Contribution from the Department of Inorganic Chemistry,
Charles University, Prague, Czechoslovakia

Metal Complexes of Thiopolycarboxylic Acids. III. Ethylenedithiodiacetic Acid*

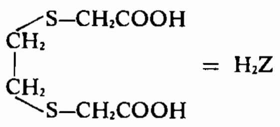
J. Podlaha and J. Podlahová

Received October 19, 1970

The complexes of ethylenedithiodiacetic acid with the first transition row metal ions were investigated in aqueous solution and in the solid state. Relatively weak 1:1 complexes are formed with all ions studied. In solution, the Ni^{2+} *and* Cu^{2+} *ions are capable of forming also 1:2 metal-to-ligand complexes. A number of solid complexes were prepared and from the study of their properties, conclusions were drawn regarding their molecular structure in the solid state and in solution.*

Introduction

As a continuation of our examination of the complex-forming ability of thiopolycarboxylic acids,[1,2] the ligand ethylenedithiodiacetic acid,



$$\begin{matrix} CH_2{-}S{-}CH_2COOH \\ | \\ CH_2{-}S{-}CH_2COOH \end{matrix} = H_2Z$$

was studied systematically in the present work. This compound is not a very original ligand and some of its complexes have been already studied.[3-10] However, the published data are either qualitative only in nature or they have been obtained under different experimental conditions, giving little if any possibility of comparison. Therefore it was the aim of the present work to study ethylenedithiodiacetate complexes under the same constant experimental conditions as thiodiacetate complexes in the previous papers.[1,2]

Experimental Section

Materials. Ethylenedithiodiacetic acid was prepared from 1,2–dichloroethane and mercaptoacetic acid.[11] The final product was recrystallized twice from hot ethyl acetate to give white crystals of m.p. 108° (lit.[3,11] 108-109°).

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

Apparatus and Methods. These are described in the previous papers.[1,2] The temperature dependence of magnetic moments was measured on a standard Gouy balance.

Analyses. The ligand content was determined by a direct titration of H_2Z with base towards phenolphtalein or by the bromate-bromide method.[2] In the presence of certain transition metals (especially Cu and Fe), the bromate-bromide method was found to give somewhat higher results owing to partial oxidation to sulphone. Therefore, the sulphur content was determined gravimetrically as $BaSO_4$ after fusion with sodium peroxide-sodium carbonate mixture.

Other analytical methods were described in the previous papers.[1,2]

Calculations. The computerized methods[1] A and B based on pH–measurements and the spectrophotometric Benesi-Hildebrand method[12] (C) were used in this work. Moreover, the stability constants of 1:2 complexes were calculated from solubility and absorptivity data according to the equations given below.

The following acid dissociation and stability constants were calculated (charges are omitted):

$$K_1^H = \frac{[H][HZ]}{[H_2Z]} \quad (1) \qquad K_2^H = \frac{[H][Z]}{[HZ]} \quad (2)$$

$$K_{MeHZ} = \frac{[MeHZ]}{[Me][HZ]} \quad (3) \qquad K_1 = \frac{[MeZ]}{[Me][Z]} \quad (4)$$

$$K_2 = \frac{[MeZ_2]}{[MeZ][Z]} \quad (5)$$

To calculate K_2 from the solubility data, the following equations were used (Method D):
total metal in the saturated solution

$$c_{Me} = [Me] + [MeZ] + [MeZ_2] \qquad (6)$$

total ligand (pH = 6)

(*) 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) Ramberg L. and Tiberg A., *Ber., 47,* 730 (1914).
(4) Larsson E.: *Svensk. Kem. Tid., 51,* 42 (1939).
(5) Tiberg A., *Ber., 49,* 2024 (1916).
(6) Tiberg A., *Ber., 49,* 2029 (1916).
(7) Tiberg A., Thesis, Univ. of Lund, 1924; *C.A., 19,* 3253 (1925).
(8) Suzuki K. and Yamasaki K., *J. Inorg. Nucl. Chem., 24,* 1093 (1962).
(9) Saini G., Ostacoli G., Campi E., and Cibrario N., *Gazz. Chim. Ital., 91,* 242 (1961).
(10) James B.R. and Williams R.J.P., *J. Chem. Soc.,* 1961, 2007.
(11) *Ger. Pat.* 840,997 (1952); *C.A., 47,* 6974 (1953).

(12) Benesi H.A. and Hildebrand J.H., *J. Am. Chem. Soc., 71,* 2703 (1949).

$$c_Z=[Z]+[MeZ]+2[MeZ_2] \tag{7}$$

$$K_1=[MeZ]P^{-1} \tag{8}$$

(P is the solubility product of MeZ at standard conditions). From the expressions (5)-(8) simple second order equations for all particles can be derived with the application of the K_1 value obtained previously.

If the absorbancy of a saturated solution is measured, the stability constant K_2 and the molar extinction coefficient ε_2 of the 1:2 complex can be calculated simultaneously as the parameters of a straight line constructed from the experimental data (Method E):

$$y=\varepsilon_2^{-1}(K_2x+1) \tag{9}$$

where

$$x=\frac{K_1[\varepsilon_o(c_{Me}-P/K_1-A+\varepsilon_1P/K_1]}{P\varepsilon_o(c_Z-c_{Me}+P/K_1)+2P(A-\varepsilon_1P/K_1)} \tag{10}$$

$$y=\frac{P(c_Z+c_{Me}-P/K_1)}{P\varepsilon_o(c_Z-c_{Me}+P/K_1)+2P(A-\varepsilon_1P/K_1)} \tag{11}$$

A - absorbancy in 1 cm cell.

$\varepsilon_o,\varepsilon_1$–molar extinction coefficients of metal ion and 1:1 complex respectively (determined previously).

Table I. The dissociation constants of H_2Z and the 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+}	Cr^{3+}	Fe^{3+}
pK_1^H	B	3.17 (0.01)									
pK_2^H	B	3.89 (0.01)									
$\log K_{MeHZ}$	A		[a]	[a]	0.7 (0.1)	2.03 (0.06)	1.95 (0.07)	3.00 (0.03)	3.94 (0.04)		
	C									5.38 (0.19)	4.35 (0.22)
$\log K_1$	A		1.40 (0.07)	1.98 (0.03)	1.05 (0.08)	2.74 (0.06)	3.10 (0.04)	4.47 (0.03)	5.66 (0.03)		
	B		1.386	1.994	1.028	2.712	3.166	4.502	5.699		
	Average		1.39 (0.07)	1.99 (0.03)	1.04 (0.08)	2.73 (0.06)	3.13 (0.04)	4.49 (0.03)	5.68 (0.03)		
$\log K_2$ [b]	D							1.34 (0.16)	2.2 (0.2)		
	E							1.53 (0.15)	1.9 (0.2)		
	Average							1.44 (0.16)	2.1 (0.2)		

[a] too low to be calculated. [b] I = 2.0.

Table II. Analytical data of the compounds prepared.

Compound (m.w.)	Appearance	metal, % calcd. (found)	Z^{2-}, % calcd. (found)	$H_2O(+OH)$, % calcd. (found)
Na_2Z (254.23)	white powder	18.09 (17.69)	81.91 (81.70)	
NaHZ (232.25)	white crystals	9.90 (9.81)	90.10 (90.15)	
$CrZ.2.5H_2O$(I) (305.28)	red powder	17.03 (17.06)	68.21 (68.40)	14.76 (14.54)[a]
$CrZ.2.5H_2O$(II) (305.28)	blue crystals	17.03 (17.13)	68.21 (68.37)	14.76 (14.50)[a]
MnZ (263.19)	pale pink powder	20.87 (19.90)	79.13 (79.41)	
$FeZ.2H_2O$ (300.13)	light green crystals	18.61 (18.65)	69.39 (69.19)	12.00 (12.34)
FeZ (264.10)	pale green powder	21.15 (21.00)	78.85 (78.94)	
$CoZ.2H_2O$ (303.21)	red-violet crystals	19.43 (19.30)	68.68 (68.32)	11.89 (12.09)
CoZ (267.19)	violet powder	22.06 (21.97)	77.94 (78.01)	
$NiZ.2H_2O$ (302.99)	green crystals	19.38 (19.48)	68.73 (68.80)	11.89 (11.56)
$CuZ.2H_2O$ (307.83)	green needles	20.62 (20.41)	67.68 (68.09)	11.70 (11.50)[a]
$CrZOH.2H_2O$ (313.29)	grayish-blue powder	16.60 (16.44)	66.47 (67.05)	16.93 (16.51)[a]
$FeZOH.2H_2O$ (317.14)	orange powder	17.59 (17.30)	65.68 (66.01)	16.73 (16.69)[a]

[a] from the difference.

The expressions (9)-(11) follow from (5)-(8) and the equation

$$A = \varepsilon_0[Me] + \varepsilon_1[MeZ] + \varepsilon_2[MeZ_2] \qquad (12)$$

Results

Composition and Stability of Complexes in Solution. The composition of the complexes in solution was determined by the Job method measuring absorbancy at proper wavelength (V^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, and Fe^{3+}) and conductivity (all divalent cations). All isomolar curves showed only one maximum corresponding to the 1:1 ratio. The formation of 1:1 complex only was implied further from the shape of formation curves calculated from pH–titrations of ligand in the presence of metal ions (10:1 to 1:5 metal-to-ligand ratio): the curves demonstrated the systems to be mononuclear and they limited to $\bar{n} = 1$ (with the exception of Ni^{2+} and Cu^{2+} where a little higher $\bar{n}$ was attained). Therefore, the calculation of stability constants was relatively simple, formation of only a small amount of the mixed species $MeHZ^+$ having been taken into account besides the MeZ complex. The $MeHZ^{2+}$ complex is the only one to be considered with tervalent cations, as follows from the Benesi-Hildebrand plots (constructed analogously to the previous paper[1]). The formation of Cr^{III} complex is very slow, the equilibrium being not attained until solutions are heated at 80° for several hours and then allowed to stand overnight.

The stability constants and the dissociation constants of the ligand (calculated from its titration curve) are summarized in Table I.

Preparation of Compounds. Sodium salts, NaHZ and Na_2Z, were obtained by the neutralization of a H_2Z suspension with the equivalent amounts of $NaHCO_3$ followed by crystallization.

The complexes of general composition $Me^{II}Z.nH_2O$ (n=2 or 0) were obtained as slightly soluble solids from the equimolar amounts of $MeSO_4$ and Na_2Z solutions. According to experimental conditions, iron and cobalt complexes were obtained either as well developed crystals of dihydrate (by a slow crystallization from 0.02 *M* solutions) or as microcrystalline anhydrous complexes (by mixing 0.2 *M*

Table III. Electronic spectra of H_2Z, its salts, and complexes.

Compound	Wavenumbers of maxima (ε_M) Solution	Solid reflectance	Assignment
H_2Z	52,100(6400)		CT
	41,700(440)	39,200	CT
Na_2Z	52,100(6000)		CT
NaHZ	52,000(6200)		CT
$VZ(H_2O)_2$	12,000(2.0)		$^4T_{2g}\leftarrow{}^4A_{2g}$
	17,900(4.5)		$^4T_{1g}(F)\leftarrow{}^4A_{2g}$
	27,700(10)sh		$^4T_{1g}(P)\leftarrow{}^4A_{2g}$
$CrZ.2.5H_2O(I)$	*a*	19,600	
$CrZ.2.5H_2O(II)$	*a*	13,300	$^5T_{2g}\leftarrow{}^5E_g$
		16,700sh [b]	
		35,700	CT
$FeZ(H_2O)_2$	11,000(4.1)	10,700	$^5E_g\leftarrow{}^5T_{2g}$
	c	38,200	CT
FeZ		10,600	$^5E_g\leftarrow{}^5T_{2g}$
		37,900	CT
$CoZ(H_2O)_2$	8,850(3.4)	*d*	$^4T_{2g}\leftarrow{}^4T_{1g}(F)$
	17,100(7.3)	16,700	$^4A_{2g}\leftarrow{}^4T_{1g}(F)$
	20,200(14.1)	19,700	$^2P,{}^2G,{}^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$
	c	36,400	CT
CoZ		16,200	$^4A_{2g}\leftarrow{}^4T_{1g}(F)$
		19,300	$^2P,{}^2G,{}^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$
		36,100	CT
$NiZ(H_2O)_2$	9,450(14.3)	*d*	$^3T_{2g}\leftarrow{}^3A_{2g}$
	15,100(8.9)	14,700	$^3T_{1g}(F)\leftarrow{}^3A_{2g}$
	25,300(19.1)	25,000	$^3T_{1g}(P)\leftarrow{}^3A_{2g}$
	38,400(6300)	37,100	CT
NiZ_2^{2-}	9,700(19.4)		$^3T_{2g}\leftarrow{}^3A_{2g}$
	15,900(12.9)		$^3T_{1g}(F)\leftarrow{}^3A_{2g}$
	26,300(34)		$^3T_{1g}(P)\leftarrow{}^3A_{2g}$
	34,700(4900)		CT
$CuZ(H_2O)_2$	12,500(74)	13,000	$^2T_{2g}\leftarrow{}^2E_g$
	30,800(2800)	29,400	CT
	37,300(4200)	38,500	CT
CuZ_2^{2-}	14,200(79)		$^2T_{2g}\leftarrow{}^2E_g$
	29,400(1800)		CT
	40,000(3400)		CT
$CrZOH.2H_2O$	17,000(28.0) [e]	17,300	$^4T_{2g}\leftarrow{}^4A_{2g}$
	23,200(29.5)	24,400	$^4T_{1g}(F)\leftarrow{}^4A_{2g}$
	c	36,800	CT
$FeZOH.2H_2O$	30,000(71)sh [e]		CT
	41,600(3200)	37,000	CT

[a] insufficient solubility; [b] centre of gravity at 14,600 cm^{-1}; [c] overlapped by a ligand CT band; [d] outside the apparatus range; [e] $MeHZ^{2+}$ complex.

Table IV. Interplanar distances and relative intensities of powder diagram lines. The compounds not entered here are amorphous.

H_2Z		Na_2Z		NaHZ		CrZ. $2.5H_2O$ (II)		MnZ		FeZ		CoZ		NiZ		FeZ. $2H_2O$		CoZ. $2H_2O$		NiZ. $2H_2O$		CuZ. $2H_2O$	
d,Å	I	d,Å	I	d,Å	I	d,Å	I	d,Å	I	d,Å	I	d,Å	I	d,Å	I	d,Å	I	d,Å	I	d,Å	I	d,Å	I
5.00	2	5.09	2	4.72	4	7.89	2	8.10	2	8.34	3	8.34	2	8.18	3	8.26	2	8.18	2	8.18	2	7.69	4
4.33	4	4.92	2	4.31	2	5.68	2			6.19	1	6.10	1	6.23	1	6.06	2	6.19	2	6.06	2	5.71	4
3.57	2	4.24	4	3.67	3	4.82	4	4.77	4	4.72	4	4.72	4	4.76	4	5.79	4	5.82	4	5.79	4	4.77	3
3.35	3	3.40	3	3.49	1	3.81	1	4.15	2	4.17	2	4.17	2	4.18	2	5.24	1	5.24	1	5.24	1	4.33	1
3.17	2	3.16	1	3.31	2	3.54	2			3.72	1	3.75	1			5.03	2	5.03	2	5.03	3	3.86	2
3.02	1	2.98	3	2.89	3	3.31	2	3.59	2	3.56	2	3.57	2	3.52	2	4.05	3	4.05	3	4.07	2	3.48	1
2.92	1	2.85	1	2.68	2	3.11	3	3.12	3	3.11	3	3.09	3	3.06	3	3.59	2	3.56	2	3.54	2	3.07	2
2.70	3	2.70	1	2.57	2	2.95	2	2.70	2	2.69	2	2.68	2							3.35	1	2.90	1
2.43	3	2.52	3	2.46	3	2.75	3	2.58	1							3.18	2	3.17	2	3.17	2	2.51	2
2.31	2	2.25	1	2.36	1	2.51	1	2.40	2	2.38	2	2.41	1					3.04	1			2.14	2
2.15	2	2.15	2	2.23	1	2.45	1					2.37	2	2.35	2	2.92	2	2.92	2	2.89	2	1.94	1
2.01	1	2.09	2	2.14	1	2.31	2	2.30	1	2.31	1							2.70	1			1.74	1
1.92	2	1.96	2	2.04	1	2.15	1	2.06	2	2.06	1			2.05	1	2.53	1	2.51	2	2.52	2		
1.84	2	1.81	2	1.96	1	2.06	2			2.00	2					2.34	2						
1.66	2	1.72	1	1.90	2	1.98	1			1.92	1	2.00	1	1.97	1	2.31	2	2.31	2	2.32	1		
1.56	1	1.61	2	1.79	1	1.93	2	1.81	1	1.78	2	1.76	1	1.76	1					2.29	1		
1.50	1	1.39	1	1.71	1	1.85	1	1.63	1	1.61	1	1.59	1	1.59	2	2.18	1	2.17	1	2.15	1		
1.45	1	1.29	1	1.61	2	1.79	2			1.46	1					2.09	1	2.09	1	2.06	1		
		1.24	1	1.31	1	1.69	1									2.00	2	2.00	2	1.97	2		
						1.62	2													1.91	1		
						1.56	1									1.81	1			1.80	1		
						1.50	1									1.72	2	1.72	1	1.71	2		
						1.42	1									1.62	1	1.61	1	1.61	1		
						1.37	1													1.43	1		
						1.32	1													1.33	1		
						1.22	1																

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.	Soly. product (I=0.1)	Solubility, —log(molar concentration), in water (I=2.0)	Na$_2$Z solutions (I=2.0) 0.01*M*	0.03*M*	0.06*M*	0.10*M*	0.30*M*	0.60*M*
H_2Z	-1.2×10^{-4} [a]		3.970 [b]						
Na_2Z	-1.4×10^{-4} [a]		58.22 [b]						
NaHZ	-1.1×10^{-4} [a]		62.30 [b]						
$CrZ.2.5H_2O$(I)	2.76 (298 K) 2.10 (196 K) 1.04 (77 K)								
$CrZ.2.5H_2O$(II)	4.87	7.67×10^{-7}	3.22	3.38	3.50	3.74	3.71	3.69	3.39
MnZ	5.92	3.80×10^{-4}	1.85	1.99	2.21	2.42	2.48	2.60	2.52
$FeZ.2H_2O$	5.11								
FeZ	5.34	1.82×10^{-6}	2.89	3.22	3.31	3.30	3.30	3.18	3.07
$CoZ.2H_2O$	4.79								
CoZ	4.88	6.64×10^{-7}	2.50	2.80	2.82	2.79	2.78	2.67	2.64
$NiZ.2H_2O$	3.16	4.62×10^{-7}	1.74	1.71	1.64	1.54	1.45	1.25	1.21
$CuZ.2H_2O$	2.19	5.92×10^{-9}	2.12	2.15	2.16	2.09	2.07	2.03	2.00
$CrZOH.2H_2O$	3.85		6.55 [c]						
$FeZOH.2H_2O$	3.24		5.96 [c]						

[a] molar susceptibility; [b] grams per 100 gr. of solution; [c] I = 0.1

solutions of reactants). These dihydrates tend to an irreversible dehydration even in contact with water. Identical anhydrous iron, cobalt, and, in addition, nickel complexes can be prepared by thermal dehydration (see below). The attempted preparation of a vanadous complex was unsuccessful owing to its high solubility and extreme tendency towards oxidation.

The chromous complex represents a special type of compound, isolated in two isomeric forms: (I), a red precipitate resulting from 0.1 *M* solutions of $CrSO_4$ and Na_2Z, isolable if handled quickly, and (II), a sky-blue crystalline material formed from the red isomer in contact with its mother solution during several hours. This second isomer is much more stable towards aerial oxidation than the first one. Both compounds possess the same composition, $CrZ\,.\,2.5H_2O$.

The tervalent metal complexes, $CrZOH\,.\,2H_2O$ and $FeZOH\,.\,2H_2O$, were prepared by mixing equimolar amounts of metal nitrate and Na_2Z in buffered solutions (pH=3). Both compounds precipitate almost completely, chromium(III) complex but only after heating to 90°.

All compounds prepared were isolated by suction, washed with water, ethanol, and ether, and dried at room temperature. Their composition, appearance,

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

Compound	ν(C-S)	ν_s(COO)	ν_a(COO)	$\delta(H_2O)$	ν(OH)
H_2Z	728s	1401s	1685vs 1720vs		3040s,vb
D_2Z[a]	729s	1398vs	1685vs 1720vs		2310s,b
Na_2Z	729s	1415vs	1590vs		
NaHZ	729s	1391vs	1635m 1737s		
$CrZ.2.5H_2O(I)$	729m	1433vs	1557vs	1635w	3410s,b
$CrZ.2.5H_2O(II)$	709s	1376vs	1585vs	1641sh	3070vs 3300s
MnZ	676s	1395vs	1588vs		
$FeZ.2H_2O$	686s	1380vs 1398vs	1582vs	1678w	3190vs,b
FeZ	686s	1392vs	1585vs		
$CoZ.2H_2O$	703s	1382vs 1400vs	1587vs	1691m	3140vs,b
CoZ	686s	1398vs	1590vs	1700s	3120vs,b
$NiZ.2H_2O$	712vs	1386vs 1399vs	1590vs		
$CuZ.2H_2O$	712s	1380vs 1406sh	1602vs	1671sh	3390vs,b
$CrZOH.2H_2O$	719m	1406sh 1432vs	1570vs	1688vw	3410vs,b
$FeZOH.2H_2O$	705m	1400sh 1439vs	1610vs	1689sh	3430s,b

[a] H_2Z recrystallized repeatedly from D_2O

Table VII. Thermal decomposition of the compounds prepared.

Compound	Dehydration			Decomposition of Z			Other processes		
	°C	DTA-effect	Product	°C	DTA-effect	Product	°C	DTA-effect	Product
H_2Z				320	endo		112	endo	melt
Na_2Z				340	endo				
				395	exo	$Na_2SO_4+Na_2CO_3$			
NaHZ				280	endo		170	endo	melt
				320	endo	$Na_2SO_4+Na_2CO_3$			
$CrZ.2.5H_2O(I)$	100	endo	$CrZ.H_2O$	190	endo	Cr oxide+sulphate	550	endo	Cr_2O_3
$CrZ.2.5H_2O(II)$	100	endo	$CrZ.2H_2O$	240	endo	Cr oxide+sulphate	560	endo	Cr_2O_3
	150	endo	CrZ						
MnZ				330	exo		790	endo	Mn_3O_4
				370	endo	$MnSO_4+Mn_3O_4$			
$FeZ.2H_2O$	150	endo	FeZ	300	endo		560	endo	Fe_2O_3
				410	exo	Fe oxide+sulphate			
FeZ				280	exo		570	endo	Fe_2O_3
				420	exo	Fe oxide+sulphate			
$CoZ.2H_2O$	165	endo	CoZ	335	exo		800	endo	Co_3O_4
				385	endo	$CoSO_4+Co_3O_4$	880	endo	CoO
				450	exo				
CoZ				350	exo		800	endo	Co_3O_4
				385	endo	$CoSO_4+Co_3O_4$	870	endo	CoO
				460	exo				
$NiZ.2H_2O$	170	endo	NiZ	290	exo		730	endo	NiO
				350	exo	$NiSO_4+NiO$			
				450	exo				
$CuZ.2H_2O$	160	endo . . . followed by	. . . .	180	exo	Cu,Cu^I,Cu^{II}	730	endo	CuO
				320	exo	oxide+sulphate			
$CrZOH.2H_2O$	30-160	endo	CrZOH	325	exo		570	endo	Cr_2O_3
				440	exo	Cr oxide+sulphate			
$FeZOH.2H_2O$	40-140	endo	FeZOH	260	exo		550	endo	Fe_2O_3
				350	exo	Fe oxide+sulphate			

and analytical data are given in Table II.

Properties of the compounds prepared. The following properties are summarized in Tables III-VII: electronic spectra (Table III), powder diagrams (Table IV), magnetic and solubility data (Table V), selected bands of IR spectra (Table VI), and thermal decomposition data (Table VII). The assignment of electronic and IR spectral bands was carried out as in the previous papers.[1,2] The spectra of mixed complexes $MeHZ^+$ could not be measured with any reasonable accuracy since these complexes amount just to a minor part of solutions.

Discussion

The character of bonding in the ethylenedithiodi-

Table VIII. Crystal field parameters of $MeZ(H_2O)_2$ complexes.

Me	Dq, cm^{-1}	B, cm^{-1}	f	β
V^{2+}	1200	588	1.03	0.77
Cr^{2+}	1460		1.03	
Fe^{2+}	1100		1.10	
Co^{2+}	960	829	1.03	0.74
Ni^{2+}	945	822	1.06	0.76
Cu^{2+}	1250		1.04	
Cr^{3+}	1700	620	1.00	0.60

acetate complexes is, to a great extent, similar to that of thiodiacetate complexes studied previously. The trend of stability constants (see Figure 1) is also analogous and consistent with the Irving-Williams series. However, as regards a certain affinity of Ni^{2+} and Cu^{2+} towards sulphur, the relative stability of nickel and copper complexes is raised even more distinctly. A number of additional arguments support the existence of sulphur-metal bonds, mainly: a general enhancement of stability constants comparing with those of α,ω—dicarboxylic acid complexes,[13] the presence of extra UV bands attributable to a charge transfer by means of this bond, and the distinct shift of the C–S stretching mode of the complexes to lower wavenumbers in comparison with the free ligand. As to the rest, the coordination of sulphur was confirmed by a X-ray single crystal structure determination of NiZ . $2H_2O$, the preliminary results of which[14] showed both the Ni–S distances to be near to 2.46 Å.

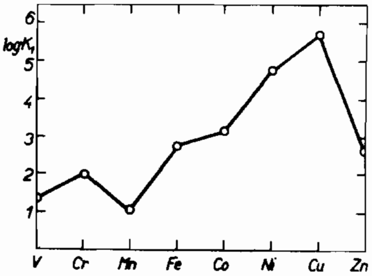
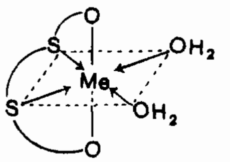


Figure 1. Trend of stability constants of 1:1 ethylenedithiodiacetate complexes in the first transition row. The value of Zn^{2+} was taken from reference 9.

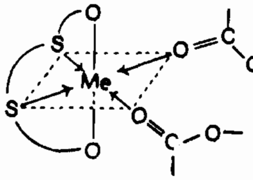
To summarize, the ethylenedithiodiacetate anion can be assumed to act as a tetradentate ligand. The absolute stability of its first transition row metal complexes, is, however, relatively low as a consequence of a limited affinity of these metals towards sulphur.

The electronic absorption and diffuse reflectance spectra are essentially identical, thus demonstrating the coincidence of a molecular structure in solid state and in solution. These spectra can be interpreted in terms of metal ions surrounded by a weak crystal field of octahedral microsymmetry. The values of magnetic moments support this conception. The electronic spectra were fitted to the Tanabe-Sugano diagrams[15] to obtain Dq, B and β crystal field parameters summarized in Table VIII. From the data of this table, the empirical parameter f was calculated[16]. According to the average value f = 1.04 the Z^{2-} anion can be placed close to 6 NCS and between water and EDTA in the spectrochemical series.

In accordance with all the results, as well as with the preliminary X-ray structure determination, the molecular structure of the MeZ.$2H_2O$ complexes can be presented as follows:

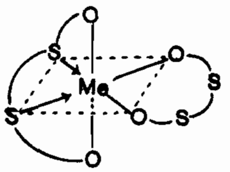


The isomorphous complexes NiZ.$2H_2O$, CoZ.$2H_2O$ and FeZ.$2H_2O$ posses this structure evidently. According to a spectral evidence[17], the complex CuZ . $2H_2O$ exhibits also six coordination. The second isomorphous set includes the anhydrous complexes MnZ, FeZ, CoZ, and NiZ. Since the spectral and magnetic data indicate that these complexes are octahedral, their coordination polyhedron must be completed by some intermolecular interaction, probably through free carboxyl oxygens, *e. g.*



Such a polymerization may well be responsible for the irreversibility of dehydration.

As regards 1:2 complexes, the second ligand is bound probably only through carboxyl oxygens as the stability of 1:2 complexes is very low.



---

(13) Sillen L.G. and Martell A.E., Stability Constants, *Chem. Soc. Spec. Publ.* No. 17, London 1964.

(14) Loub J. and Podlahová J., *Inorg. Nucl. Chem. Lett.*, *7*, 409 (1971).

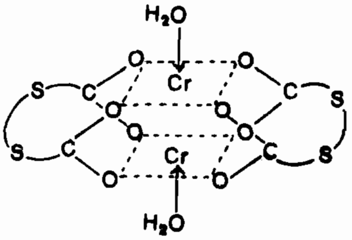
(15) Figgis B.N., Introduction to Ligand Fields. Interscience Publ., N.Y. 1966.

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

(17) Lever A.B.P., Inorganic Electronic Spectroscopy. Elsevier, Amsterdam 1968.

As in the case of thiodiacetate complexes, chromium(III) and iron(III) complexes of ethylenedithiodiacetic acid seem also be high polymers linked through bridging OH groups.

The two forms of the chromous complex represent an interesting example of magnetic isomerism. The blue form (II) is a magnetically normal high spin complex possessing evidently a structure analogous to the dihydrate type with coordinated sulphur. On the other hand, the red form (I) is antiferromagnetic, shows no bands responsible for a S-Cr bond both in UV and IR spectra, and its colour is reminiscent of that of chromous acetate. The structure of this red form can be viewed as a dimer containing non-coordinated sulphur, and a direct Cr-Cr bond:



The dehydration of both forms is in accordance with the structures proposed. In this respect, ethylenedithiodiacetic acid is an interesting ligand, both forms of its chromous complex being stable in solid state.