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Metal Complexes of Thiopolycarboxylic Acids. V. Ethyliednetetrathiotetraacetic Acid

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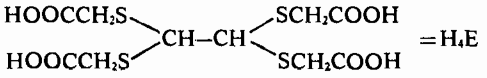
The title compound forms weak 1:1 and 2:1 (metal-to-ligand) complexes with bivalent transition metal ions from Mn to Cu. Both types were studied in solution and in solid state, and from the properties of the complexes conclusions were drawn regarding their molecular structure.

Introduction

Ethylidenetetrathiotetraacetic acid,



$$\begin{matrix} HOOCCH_2S \\ HOOCCH_2S \end{matrix} \!\!>\! CH{-}CH \!<\!\! \begin{matrix} SCH_2COOH \\ SCH_2COOH \end{matrix} = H_4E$$

was described first by Ritter and Lower.[1] Its coordination properties towards metals were studied by several authors,[2,3] and solid complexes, $M_2E.nH_2O$ (M = Co, Ni and Cu), were isolated.[4,5] As a continuation of the previous papers of this series,[6-9] a systematic examination of this potentially octadentate ligand and its transition metal complexes was undertaken in this work.

Experimental Part

Materials

The ligand, H_4E, was synthesized according to Longo *et al.*[3] It formed white crystals of m.p. 201-202° (lit.,[1,2,4] 189-204°). Other materials were prepared as described previously.[6,7]

Apparatus and Methods

These were described in the previous papers.[6-8]

Analytical

Since the bromate-bromide method used previously[7] was found to give unsatisfactory results with H_4E, a method was developed based on an oxidation of the ligand by an excess of permanganate in $3N{-}H_2SO_4$. After stirring for 20 min. at room temperature, the excess of permanganate was back-titrated. An empirical ratio of 29.3 equivalents of permanganate per mole of H_4E is reproducible accurately at these conditions. The purity of H_4E was further controlled by an elementer microanalysis and an alcalimetric equivalent weight determination. Metals were determined by standard volumetric and/or gravimetric procedures.

Calculations

The following acid dissociation and stability constants were calculated:

$$K_1^H = \frac{[H].[H_3E]}{[H_4E]} \qquad K_2^H = \frac{[H].[H_2E]}{[H_3E]}$$

$$K_3^H = \frac{[H].[HE]}{[H_2E]} \qquad K_4^H = \frac{[H].[E]}{[HE]} \qquad K_1 = \frac{[ME]}{[M].[E]}$$

(charges are omitted)

A computerized[10] Bjerrum's method based on pH—titrations was used to determine K_i^H. The stability constant K_1 was found as an intercept of a straight line calculated from a formation curve.[11] The pH—titration data corresponding to the presence of metal ions were treated by a computer to calculate formation curves.[10]

From the constants obtained, the formation curves can be back—calculated perfectly.

Results

Composition and Stability of Complexes in Solution

Apparent changes of absorption spectra of metal ions caused by the presence of the ligand (pH = 6—7) made it possible to choose wavelengths suitable to a determination of the composition of complex by the Job metod. The results, summarized in Figure 1, clearly show the formation of only 1:1 complex with

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[1] Ritter J.J., Lower M.J., *J. Am. Chem. Soc.*, *74*, 5576 (1952).
[2] Saini G., Ostacoli G., Campi E., and Cibrario N., *Gazz. Chim. Ital.*, *91*, 904 (1961).
[3] Longo F.R., Ventresca A., Drach J.E., McBride J., and Sauers R.F., *Chem. Analyst*, *54*, 101 (1965).
[4] Geary W.J. and Malcolm D.E., *J. Chem. Soc.*, (A), 798 (1970).
[5] Ouchi A., Ohashi Y., Takeuchi T., and Yoshino Y.: *Bull. Chem. Soc. Japan*, *43*, 1088 (1970).
[6] Podlaha J. and Podlahová J., *Inorg. Chim. Acta*, *4*, 521 (1970).
[7] Podlaha J. and Podlahová J., *Inorg. Chim. Acta*, *4*, 549 (1970).
[8] Podlaha J. and Podlahová J., *Inorg. Chim. Acta*, *5*, 413 (1971).
[9] Podlaha J. and Podlahová J., *Inorg. Chim. Acta*, *5*, 420 (1971).
[10] Romary J.K. Donelly D. L., and Andrews A.C., *J. Inorg. Nucl. Chem.*, *29*, 1805 (1967).
[11] Rossotti F.J.C. and Rossotti H., The Determination of Stability Constants. Mc-Graw-Hill, New York 1961.

the exception of Fe^{2+}, where, on the contrary, only 2:1 complex demonstrates itself on the curve.

The dissociation constants of the ligand and the stability constants of the 1:1 metal complexes are presented in Table I. A shift of formation curves with an increasing metal–to–ligand ratio was invariantly observed indicating the systems to be polynuclear regarding a metal. Therefore, the stability constants were calculated from formation curves related to the two–fold excess of the ligand, where perfectly linear fits for K_1 were obtained confirming that only 1:1 complex is formed under these conditions (see Figure 2). However, none of the numerous binuclear (protonised) complexes of the M_2E and/or MH_nE type taken tentatively into account gave any reliable set of stability constants from the other formation curves, probaly because of an extreme sensitivity of the systems to experimental errors. No 2:1 stability constants are therefore presented.

Table I. The dissociation constants of H_4E and the stability constants of its 1 : 1 complexes at 25° and I = 0.1.

$pK_1^H = 2.80 \pm 0.10$	$\log K_{MnE} = 1$
$pK_2^H = 3.50 \pm 0.09$	$\log K_{FeE} = 1.9 \pm 0.1$
$pK_3^H = 3.87 \pm 0.09$	$\log K_{CoE} = 2.2 \pm 0.1$
$pK_4^H = 4.54 \pm 0.07$	$\log K_{NiE} = 4.02 \pm 0.04$
	$\log K_{CuE} = 5.29 \pm 0.04$

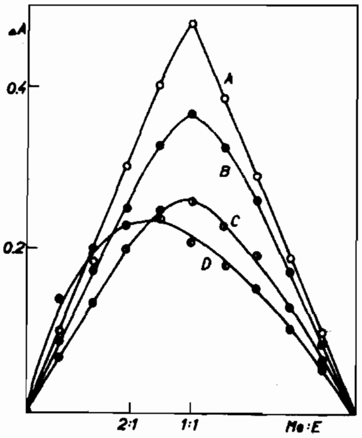

Figure 1. The Job plots in the systems M^{2+}—E^{4-} at pH=6: A: Cu^{2+}, 327 nm, 0.0005 *M*; B: Ni^{2+}, 270 nm, 0.0005 *M*; C: Co^{2+}, 610 nm, 0.05 *M*; D: Fe^{2+}, 850 nm, 0.08 *M*.

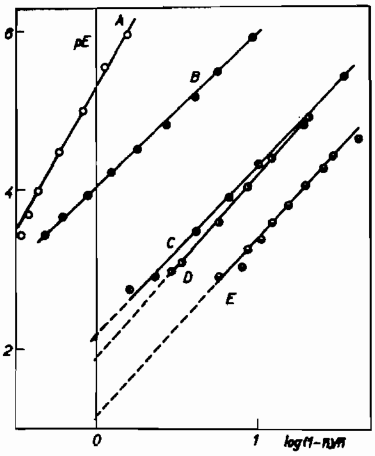

Figure 2. The graphical determination of pK_1: A: Cu^{2+}, B: Ni^{2+}, C: Co^{2+}, D: Fe^{2+}, E: Mn^{2+}.

Preparative Part

In a number of cases a careful adjustment of experimental conditions (see Table II) was found essential in order to obtain pure compounds.

Sodium salts were obtained by a neutralisation of H_4E with $NaHCO_3$ followed by a crystallization.

The complexes $MH_2E \cdot nH_2O$ were prepared by slow crystallization of solutions containing equivalent amounts of the disodium salt and metal perchlorate. The nickel complex required somewhat modified conditions in order to prevent the formation of Ni_2E and H_4E.

The $M_2E \cdot nH_2O$ complexes were obtained mostly as precipitates by mixing Na_4E and metal perchlorate solutions in the appropriate ratio.

The preparation and the handling of the ferrous complexes were carried out under nitrogen.

All the compounds were isolated by suction, washed with a proper solvent (see Table II) and dried at room temperature.

Properties of the Compounds

The following properties are summarized in Tables II-VII: composition, appearance, the conditions of the preparation (Table II), analytical, magnetic and solubility data (Table III), electronic spectra (Table IV), powder diagrams data (Table V), i.r. spectra (Table VI) and thermal decomposition data (Table VII).

Discussion

In solution, H_4E behaves as a tetrabasic acid. Its acid dissociation constants as determined in the present work are substantially identical with those of Geary and Malcolm,[4] but different from those of Longo *et al.*[3] and Munoz *et al.*[12]. As in similar cases, such a set of close equilibrium constants represent a system which can be treated reliably only by a computer, being still critically dependent on experimental errors. This reflects on relatively high standard deviations of the constants. The absolute magnitude of the dissociation constants responce well to a dissociation of the carboxylic protons. In solid state, however, distinct evidence for a hydrogen bond between carboxyl and sulphur was obvious as the i.r. S–H stretching band which is isotopically shifted on deuteration.

The ligand forms 1:1 complexes with transitions metal ions in solution. The trend of stability constants is consistent with Irving-Williams series, and the values of nickel and copper complexes agree approximately with those obtained by other authors[2,4] taking into account somewhat different experimental conditions. In addition, some evidence supporting

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(12) Munoz O.S. and Weinert S.O., *Rev. Real Acad. Cienc. Exactas, Fis. Natur. Madrid, 61,* 573 (1967). cf. *C.A., 69,* 90437 z (1968).

Table II. The conditions of the preparation and the appearance of the compounds.

Compound Appearance	Starting materials (moles) [a] A	 B	ml of H_2O A+B °C	ml of non-aqueous solvent	crystal-lization	yield %
$Na_2H_2E . 2H_2O$	H_4E	$NaHCO_3$	250+0	250	+5°	75
white crystals	0.05	0.1	80°	EtOH	5 days	
$Na_4E . 2H_2O$	H_4E	$NaHCO_3$	75+0	150	25°	65
white powder	0.05	0.2	80°	MeOH	24 hours	
$H_2MnE . 6H_2O$	Na_2H_2E	$Mn(ClO_4)_2$	240+10	—	25°	75
pale pink n.	0.025	0.025	25°		24 hours	
$H_2FeE . 6H_2O$	$Fe(ClO_4)_2$	Na_2H_2E	100+100	150	+5°	65
pale yellow c.	0.025	0.025	25°	EtOH	24 hours	
$H_2CoE . 6H_2O$	Na_2H_2E	$Co(ClO_4)_2$	50+10	—	25°	80
pink needles	0.025	0.025	40°		24 hours	
$H_2NiE . 6H_2O$	NaH_3E	$Ni(ClO_4)_2$	50+10	60	+5°	35
pale green c.	0.040	0.025	80°	acetone	75 min.	
$H_2CuE . 2H_2O$	Na_2H_2E	$Cu(ClO_4)_2$	25+10	—	25°	50
grass green p.	0.025	0.025	30°		2 days	
$Mn_2E . 12H_2O$	Na_4E	$Mn(ClO_4)_2$	50+20	—	+5°	60
pale pink c.	0.025	0.050	40°		3 days	
$Fe_2E . 2H_2O$	$Fe(ClO_4)_2$	Na_4E	100+60	120	precipitate	45
pale ocre p.	0.090	0.033	25°	EtOH		
		$+2gNH_4ac$				
$Co_2E . 8H_2O$	$Co(ClO_4)_2$	Na_4E [b]	10+24	—	»	85
pink powder	0.075	0.025	100°			
$Ni_2E . 8H_2O$	$Ni(ClO_4)_2$	Na_4E	10+30	—	»	40
pale green p.	0.055	0.025	50°			
$Cu_2E . 5H_2O$	$Cu(ClO_4)_2$	Na_4E	30+30	—	»	75
grass green p.	0.050	0.025	25°			
$Cu_2E . 8H_2O$	obtained by a recrystallization		of the pentahydrate		25°	95
blue powder					14 days	

Appearance: n. = needles, c. = crystals, p. = powder. [a] B added to A; [b] at pH=11.

Table III. The analytical, magnetic and solubility data of the compounds prepared.

Compound m.v.	H,% calcd. (found)	metal,% calcd. (found)	E,% calcd. (found)	H_2O,% calcd. (found)	$\mu_{eff.}$,B.M. at 20°	Solubility g/100g of water at 25°
H_4E	1.032	—	98.97	—	-268.10^{-6} [a]	0.081
390.46	(1.03)		(98.7)			
$Na_2H_2E . 2H_3O$	0.426	9.77	82.14	7.66	-278.10^{-6} [a]	[b]
470.47	(0.43)	(9.78)	(82.3)	(8.07)		
$Na_4E . 2H_2O$	—	17.88	75.12	7.00	-260.10^{-6} [a]	58.3
514.43		(18.22)	(75.8)	(6.96)		
$H_2MnE . 6H_2O$	0.366	9.96	70.06	19.61	5.96	0.93
551.57	(0.36)	(9.81)	(70.2)	(19.1)		
$H_2FeE . 6H_2O$	0.365	10.11	69.94	19.58	5.33	1.38
552.48	(0.37)	(10.55)	(69.2)	(18.5)		
$H_2CoE . 6H_2O$	0.363	10.61	69.56	19.47	5.00	0.40
555.56	(0.37)	(10.18)	(68.9)	(19.6)		
$H_2NiE . 6H_2O$	0.363	10.57	69.58	19.48	3.30	0.76
555.34	(0.37)	(10.11)	(69.4)	(19.5)		
$H_2CuE . 2H_2O$	0.413	13.02	79.18	7.38	1.73 (298°K)	[d]
488.03	(0.42)	(12.24)	(79.6)	(7.7) [c]	1.48 (77°K)	
$Mn_2E . 12H_2O$	—	15.42	54.23	30.35	5.87	12.3
712.55		(15.01)	(53.5)	(30.2)		
$Fe_2E . 8H_2O$	—	17.39	60.16	22.44	4.88 (298°K)	25
642.29		(17.44)	(61.0)	(21.6) [c]	4.48 (77°K)	
$Co_2E . 8H_2O$	—	18.18	59.59	22.23	4.75	3.14
648.45		(18.73)	(59.5)	(21.6)		
$Ni_2E . 8H_2O$	—	18.12	59.63	22.25	3.28	14.0
648.01		(17.17)	(59.5)	(21.6)		
$Cu_2E . 5H_2O$	—	21.05	64.02	14.93	1.80	[e]
603.61		(20.4)	(64.0)	(15.6) [c]		
$Cu_2E . 8H_2O$	—	19.32	58.76	21.93	1.70	0.13
657.67		(19.9)	(58.0)	(22.1) [c]		

[a] molar susceptibility; [b] disproportionation: $2Na_2H_2E \leftrightarrows H_4E+Na_4E$; [c] from the difference; [d] reduction of Cu^{II}; [e] conversion to octohydrate.

a formation of 2:1 complexes in solution was obtained, but their stability constants could not be calculated from experimental data with certainty.

Both types of complexes were studied in solid state. In addition to the previously known 2:1 complexes, the analogous manganous and ferrous com-

Table IV. The electronic spectra of the compounds studied.

Compound	Solution cm⁻¹	(log ε)	Attribution	Compound	Solid (diffuse reflectance) cm⁻¹	Compound	cm⁻¹
H_4E	33,900	(1.0)	CT (ligand)	H_4E	34,500		
	45,500	(3.46)	»		40,000		
Na_2H_2E	33,900	(1.0)	CT (ligand)	$Na_2H_2E . 2H_2O$	34,500		
	45,500	(3.46)	»		40,000		
Na_4E	33,900	(1.0)	CT (ligand)	$Na_4E . 2H_2O$	34,500		
	45,500	(3.46)	»		40,000		
MnE^{2-}	33,900	(1.0)	CT (Mn←S)	$H_2MnE . 6H_2O$	32,300	$Mn_2E . 12H_2O$	33,300
	45,500	(3.46)	CT (ligand)		44,400		44,400
FeE^{2-}	11,000	(0.47)	$^5E_g \leftarrow {}^5T_{2g}$	$H_2FeE . 6H_2O$	10,200	$Fe_2E . 8H_2O$	10,400
	34,500	(1.90)	CT (Fe←S)		31,000		31,000
	45,500	(3.43)	CT (ligand)		38,500		38,500
CoE^{2-}	8,700	(0.64)	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	$H_2CoE . 6H_2O$	10,000	$Co_2E . 8H_2O$	10,000
	17,200	(0.80)	$^4A_{2g} \leftarrow {}^4T_{1g}$		15,600		15,600
	20,000	(1.09)	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$		19,000		19,000
	35,100	(2.08)	CT (Co←S)		33,300		38,500
	45,500	(3.47)	CT (ligand)		43,500		41,700
NiE^{2-}	9,400	(1.36)	$^3T_{2g} \leftarrow {}^3A_{2g}$	$H_2NiE . 6H_2O$	10,000	$Ni_2E . 8H_2O$	10,000
	15,300	(0.92)	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$		14,900		15,100
	25,300	(1.30)	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$		25,000		25,000
	37,000	(2.98)	CT (Ni←S)		37,000		37,000
	45.500	(3.49)	CT (ligand)		45,400		45,400
CuE^{2-}	12,700	(1.78)	$^2T_{2g} \leftarrow {}^2E_g$	$H_2CuE . 2H_2O$	13,300	$Cu_2E . 5H_2O$	13,000
	30,300	(3.01)	CT (Cu←S)		25,600		29,000
	37,000	(3.22)	CT (Cu←S)		37,700		37,000
	45,500	(3.49)	CT (ligand)		43,500		45,400
			$^2T_{2g} \leftarrow {}^2E_g$			$Cu_2E . 8H_2O$	12,800
			CT (Cu←S)				35,700
			CT (Cu←S)				38,500
			CT (ligand)				45,400

Table V. The interplanar distances and the relative intensities of the powder diagram lines.

H_4E		$Na_2H_2E . 2H_2O$		$Na_4E . 2H_2O$		Na_4E		$H_2MnE . 6H_2O$		$H_2FeE . 6H_2O$		$H_2CoE . 6H_2O$		$H_2NiE . 6H_2O$		$Mn_2E . 12H_2O$		$Cu_2E . 8H_2O$		Mn_2E	
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
6.80	1	6.06	1	5.99	2	6.14	2	8.04	3	7.37	1	7.19	3	6.91	4	6.60	1	7.13	3	5.03	1
5.03	2	5.30	1	5.03	1	4.28	2	5.68	2	5.64	1	5.63	1	6.65	1	5.09	3	6.14	3	4.69	2
4.77	2	4.52	1	4.37	2	3.80	4	5.03	1	4.92	3	4.87	1	5.12	2	4.77	4	5.53	1	3.81	2
4.25	2	4.11	2	3.82	4	3.39	1	4.62	3	4.44	1	4.53	2	4.50	4	4.31	2	5.03	2	3.53	1
3.80	4	3.64	2	3.63	4	3.08	3	4.33	1	4.23	1	4.13	2	3.82	2	3.95	3	4.46	3	2.94	2
3.53	1	3.15	4	3.36	2	2.86	2	3.77	2	3.84	2	3.70	2	3.56	2	3.81	1	3.95	1	2.74	2
3.18	4	3.02	1	3.28	1	2.58	3	3.52	1	3.60	2	3.48	1	3.33	1	3.37	1	3.60	4	2.51	1
2.87	1	2.73	1	3.01	3	2.44	2	3.26	4	3.31	4	3.14	4	3.12	2	3.16	3	3.25	1	2.29	1
2.74	4	2.51	3	2.87	3	2.30	1	3.09	1	3.06	1	3.08	1	2.89	3	2.94	3	2.91	2	2.26	1
2.51	3	2.34	1	2.74	1	2.16	1	2.83	2	2.74	3	2.81	2	2.71	2	2.75	2	2.58	2	2.08	1
2.38	2	2.27	2	2.61	3	2.01	1	2.68	2	2.54	2	2.66	2	2.57	1	2.48	1	2.40	3	1.99	1
2.26	2	2.18	1	2.54	3	1.82	1	2.55	1	2.36	2	2.51	1	2.40	3	2.36	2	2.28	1	1.88	1
2.08	1	2.02	2	2.42	3	1.76	1	2.45	2	2.20	2	2.41	1	2.23	2	2.26	1	2.17	1	1.65	1
2.00	1	1.92	1	2.31	1	1.70	1	2.34	2	2.09	1	2.32	1	2.06	2	2.12	3	2.07	2	1.60	1
1.84	1	1.84	1	2.22	2	1.53	1	2.19	2	1.87	2	2.18	2	1.89	2	2.03	1	1.87	1		
1.74	1	1.73	2	2.15	1			2.10	1	1.78	1	2.01	1	1.83	1	1.96	1	1.75	1		
1.67	1	1.64	1	2.02	3			1.99	1	1.64	2	1.86	1	1.77	1	1.83	2	1.62	1		
1.61	1	1.57	1	1.87	1			1.91	1			1.75	1	1.64	2	1.71	1	1.55	1		
		1.52	1	1.81	2			1.85	1			1.63	1	1.58	1	1.62	1	1.41	1		
		1.47	1	1.75	2			1.78	2					1.52	1	1.56	1				
		1.42	1	1.70	1			1.65	1					1.46	1	1.51	1				
		1.36	1	1.62	1			1.61	1					1.38	1	1.42	1				
		1.32	1	1.55	2			1.51	1					1.36	1						
				1.51	1									1.32	1						
				1.44	1																
				1.26	1																

plexes were prepared. A different stage of hydration of our cobalt, nickel and copper complexes as compared with those of Geary and Malcolm[4] and Ouchi *et al.*[5] is caused evidently by different methods of isolation. Moreover, a series of the previously unknown 1:1 complexes was prepared in the crystalline state.

The electronic spectra of both types of complexes were interpreted in terms of weak octahedral crystal field formalism.[13] The crystal field parameters calculated from the spin–allowed bands are presented in Table VIII. According to the Table, the ligand can be located into the spectrochemical and nephel-

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

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

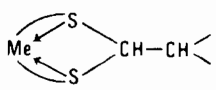
Compound	ν(C–S)	$ν_s$(COO)	$ν_a$(COO)	$ν_s$(COOH)	$ν_a$(COOH)	$ν(H_2O)$	ν(S–H) ν(S–D)	ν(O . . . H) ν(O . . . D)
H_4E	660 s	1380 vs 1410 vs	—	1290 vs	1710 vs		2565 m	3100 vs
D_4E [a]	660 s	1383 s 1395 s	—	1288 s	1712 vs	—	2565 m 2070 w	3100 m 2380 m
$Na_2H_2E . 2H_2O$	670 m	1392 vs	1570 vs	1253 vs	1700 s	3430 s		
$Na_2D_2E . 2D_2O$ [a]	665 vw	1387 vs 1390 vs	1565 vs	1253 vs	1700 s	3425 m		
Na_2H_2E	680 m	1380 m sh	1604 m	1245 m sh	1714 m	—		
$Na_4E . 2H_2O$	685 m	1408 vs	1590 vs 1610 vs	—	—	3430 vs		
Na_4E	685 m	1409 vs	1590 vs	—	—	—		
$H_2MnE . 6H_2O$	695 m	1405 vs	1585 vs 1620 s sh	1252 m	1710 s	3440 vs		
$H_2FeE . 6H_2O$	700 m	1413 vs	1570 vs 1620 s sh	1252 m	1724 s	3450 vs		
$H_2CoE . 6H_2O$	699 m	1405 vs	1570 vs 1620 s sh	1250 m	1712 s	3460 vs		
$H_2NiE . 6H_2O$	698 m	1405 vs	1570 vs 1620 s sh	1250 m	1712 s	3460 vs		
$H_2CuE . 2H_2O$	715 m	1408 vs	1570 vs 1620 s sh	1290 s	1714 s	3440 vs		
H_2MnE	694 m	1404 vs	1585 vs 1620 vs sh	1252 m	1714 m	—		
H_2FeE	705 m	1408 vs	1583 vs 1615 s sh	1292 m	1714 vs	—		
H_2CoE	712 m	1405 vs	1585 vs 1620 vs sh	1290 m	1728 s	—		
H_2NiE	712 m	1404 vs	1585 vs 1630 vs sh	1290 s	1723 s	—		
$Mn_2E . 12H_2O$	719 s	1400 vs	1572 vs 1598 vs sh	—	—	3485 s		
$Fe_2E . 8H_2O$	705 s	1410 vs	1588 vs 1598 s sh	—	—	3440 vs		
$Co_2E . 8H_2O$	708 s	1403 vs	1587 vs 1625 vs sh	—	—	3440 vs		
$Ni_2E . 8H_2O$	712 m	1392 vs	1587 vs 1632 vs sh	—	—	3440 vs		
$Cu_2E . 5H_2O$	717 m	1405 vs	1590 vs 1630 vs sh	—	—	3440 vs		
$Cu_2E . 8H_2O$	713 m	1382 vs	1590 vs 1630 vs sh	—	—	3440 vs		
Mn_3E	705 m	1402 vs	1585 vs 1620 s sh	—	—	—		

[a] after repeated recrystallization from D_2O.

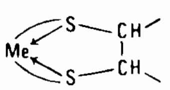
auxetic series at the same place as ethylenedithiodiacetic acid.[8]

The evidence of an octahedral coordination follows further from the magnetic properties and the i.r. spectra of the complexes. In such an arrangement, carboxylic oxygens are coordinated to the metal through a bond which is essentially ionic as follows from the position of $ν_{as}$(COO) band in the i.r. spectra.[14] A coordination of sulphur to the metal reflects on the presence of the extra u.v. charge transfer bands in the electronic spectra, the intensity of which is in an obvious correlation with the stability constants. The further argument for the presence of sulphur–metal bonds is a distinct shift of the C–S streching frequency in the i.r. spectra of the complexes.

One must consider two possible types of the metal–ligand bonding in the complexes which can be presented as follows:



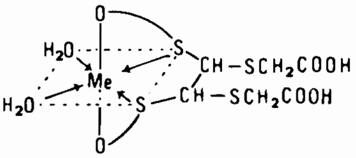
(A)



(B)

The results obtained in this work do not permit to take a decision between these two forms. The form B is, however, evidently more probable because of steric requirements and is supported by the position of the ligand in the spectrochemical series.

The following conception of the molecular structure can be given as corresponding to the properties of the complexes. 1 : 1 *complexes*: the metal ion is bound to one half of the ligand molecule, the second being protonized. The coordination around the metal is completed by two water molecules in *cis*-position (analogously to the nickel-ethylenedithiodiacetate complex[15]), which are not readily lost:



2 : 1 *complexes*: two metal ions exhaust the coordination ability of the ligand by bonding to the both hal-

Table VII. The thermal decomposition of the compounds prepared.

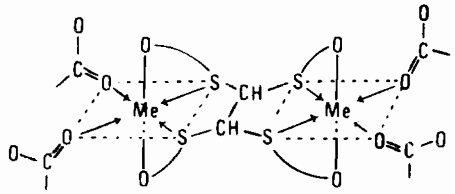
Compound	Dehydration			Decomposition of E		Other processes		
	°C	DTA effect	Product	°C	DTA effect	°C	DTA effect	Product
H_4E				200	*endo*	620	*endo*	
				415	*exo*			
$Na_2H_2E \cdot 2H_2O$	150	*endo*	Na_2H_2E	245	*endo*	580	*exo*	Na_2SO_4
				280	*exo*			
$Na_4E \cdot 2H_2O$	80	*endo*	[a]	270	*endo*	400	*exo*	Na_2SO_4
	210	*endo*	Na_4E	330	*exo*			
$H_2MnE \cdot 6H_2O$	110	*endo*	$H_2MnE \cdot 3H_2O$	320	*endo*	780	*endo*	Mn_3O_4
	185	*endo*	H_2MnE	495	*exo*			
$H_2FeE \cdot 6H_2O$	110		$H_2FeE \cdot 2H_2O$	190	*endo*	680	*endo*	Fe_2O_3
	130	*endo*	H_2FeE	470				
$H_2CoE \cdot 6H_2O$	120		$H_2CoE \cdot 2H_2O$	200	*endo*	800	*endo*	Co_3O_4
	140	*endo*	H_2CoE	480	*exo*	880	*endo*	CoO
$H_2NiE \cdot 6H_2O$	110		$H_2NiE \cdot 2H_2O$	220	*exo*	740	*endo*	NiO
	150	*endo*	H_2NiE	360	*exo*			
$H_2CuE \cdot 2H_2O$	80	*endo*	H_2CuE [b]	140	*exo*	720	*endo*	CuO
				240	*exo*			
$Mn_2E \cdot 12H_2O$	60	*endo*	$Mn_2E \cdot 2H_2O$	240	*exo*	850	*endo*	Mn_3O_4
	110	*endo*	Mn_2E	380	*exo*			
$Fe_2E \cdot 8H_2O$	80	*endo*	Fe_2E [b]	230	*exo*	570	*endo*	Fe_3O_4
				450				
$Co_2E \cdot 8H_2O$	100	*endo*	Co_2E [b]	230	*exo*	800	*endo*	Co_3O_4
				380	*exo*	880	*endo*	CoO
$Ni_2E \cdot 8H_2O$	105	*endo*	Ni_2E [b]	250	*exo*	750	*endo*	NiO
				450	*exo*			
$Cu_2E \cdot 5H_2O$	100	*endo*	Cu_2E [b]	170	*exo*	780	*endo*	CuO
				310	*exo*			
$Cu_2E \cdot 8H_2O$	150	*endo*	Cu_2E [b]	200	*exo*	780	*endo*	CuO
				320	*exo*			

[a] absorbed moisture; [b] the dehydration is not fully completed before the start of the decomposition.

Table VIII. The crystal field parameters of the complexes.

M	D_q, cm^{-1}	B, cm^{-1}	F	β
Fe^{2+}	1,100	—	1.10	—
Co^{2+}	952	830	1.03	0.74
Ni^{2+}	940	840	1.06	0.78
Cu^{2+}	1,270	—	1.06	—
			Average . . . 1.06	

ves of its molecule. The coordination sphere of the metals is completed probably by intermolecular bridges formed through non–bonding carboxyl oxygens, e.g.:



Such polymeric framework may well be responsible for the amorphous character of the precipitates and is further supported by the one–stage dehydration having no effect on the electronic spectra.

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(14) Nakamoto K., Infrared Spectra of Inorganic and Coordination Compounds. Willey and Sons, New York 1963.

(15) Loub J. and Podlahová J., *Inorg. Nucl. Chem. Letters, 7,* 409 (1971).