15.22)[a]
$MnT.2H_2O$ (359.35)	pale pink powder	15.29 (15.35)	74.68 (75.12)	10.03 (9.81)
$FeT.2H_2O$ (360.26)	greenish powder	15.50 (15.29)	74.50 (74.81)	10.00 (9.77)
$CoT.2H_2O$ (363.34)	red-violet crystals	16.22 (15.88)	73.86 (74.06)	9.92 (10.18)
$NiT.3H_2O$ (381.14)	blue-green crystals	15.40 (15.00)	70.42 (70.09)	14.18 (14.92)[a]
$CuT.H_2O$ (349.93)	green crystals	18.16 (18.23)	76.69 (76.02)	5.15 (5.75)[a]
$CrTOH.2H_2O$ (373.42)	grayish-blue powder	13.93 (14.19)	71.87 (71.62)	14.20 (14.19)[a]
$FeTOH.2H_2O$ (377.27)	orange powder	14.80 (14.56)	71.14 (72.10)	14.06 (13.34)[a]

[a] from the difference.

Table III. Electronic spectra of diethylenetrithiodiacetate complexes.

Compound	Wavenumbers of maxima (ε_M) Solution	 Solid reflect.	Assignment
H_2T	48,500(7300)		CT
	37,200(620)sh	36,800	CT
$Na_2T.3H_2O$	49,100(7000)		CT
$NaHT.H_2O$	48,800(7100)		CT
$VT(H_2O)_n$	12,100(2.4)		$^4T_{2g}\leftarrow{}^4A_{2g}$
	18,050(5.2)		$^4T_{1g}(F)\leftarrow{}^4A_{2g}$
	27,400(9)sh		$^4T_{1g}(P)\leftarrow{}^4A_{2g}$
$CrT.3H_2O$	*a*	19,400	
$FeT.2H_2O$	10,300(4.4)	10,200	$^5E_g\leftarrow{}^5T_{2g}$
	b	38,600sh	CT
$CoT.2H_2O$	9,100(8.2)	*c*	$^4T_{2g}\leftarrow{}^4T_{1g}(F)$
	17,600(3.8)sh	17,400sh	$^4A_{2g}\leftarrow{}^4T_{1g}(F)$
	19,800(11.3)	19,700	$^2P,{}^2G,{}^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$
	32,800(690)	33,100	CT
$NiT.3H_2O$	9,950(31)	*c*	$^3T_{2g}\leftarrow{}^3A_{2g}$
	16,300(11.5)	16,400	$^3T_{1g}(F)\leftarrow{}^3A_{2g}$
	26,300(32)	25,800	$^3T_{1g}(P)\leftarrow{}^3A_{2g}$
	37,000(4700)	37,000	CT
$CuT.H_2O$	13,100(110)	12,900	$^2T_{2g}\leftarrow{}^2E_g$
	27,700(3800)	27,200	CT
$CrTOH.2H_2O$	*a*	17,200	$^4T_{2g}\leftarrow{}^4A_{2g}$
		24,800	$^4T_{1g}(F)\leftarrow{}^4A_{2g}$
		40,000sh	CT
$FeTOH.2H_2O$	36.200(820)sh [d]	35,700	CT
	41,700(1150)		CT

[a] insufficient solubility; [b] overlapped by a ligand CT band; [c] outside the apparatus range; [d] $FeHT^{2+}$ complex.

Table IV. Interplanar distances and relative intensities of powder diagram lines.

H_2T		$Na_2T.3H_2O$		$NaHT.H_2O$		$MnT.2H_2O$		$FeT.2H_2O$		$CoT.2H_2O$		$NiT.3H_2O$		$CuT.H_2O$	
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	5.10	1	4.66	4	5.58	1	8.02	2	7.96	3	7.90	1	7.78	3
4.28	4	4.77	2	4.27	2	4.39	3	6.85	2	7.18	2	7.18	1	6.94	1
3.62	1	4.45	3	3.89	1	4.07	2	5.78	3	6.35	2	6.27	1	6.12	1
3.39	2	4.34	3	3.57	3	3.75	1	4.65	1	5.66	4	5.62	3	5.53	4
3.27	1	3.76	3	2.85	4	3.48	2	4.41	4	4.91	2	4.88	2	4.82	3
2.96	1	3.46	1	2.65	2	3.23	1	4.17	3	4.46	2	4.43	2	4.30	3
2.65	2	3.26	1	2.52	1	3.04	1	4.01	2	3.99	1			3.95	1
2.43	2	3.12	1	2.22	2			3.78	3	3.65	1			3.33	1
2.22	1	2.96	1	2.10	1			3.52	3	3.12	2	3.11	1	3.13	2
1.84	1	2.83	4	2.06	1			3.23	2	2.99	1			3.04	2
		2.62	3	1.96	1			3.06	1	2.90	1			2.88	2
		2,53	2	1.89	1			2.89	2	2.43	1			2.68	1
		2.11	1					2.76	1	2.34	1			2.52	1
		1.87	2					2.59	3	2.23	2	2.22	1	2.33	3
		1.74	1					2.46	2	1.97	2	1.98	1	2.18	3
								2.34	2	1.87	1			2.11	1
								2.18	1	1.73	1			1.91	1
								2.07	1					1.83	1
								1.91	2					1.74	1
								1.84	1						
								1.79	1						
								1.51	1						

Properties of the Compounds Prepared. The following properties are summarized in Tables III-VII: electronic spectra (Table III), powder diagram lines (Table IV), magnetic and solubility data (Table V), IR spectra (Table VI), and thermal decomposition data (Table VII).

Discussion

To compare diethylenetrithiodiacetic acid with the ligands studied previously, two contradictory factors can be pointed out as influencing the complex-forming ability of this ligand: (a), the presence of three sulphur atoms which should result in an enhanced stability of complexes if all the sulphur atoms are bound to the metal, and (b), the steric hindrance resulting when not all the sulphur atoms are coordinated. The trend of stability constants (see Figure 1) in comparison with those of previous ligands clearly shows that (a) is the case for Ni^{2+} and Cu^{2+} whereas (b) appears to take place with other cations studied. Such a distinction between the two types of cations studied is supported further by other properties of complexes, namely the intensity of UV charge transfer bands connected with a S—Me bond, the magnitude of the shift

Table V. Magnetic and solubility data (at 25°) of the compounds prepared. The solubility products are calculated by using stability constants from Table I.

Compound	μ_{eff}, B.M.	Solubility in 0.1M $NaClO_4$ (KCl) mol/l	soly. product
H_2T	-1.7×10^{-4} [a]	0.2055 [b]	
$Na_2T.3H_2O$	-1.7×10^{-4} [a]	13.36 [b]	
$NaHT.H_2O$	-2.0×10^{-4} [a]	49.36 [b]	
$CrT.3H_2O$	2.05 (298 K) 0.72 (77 K)	4.17×10^{-6}	1.70×10^{-11}
$MnT.2H_2O$	5.97	9.76×10^{-3}	6.24×10^{-5}
$FeT.2H_2O$	5.40	8.26×10^{-3}	3.42×10^{-5}
$CoT.2H_2O$	4.91	3.09×10^{-3}	4.73×10^{-6}
$NiT.3H_2O$	3.18	1.02×10^{-3}	1.90×10^{-8}
$CuT.H_2O$	1.95	2.66×10^{-2}	3.30×10^{-8}
$CrTOH.2H_2O$	3.86	7.16×10^{-7}	
$FeTOH.2H_2O$	3.35	9.54×10^{-5}	

[a] molar susceptibility; [b] grams per 100 gr. of solution.

Table VI. Selected IR bands (cm^{-1}) of the compounds prepared.

Compound	ν(C-S)	ν_s(COO)	ν_a(COO)	δ(H_2O)	ν(OH)
H_2T	716s	1406s	1700sh 1730vs		3100vs,b
D_2T [a]	718s	1403s	1700sh 1730vs		2320s
$Na_2T.3H_2O$	720s	1402vs	1602vs	1675sh	3430s,b
$NaHT.H_2O$	716m	1415vs	1600s 1737s	1660sh	3180w,b 3450s,b
$CrT.3H_2O$	722m	1412vs	1581vs	1635w	3210w,b 3380s,b
$MnT.2H_2O$	705s	1410vs	1596vs	1650sh	3440vs,b
$FeT.2H_2O$	709s	1417vs	1598vs	1658sh	3440vs,b
$CoT.2H_2O$	704s	1403vs	1609vs	1682sh	3280sh 3440vs,b
$NiT.3H_2O$	680s	1394vs	1610vs	1698sh	3450vs,b
$CuT.H_2O$	667w 692s	1385vs	1612vs	1695sh	3270sh 3450vs,b
$CrTOH.2H_2O$	716m	1416vs	1595vs	1625sh	3200m,b 3450vs,b
$FeTOH.2H_2O$	719s	1412vs	1601vs	1633sh	3220m,b 3430s,b

[a] H_2T recrystallized repeatedly from D_2O.

of C–S stretching frequency in the IR spectra, and the strength of the crystal field (see below).

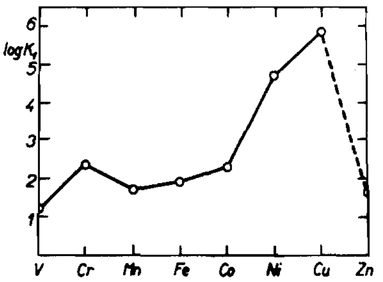


Figure 1. Trend of stability constants of diethylenetrithiodiacetate complexes in the first transition row. The value of Zn^{2+} is estimated from unpublished results.

The type of bonding in diethylenetrithiodiacetate complexes must be therefore considered as metal-dependent: the ligand acts as pentadentate towards Ni^{2+} and Cu^{2+}, while one or more sulphur atoms are not coordinated in the complexes with other metals studied, probably for steric reasons caused by a lowered affinity of these metals towards sulphur.

The electronic absorption spectra in solution are essentially identical with the diffuse reflectance spectra indicating the structure to be the same in solution and in the solid state. As with the previous ligands, the spectra have been interpreted in a weak octahedral crystal field formalism.[5] The parameters Dq and B obtained from the Tanabe-Sugano diagrams as well as the nephelauxetic ratio β are presented in Table VIII, from which the spectra of complexes can be satisfactorily back-calculated. The empirical parameter f derived after Jørgensen[6] clearly divides the metals studied into two groups mentioned above according to the number of sulphur atoms proposed to be coordinated. As a consequence, the position of diethylenetrithiodiacetate ion in the spectrochemical series cannot be determined unambiguously.

Analogously, neither can the molecular structure of the diethylenetrithiodiacetate complexes be formulated in such a reliable manner as that of the ligands

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(5) Figgis B.N., Introduction to Ligand Fields. Interscience Publ., N.Y. 1966.

(6) Jørgensen C.K., Absorption Spectra and Chemical Bonding in Complexes. Pergamon Press, Oxford 1962.

Table VII. Thermal decomposition of the compounds prepared.

Compound	Dehydration °C	DTA-effect	Product	Decomposition of T °C	DTA-effect	Product	Other processes °C	DTA-effect	Product
H_2T				260	endo		110	endo	melt
				300	exo				
$Na_2T.3H_2O$	40	endo	$Na_2T.H_2O$	280	exo	$Na_2SO_4+Na_2CO_3$			
	100	endo	Na_2T						
$NaHT.H_2O$	70	endo	NaHT	280	exo	$Na_2SO_4+Na_2CO_3$			
$CrT.3H_2O$	90	endo	$CrT.H_2O$	260	exo	Cr oxide+sulphate	550	endo	Cr_2O_3
$MnT.2H_2O$	70	endo	$MnT.H_2O$	280	exo		840	endo	Mn_3O_4
	160	endo	MnT	380	exo	$MnSO_4+Mn_3O_4$			
$FeT.2H_2O$	130	endo	FeT	280	exo		570	endo	Fe_2O_3
				340	exo	Fe oxide+sulphate			
$CoT.2H_2O$	150	endo	CoT	300	exo		750	endo	Co_3O_4
				420	exo	$CoSO_4+Co_3O_4$	920	endo	CoO
$NiT.3H_2O$	60	endo	$NiT.H_2O$	300	exo		730	endo	NiO
				420	exo	$NiSO_4+NiO$			
$CuT.H_2O$				220	exo	Cu,Cu^{I},Cu^{II}	690	endo	CuO
				300	exo	oxide+sulphate			
				330	exo				
$CrTOH.2H_2O$	40-200	endo	CrTOH	290	exo		550	endo	Cr_2O_3
				340	exo	Cr oxide+sulphate			
$FeTOH.2H_2O$	40-190	endo	FeTOH	190	exo		630	endo	Fe_2O_3
				280	exo	Fe oxide+sulphate			
				320	exo				

Table VIII. Crystal field parameters of diethylenetrithiodiacetate complexes.

Me	Dq, cm^{-1}	B, cm^{-1}	f	β
V^{2+}	1220	573	0.99	0.75
Fe^{2+}	1030		1.03	
Co^{2+}	950	798	1.02	0.71
Ni^{2+}	995	855	1.12	0.79
Cu^{2+}	1310		1.09	
Cr^{3+}	1720	650	1.01	0.63

studied previously. Very probably, the nickel and copper complexes contain a pentadentate T^{2-} anion, the sixth position of the coordination polyhedron being occupied by a molecule of water which cannot be removed by heating without decomposing the ligand. However, the dehydration of other complexes is too different to permit any reliable conclusions regarding the number of coordinated water molecules and hence the number of coordination sites occupied by the ligand.

The character of chromium(III) and iron(III) complexes is quite analogous to that of previous thiodicarboxylate complexes thus representing these compounds as high polymers linked through OH bridges.

As regards Cr^{II}, the only complex which could be prepared is the antiferromagnetic $CrT . 3H_2O$ analogous to $CrZ . 2.5H_2O(I)$[3] and possessing probably the same dimeric structure with a direct Cr—Cr bond.