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Metal Complexes of Thiopolycarboxylic Acids. I. Complexes of Thiodiacetic Acid in Solution

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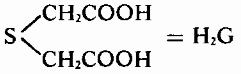
The complexes of thiodiacetic acid with the first transition row metal ions were investigated in the diluted aqueous solution. The 1:1 and 1:2 (metal-to-ligand) complexes are formed with all metals studied with the exception of V^{2+}, Mn^{2+}, Cr^{3+}, and Fe^{3+}, where only 1:1 complexes appear to exist. The stability constants, calculated from potentiometric and spectrophotometric data, agree well with the Irving-Williams series. From the electronic spectra of the complexes, the pseudo-octahedral crystal field parameters were calculated and the ligand was placed into the spectrochemical and nephelauxetic series.

Introduction

Among the great variety of metal chelates those containing heavy donor atoms have been investigated relatively rarely. As the affinity of some metals towards sulphur is very distinct, it seemed to us interesting to substitute the nitrogen atoms of some aminopolycarboxylic acids by sulphur and to study the complex-forming ability of thiopolycarboxylic acids so formed. The simplest compound of this type is thiodiacetic (thiodiglycollic) acid



$$\mathrm{S}\left\langle\begin{array}{l}\mathrm{CH_2COOH}\\ \mathrm{CH_2COOH}\end{array}\right. = \mathrm{H_2G}$$

Some data concerning the stability of thiodiacetate complexes are compiled or presented in original reports.[1,2] However, they were obtained using different methods of measurement and/or calculation so that they cannot be compared unambiguously. Moreover, complexes formed in solution often were not characterized at all. Therefore it was the aim of the present work to study the equilibrium stability and the electronic spectra of the thiodiacetate complexes of bivalent and tervalent first transition row metal cations at the constant experimental conditions.

Experimental Section

Materials. Thiodiacetic acid[3]: 90.5 ml of 80% mercaptoacetic acid (one mole) was mixed cautiously with the solution of 80 g NaOH (two moles) in 200 ml of water in a stream of nitrogen with stirring and cooling. One mole of sodium chloroacetate (94.5 g of $ClCH_2$-COOH neutralized with 84 g of $NaHCO_3$) in 200 ml of water was added, the resulting solution was refluxed for 2 hours and allowed to stand overnight. pH was then adjusted with concentrated HCl to 1, the solution was evaporated on the water bath and the rest dried carefully at 80 °C. The resulting mixture of H_2G and NaCl was refluxed twice with 500 ml of acetone, the solvent was evaporated from the clear filtrate in vacuo at 30 °C and the crude product was recrystallized from the hot 1:2 benzene-glacial acetic acid mixture. After cooling the white crystals deposited were collected, washed with petroleum ether and dried at 100°C. Yield, 98 g (65%), m.p. 129°C (lit.:[3] 129°C), equivalent weight (NaOH titration towards phenolphtalein), 75.12 (calcd. 75.08).

Approximately 1 *M* solutions of metal perchlorates were obtained from basic metal carbonates or freshly precipitated hydroxides and a slight excess of 30% perchloric acid. The content of metals was determined with standard gravimetric and volumetric procedures and the content of free perchloric acid by the use of Gran's method[4] and by the titration of total perchloric acid formed on the column of Dowex-50 exchanger. The results so obtained were in a good mutual agreement (± 0.3 relat.%). The ferrous perchlorate solution was prepared by the reaction of $FeSO_4$ and $Ba(ClO_4)_2$ solutions with the exclusion of air. Separated $BaSO_4$ was filtered off and the solution was stabilized with some $HClO_4$.

Vanadous and chromous sulphates were prepared by electrolytical reduction of $VOSO_4$ and $Cr_2(SO_4)_3$ solutions on the mercury pool following by the slow crystallization from an ethanolic-water solution in the nitrogen atmosphere. The well-developed crystals of $VSO_4 . 7H_2O$ and $CrSO_4 . 5H_2O$ so obtained were kept under the layer of ethanol and were relatively stable towards aerial oxidation. Tervalent cations could not be detected in the freshly prepared sulphates as well as in the ferrous perchlorate solution by customary methods.

The sodium hydroxide standard solution (free of carbonates) was prepared from the clear concentrated NaOH solution and previously boiled-off water. It was standardized against oxalic acid.

All other materials were the commercial C.P. chemicals of the firm Lachema.

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Apparatus and Methods. The pH-measurements were carried out in a closed thermostated vessel equipped with joints for electrodes, a burette and an inert gas inlet and outlet. The Radiometer glass G 202 B electrode and the calomel K 401 electrode were connected to the Radiometer 25 SE instrument and the system was standardized against a set of standard buffer solutions (pH from 1.65 to 9.16). The precision of the pH-measurements was ±0.01 pH at 25±0.1°C and ionic strength $I=0.1$. The pH-values were converted to the hydrogen-ion concentration assuming the activity coefficient of H^+ to be 0.83 at these conditions.[5] To mantain an inert atmosphere and to stir the solutions a slow stream of purified nitrogen was bubbled through. The ionic strength of solutions was adjusted to 0.1 by the addition of required amounts of sodium perchlorate (potassium chloride in the case of easily oxidizable chromous and vanadous salts). The presence of V^{II} and Cr^{II} sulphatocomplexes was neglected since their formation had been found to be very limited even with excess of sulpate ion.[6] The initial solutions contained various amounts and various stoichiometric ratios of a metal salt and thiodiacetic acid. The starting volume was invariably 50 ml and the solutions were titrated with standard 0.1 N–NaOH added from a standardized 10 ml-burette by 0.2 ml steps. The resultant titration curves, some typical of which are presented in Figure 1, are the averages of at least two independent runs agreeing within better than 0.03 pH.

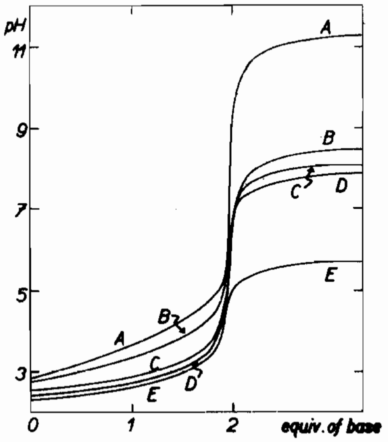

Figure 1. The titration curves of $0.005M$–H_2G (curve A) and $0.005M$–$H_2G+0.01M$ metal: Mn^{2+} (curve B), Co^{2+} (curve C), Ni^{2+} (curve D), Cu^{2+} (curve E).

Th electronic spectra in solutions were taken at 25±1 °C on the Unicam S.P. 800, CF-4 (Optica, Milano), and VSU-1 (Zeiss, Jena) instruments using 2 to 40 mm silica and glass cells, over the range 5,000-53,000 cm^{-1} (186-2000 nm). Air-sensitive solutions were handled in a glove box flushed with purified nitrogen. The ionic strength of solutions was adjusted to 0.1 with $NaClO_4$ or KCl. To attain an equilibrium, all solutions containing Cr^{3+} must be heated at 80 °C for six hours.

Calculations. From the known total concentration of metal, ligand and acidic hydrogen, and from the measured free hydrogen ion concentration, the dissociation constants of the ligand and the stability constants of bivalent metal ion complexes were calculated using different methods A-D:

$$K_1^H = \frac{[H^+][HG^-]}{[H_2G]} \qquad K_2^H = \frac{[H^+][G^{2-}]}{[HG^-]}$$

(calculated from the data at $c_{Me}=0$)

$$K_{MeHG} = \frac{[MeHG^+]}{[Me^{2+}][HG^-]} \qquad K_1 = \frac{[MeG]}{[Me^{2+}][G^{2-}]}$$

$$K_2 = \frac{[MeG_2^{2-}]}{[MeG][G^{2-}]}$$

The method A served for the simultaneous calculation of K_1 and K_{MeHG} according to Schwarzenbach and Ackermann[7] from the data belonging to the 5 to 10-fold excess of a metal ion. The calculations were carried out on the Minsk 15 (USSR) digital computer.

The method B is Calvin's extension[8] of Bjerrum's original method[9] as programmed by Romary *et al.*[10] for the IBM 7040 computer. Using this method, the constants K_1 and K_2 (or K_1^H and K_2^H) were calculated simultaneously by a method of successive approximations.

The method C is an adaptation of the least squares method of Irving and Rossotti.[11] The simultaneously calculated K_1 and K_2 constants were found as intercepts of a straight line constructed from the experimental data.

The method D for the calculation of K_2 only was a simple algebraic procedure treating the ligand-excess experimental data and using the from the previous methods obtained value of K_1.

The stability constants of Cr^{3+} and Fe^{3+} complexes were determined spectrophotometrically in strongly acidic solutions in order to prevent hydrolysis of metal ions. The data of the absorptivity of solutions containing various amounts of metal perchlorate and thiodiacetic acid and a constant amount of perchloric acid were treated according to Benesi and Hildebrand[12] to obtain the equilibrium constant

$$K = \frac{[MeHG^{2+}][H^+]}{[Me^{3+}][H_2G]}$$

and the stability constant

$$K_{MeHG} = \frac{[MeHG^{2+}]}{[Me^{3+}][HG^-]} = \frac{K}{K_1^H}$$

The given formulation of the equilibrium constant K is supported by the fact the HG^- ion is the only of all possible forms of the ligand giving a linear Benesi-Hildebrand plot.

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Results

Composition and stability of complexes. The approximate composition of thiodiacetate complexes was determined spectrophotometrically by the Job method. Isomolar solutions contained metal salts and ligand at pH=6.5 (pH=1 in the case of Cr^{3+} and Fe^{3+}) and their absorbance was read at a proper wavelength chosen from changes of the metal ion spectrum caused by the addition of a ligand excess.

The results are summarized in Table I and demonstrated with the typical Co^{2+} plots (Figure 2). In several cases, the position of the maximum was wavelength-depending.

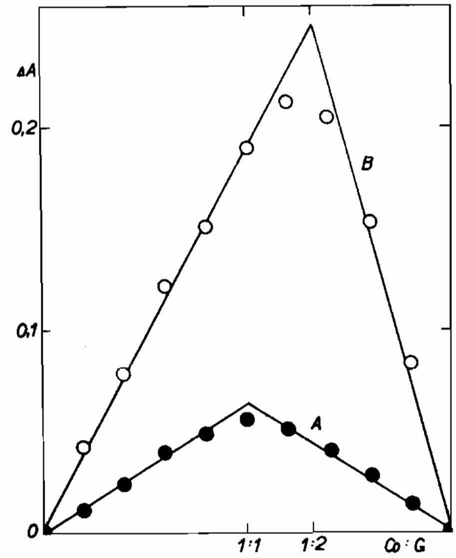

Figure 2. The Job curves of Co^{2+}—G^{2-} system. Curve A—530 nm, curve B—620 nm.

It follows from Table I that the simultaneous presence of at least two complexes must be considered in the treatment of the majority of titration curves. Using the Method B, formation curves were at first calculated and their inspection showed that

a) all systems are mononuclear regarding to metal since the formation curves are independent on the total metal concentration,

b) the maximum ligand number is two since the curves limited to $\bar{n}=1$ for V^{2+} and Mn^{2+}, to $1<\bar{n}<2$ for Cr^{2+} and Fe^{2+}, and to $\bar{n}=2$ for other bivalent cations. This observation is in accordance with the previous spectrophotometric results.

Table I. The molar ratios (metal-to-ligand) related to the Job curves maxima

Metal ion	λ, nm	Molar ratio
V^{2+}	210	1:1
Cr^{2+}	*a*	*a*
Mn^{2+}	*a*	*a*
Fe^{2+}	940	1:1+1:2
Co^{2+}	530	1:1
	620	1:2
Ni^{2+}	390	1:1+1:2
	620	1:2
Cu^{2+}	330	1:1
	350	1:1+1:2
	680	1:2
	740	1:2
Cr^{3+}	410	1:1
Fe^{3+}	330	1:1
	370	1:1

[a] Limited solubility or absorptivity or both.

However, the continuing treatment of the formation curves showed the necessity of taking into consideration a presence of mixed complexes of the $MeHG^+$ type, formation of which took place only in an excess of metal in weakly acidic solutions. Therefore the stability constants of these mixed complexes were calculated using the Method A. Mixed complexes are not formed in the case of V^{2+} and Cr^{2+}.

The Benesi-Hildebrand plots in the systems Cr^{3+}—H_2G—0.02 *M*—$HClO_4$ and Fe^{3+}—H_2G—0.1 *M*-$HClO_4$ are presented on the Figure 3.

The dissociation constants of H_2G and the stability constants of its complexes calculated by the methods mentioned are summarized in Table II and III. The standard deviations of the constants were calculated by conventional methods of mathematical statistics.[13]

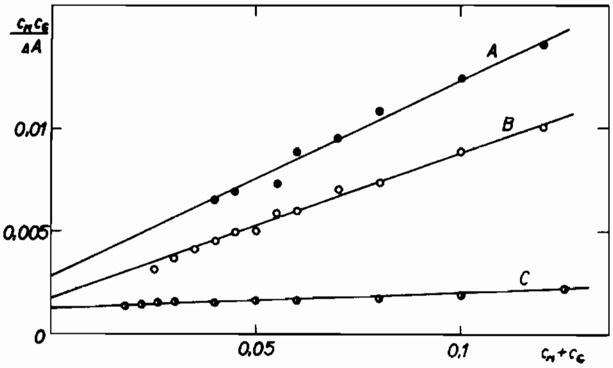

Figure 3. The Benesi-Hildebrand plots of Cr^{3+}—H_2G and Fe^{3+}—H_2G systems. A—0.02*M*—Cr^{3+}, 410 nm. B—0.02*M*—Cr^{3+}, 580 nm. C—0.005*M*—Fe^{3+}, 370 nm.

Electronic spectra. Before the measurement of an electronic spectrum of a complex particle, the suitable composition of the solution was calculated from the stability constants in order to attain the maximal concentration of the respective complex particle. A correction was made for the other absorbing particles and the net spectra of individual complexes were calculated with the exception of following three cases:

a) reliable spectra of $MeHG^+$ could not be obtained because of a very limited concentration of these complexes even at the most favourable conditions,

b) in the case of Cr^{2+} and Mn^{2+} there are unfavourable relations between solubility and absorptivity of the complexes formed,

c) the measurements of the far U.V. spectra of MeG_2^{2-} complexes were obstructed by a strong absorption of the necessary ligand excess.

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Table II. Dissociation constants of thiodiacetic acid

Medium	0.1*M*—$NaClO_4$		0.1*M*—KCl		
Method of calculation	B	C	B	C	Average
pK_1^H	3.128	3.13±0.05	3.134	3.09±0.04	3.12±0.06
pK_2^H	4.151	4.14±0.03	4.149	4.12±0.04	4.14±0.05

Table III. Stability constants of thiodiacetate complexes. Standard deviations are given in parentheses

Constant	Method	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cr^{3+}	Fe^{3+}
log K_{MeHG}	Benesi-Hild.								4.85	3.63
									(0.21)	(0.17)
	A			0.6	1.61	1.72	2.15	2.63		
				(0.2)	(0.10)	(0.08)	(0.09)	(0.06)		
log K_1	A	1.63	2.93	1.74	2.94	3.55	4.20	4.66		
		(0.09)	(0.07)	(0.13)	(0.06)	(0.07)	(0.08)	(0.04)		
	B	1.743	3.002	1.688	2.869	3.514	4.189	4.670		
	C	1.80	3.06	1.70	2.87	3.45	4.22	4.59		
		(0.10)	(0.12)	(0.08)	(0.09)	(0.07)	(0.03)	(0.03)		
	Average	1.73	3.00	1.72	2.88	3.51	4.20	4.65		
		(0.13)	(0.14)	(0.15)	(0.11)	(0.10)	(0.09)	(0.05)		
log K_2	B		2.401		2.372	2.611	2.783	2.850		
	C		2.43		2.30	2.86	2.87	2.87		
			(0.08)		(0.11)	(0.09)	(0.08)	(0.04)		
	D		2.35		2.46	2.60	2.77	2.82		
			(0.11)		(0.06)	(0.05)	(0.05)	(0.03)		
	Average		2.39		2.36	2.68	2.81	2.85		
			(0.14)		(0.12)	(0.11)	(0.10)	(0.05)		

Table IV. Electronic spectra of thiodiacetate complexes

Complex	cm^{-1} (ε_M)	Assignment	cm^{-1} (ε_M)	Complex
Ligand				
pH = 2	48,800(720)	CT		
	42,600(330)	CT		
pH = 7	48,200(920)	CT		
$VG(H_2O)_3$	11,900(1.8)	$^4T_{2g} \leftarrow {}^4A_{2g}$		
	17,850(3.9)	$^4T_{1g}(F) \leftarrow {}^4A_{2g}$		
	27,550(8) sh	$^4T_{1g}(P) \leftarrow {}^4A_{2g}$		
$FeG(H_2O)_3$	10,900(2.8)	$^5E_g \leftarrow {}^5T_{2g}$	11,100(3.6)	FeG_2^{2-}
	9,100(2.9)	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	9,400(3.2)	CoG_2^{2-}
	16,100(2) sh	$^4A_{2g} \leftarrow {}^4T_{1g}(F)$	16,500(3) sh	
	18,500(8.7)	^2P, ^2G, $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	18,900(7.6)	
$CoG(H_2O)_3$	21,500(6) sh		22,700(6) sh	
	9,250(10.2)	$^3T_{2g} \leftarrow {}^3A_{2g}$	9,800(6.3)	NiG_2^{2-}
	14,300(4.8)	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	15,600(9.9)	
	25,300(12.2)	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	25,600(32.2)	
$NiG(H_2O)_3$	39,200(1760)	CT	overlapped	
$CuG(H_2O)_3$	12,200(36)	$^2T_{2g} \leftarrow {}^2E_g$	13,300(54)	CuG_2^{2-}
	30,500(790)	CT	28,600(2200)	
	40,100(3400)	CT	36,700(4200)	
$FeHG^{2+}$	41,600(3400)	CT		
$CrHG^{2+}$	17,100(17.5)	$^4T_{2g} \leftarrow {}^4A_{2g}$		
	23,400(17.8)	$^4T_{1g}(F) \leftarrow {}^4A_{2g}$		
	37,000(10) sh	$^4T_{1g}(P) \leftarrow {}^4A_{2g}$		

The net electronic spectra are summarized in Table IV together with the attribution of the absorption bands to different types of electron transfer.

Discussion

As follows from the Figure 4, thiodiacetate complexes adhere well to the Irving-Williams series consistently with the fact that the affinity towards sulphur of the ions studied is not different enough to change the customary trend of stability constants in the first transition row. Taking into acocunt the values of stability constants, thiodiacetate ion can be assumed to act as a terdentate ligand, binding being realized through two carboxyl oxygens and the sulphur atom. Namely, thiodiacetate complexes are distinctly more stable than the structurally analogous glutarate complexes.[1] This effect can be attributed unambiguously to the formation of metal-sulphur bond. Moreover, the increase of stability is most distinctly pronounced in the case of Ni^{2+} and Cu^{2+} — the ions possessing the

Table V. Crystal field parameters of thiodiacetate complexes

Me	MeG(H₂O)₃ Dq, cm⁻¹	MeG(H₂O)₃ B, cm⁻¹	MeG(H₂O)₃ β	MeG₂²⁻ Dq, cm⁻¹ calcd.	MeG₂²⁻ Dq, cm⁻¹ exptl.	MeG₂²⁻ B, cm⁻¹	MeG₂²⁻ β
V^{2+}	1190	574	0.75	1230			
Fe^{2+}	1090			1180	1150		
Co^{2+}	985	745	0.73	1040	1025	750	0.73
Ni^{2+}	925	875	0.81	960	970	816	0.76
Cu^{2+}	1220			1240	1330		
Cr^{2+}	1710	631	0.61	1720			

strongest affinity towards sulphur from the ions studied.[14]

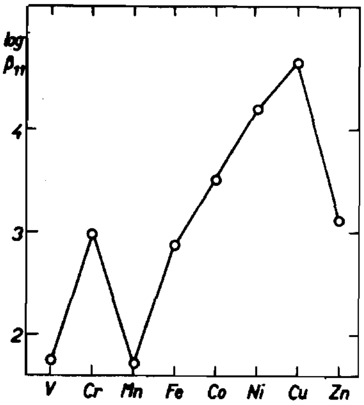

Figure 4. The trend of the stability constants of 1:1 thiodiacetate complexes in the first transition row. The value of Zn^{2+} was taken from Ref. 2.

The ligand in the mixed complexes $MeHG^{n+}$ is probably only bidentate, proton being added to one carboxyl group, since the values of proton dissociation constants, defined as

$$K^H = \frac{[H^+][MeG]}{[MeHG^+]} = \frac{K_2^H K_1}{K_{MeHG}}$$

are typical for a slightly acidified carboxyl.

The electronic spectra of the complexes can be fitted reasonably only to the octahedral crystal field diagrams. The pseudo-octahedral crystal field is proposed to be generated either by one G^{2-} ion and three water molecules (1:1 complexes) or by two G^{2-} ions (1:2 complexes). From the attribution of d–d transitions according to the Tanabe-Sugano diagrams[15] as modified for Co^{2+} and Ni^{2+} by Reedijk *et al.*,[16,17] the crystal field parameters were calculated and summarized in Table V. In this Table, the experimental values of MeG_2^{2-} complexes are compared with those calculated from the $MeG(H_2O)_3$ spectra and from the compiled parameters of hexaquoions[15] by the use of the rule of average environment. Besides the d–d transitions, the spectra of nickel and copper complexes exhibit intense U.V. bands attributable to a charge transfer, probably from sulphur to a metal 3d orbital.

Using tabulated ligand field parameters, the empirical constants f and h[15] of thiodiacetate ion can be calculated . These constants make it possible to estimate crystal field strengths of hitherto unmeasured combinations. The average values of f = 1.10 and h = 1.9 for MeG_2^{2-} complexes have resulted from the Table VI, the data of which were calculated from free ion f and h parameters[15] and from the Table V.

Table VI. The f and h parameters of MeG_2^{2-} complexes

Cation	f	h
V^{2+}	1.08	
Fe^{2+}	1.11	
Co^{2+}	1.10	1.83
Ni^{2+}	1.09	2.03
Cu^{2+}	1.11	
Average	1.10	1.9

Finally, on the basis of published spectral data[15,18,19] and the f and h values mentioned, thiodiacetate ion was placed into the spectrochemical and nephelauxetic series:[15]

$$6H_2O < 6NCS < 2G < 3acac \approx EDTA < 3gly < 6NH_3$$

(spectrochemical)

$$3en \approx 3ox < 2G < 6Cl \approx 6CN$$

(nephelauxetic)

An analogous classification for HG^- ion is not possible because of lack of experimental data.

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