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

Metal Complexes of Thiopolycarboxylic Acids. II. Solid Salts and Complexes of Thiodiacetic Acid

J. Podlaha and J. Podlahová

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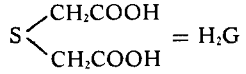
Solid sodium salts of thiodiacetic acid and its 1:1 and 1:2 (metal-to-ligand) complexes with first transition row metals have been prepared in the solid state. According to the properties of these compounds thiodiacetate ion appears to act as a terdentate ligand forming solid complexes of a pseudo-octahedral symmetry.

Introduction

Hitherto published data concerning solid thiodiacetic acid,



$$S\begin{matrix}\diagup CH_2COOH\\ \diagdown CH_2COOH\end{matrix} = H_2G$$

its salts, and complexes are limited and mostly only qualitative in nature. As an exception, the structure of H_2G as single crystal has been determined[1] and the complex salt, $K_2NiG_2 . 4H_2O$, has been prepared and examined by spectral and magnetic methods.[2] Sparingly soluble thiodiacetates of Ca^{2+}, Ba^{2+}, Zn^{2+}, Sn^{2+}, Pb^{2+}, Cu^{2+}, Ag^{+}, Hg_2^{2+}, Pt^{2+}, and Zr^{4+} have been described by other authors[3-10] without, however, having been characterized in detail.

As the simplest sulphur analogon of aminopolycarboxylic acids, the behavior of thiodiacetic acid towards the first trasition row metal ions has been studied in our preceeding paper[11] and the formation of 1:1 and 1:2 complexes has been established in aqueous solution. It was the aim of the present work to prepare solid salts and transition metal complexes of thiodiacetic acid and to examine their properties regarding to relationships between these compounds in the solid state and in solution.

Experimental part and Results

Materials. The synthesis of thiodiacetic acid, metal perchlorate solutions, vanadous and chromous sulphates has been described in the previous paper.[11] Other chemicals used were commercial C.P. materials of the firm Lachema. For the work with easy oxidizable materials all solvents were freed of air and oxidative impurities by flushing with pure nitrogen (water) or treating with sodium metal followed by the distillation (ethanol and ether).

Apparatus and Methods. The synthesis and handling of air-sensitive compounds were performed in the atmosphere of purified nitrogen either in standard closed all-glass systems or in a glove box.

The powder diagrams were taken on a Mikrometa 2 (Chirana) apparatus with a cobalt lamp, an iron filter and a camera of 57.3 mm in diameter. The intensity of the lines was estimated visually according to the scale from 1 (weakest) to 4 (strongest).

The magnetic susceptibility was measured at 25°C on a Faraday balance calibrated with $CuSO_4 . 5H_2O$, $CoHg(SCN)_4$ and water.

The thermal decomposition of compounds was studied by the simultaneous GTA and DTA methods on a Derivatograph instrument[12] using approximately 0.1 g of a compound, the temperature increase of 4°C/min and the range from 25 to 1000°C.

For the determination of solubility the samples were occasionally shaken for several weeks with a suitable amount of solvent in a nitrogen-filled sealed ampoule at 25 ± 0.1°C. After separation of the phases, the composition of the saturated solution, as well as of the solid, was determined by volumetric and/or colorimetric procedures.

The solid reflectance spectra were measured over the range 220-1000 nm on the VSU-1 instrument (Zeiss, Jena) with magnesium oxide as a standard and diluent.

The infra-red spectra were taken in KBr-discs on the UR-20 spectrophotometer (Zeiss, Jena) over the range 400-4000 cm^{-1}. Using control Nujol mulls for typical compounds, the KBr-disc technique was found to be applicable.

Analytical. The thiodiacetate content was determined volumetrically by oxidation to sulphoxide in 3N–HCl with a bromate-bromide solution.[13] The interferring Cr^{2+} ions were air-oxidized to Cr^{3+}, iron was precipitated as $Fe(OH)_3$ and copper as CuS before the titration.

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Metals were analyzed either complexometrically (Mn, Co, Ni, Cu) or gravimetrically as oxides after the ignition of a sample (Cr, Fe). The content of Cr^{2+} and Fe^{2+} was found to be 100±1% of total metal as determined by the potentiometric titration with vanadate.

The sodium content was calculated from the results of the argentometric titration of sodium chloride obtained on a Dowex-2 column (200 mesh, Cl-form). In the presence of transition metal, sufficient ethylenediaminetetraacetic acid was added before the exchange reaction to keep the metal as anion and the hydrochloric acid so formed was expelled from the eluate by evaporation to dryness.

The water content was determined either from the weight loss on drying at a proper temperature (determined from the GTA-curve) or from the difference.

All analytical data presented are the averages of at least three individual determinations.

Preparation of compounds. $Na_2G . 3H_2O$: 30% water solution of H_2G was neutralized with 30% NaOH to pH = 6 with intense stirring and cooling. The volume of the solution was reduced strongly on a water-bath to a clear viscous liquid which was added dropwise to an excess of absolute ethanol. The white precipitate was collected by suction, washed with ethanol and ether, and air-dried. Yield, 90% of white crystalline powder.

$NaHG . H_2O$: 30.0 g of H_2G (0.2 mole) and 16.8 g of $NaHCO_3$ (0.2 mole) were dissolved in 50 ml of water, the solution was heated gently to expel CO_2 and left aside to a slow crystallization. Small crystals so formed were collected, washed with a little cold water and air-dried. The salt cannot be washed with ethanol because of solvolysis. Yield, 65% of white crystals.

$MeG . nH_2O$ (n for Mn = 1, Co = 1, Ni = 3, Cu = 1): 25 ml of $1M$–$Me(ClO_4)_2$ containing some ammonium acetate to keep pH about 6 was added to 25 ml of $1M$–Na_2G. The formation of a crystalline precipitate began after several seconds and was completed by standing overnight. The product was then collected by suction, washed with water, ethanol and ether and air-dried. Yield, 70 to 85% of a pale-pink (Mn), purple (Co), green (Ni), and greenish-blue (Cu) microcrystalline material.

$FeG . H_2O$: under an inert atmosphere 25 milimoles of $FeSO_4$ $7H_2O$ and 25 milimoles of $Ba(ClO_4)_2 . 3H_2O$ were allowed to react in 20 ml of boiling water. Separated $BaSO_4$ was filtered off and 25 ml of $1M$–Na_2G was added to the cold filtrate with vigorous stirring in order to prevent the formation of supersaturated solution. After the first turbidity appeared, the solution was left to stand overnight under nitrogen. The crystalline precipitate was then collected, washed with ethanol and ether, and dried in a stream of nitrogen. Yield, 80% of a very pale green crystalline material, somewhat unstable in air.

$CrG . 1 . 5H_2O$: under an inert atmosphere 20 milimoles of $CrSO_4 . 5H_2O$ was dissolved in 50 ml of ice-cold water, 100 ml of ice-cold $0.2M$–Na_2G was added at once and the mixture was left overnight at 5°C under nitrogen. The product, which separated out, was collected, washed with water, ethanol, and ether and dried in a stream of nitrogen. Yield, 90% of a sky-blue crystalline powder, relatively stable towards aerial oxidation (some 3% of Cr^{2+} are oxidized during two-day-exposure to air).

Attempts to prepare the vanadous complex were unsuccessful owing to its high solubility and extreme sensitivity to oxidation.

$CrGOH . 2 . 5H_2O$, $FeGOH . 3H_2O$: 40 ml of boi-

Table I. Analytical data of the compounds prepared

Compound (m.w.)	% Na Calcd. (Found)	% Me Calcd. (Found)	% G Calcd. (Found)	% H_2O(+OH) Calcd. (Found)
$Na_2G . 3H_2O$	18.53		59.70	21.77
(248.15)	(18.18)		(60.73)	(21.09)
$NaHG . H_2O$	12.09		77.90	9.48
(190.16)	(12.12)		(77.69)	(9.67)
$CrG . 1 . 5H_2O$		22.89	65.21	11.90
(227.16)		(22.74)	(65.42)	(11.84)
$MnG . H_2O$		24.84	66.99	8.17
(221.10)		(24.70)	(66.19)	(9.11)
$FeG . H_2O$		25.16	66.73	8.11
(222.01)		(24.97)	(67.03)	(8.00)
$CoG . H_2O$		26.18	65.81	8.01
(225.09)		(25.55)	(65.34)	(9.11)
$NiG . 3H_2O$		22.50	56.78	20.72
(260.90)		(22.61)	(56.02)	(21.37)
$CuG . H_2O$		27.66	64.49	7.85
(229.70)		(27.75)	(64.11)	(8.14)
$CrGOH . 2 . 5H_2O$		19.83	56.50	23.67
(262.18)		(20.00)	(56.78)	(23.22)
$FeGOH . 3H_2O$		20.31	53.86	25.83
(275.05)		(20.20)	(53.87)	(25.93)
$Na_2CoG_2 . 8H_2O$	8.43	10.81	54.33	26.43
(545.32)	(8.53)	(10.45)	(53.89)	(27.13)
$Na_2NiG_2 . 8H_2O$	8.44	10.77	54.35	26.44
(545.10)	(8.39)	(10.78)	(54.23)	(26.60)
$Na_2CuG_2 . 8H_2O$	8.36	11.55	53.88	26.21
(549.93)	(8.86)	(11.30)	(54.15)	(25.69)

Table II. Magnetic and solubility data of thiodiacetate compounds at 25 °C. Solubility products are calculated using stability constants[11]

Compound	μ_{eff}, B.M.	Solubility in 0.1 *M*—$NaClO_4$ (KCl) mol/ℓ	Solub. product
H_2G	-8.9×10^{-5} [a]	36.78 [b]	
$Na_2G . 3H_2O$	-8.7×10^{-5} [a]	51.31 [b]	
$NaHG . H_2O$	-6.2×10^{-5} [a]	48.52 [b]	
$CrG . 1 . 5H_2O$	4.77	2.13×10^{-3}	2.56×10^{-6}
$MnG . H_2O$	5.93	2.79×10^{-2}	2.30×10^{-4}
$FeG . H_2O$	5.31	5.90×10^{-3}	2.00×10^{-5}
$CoG . H_2O$	4.96	7.94×10^{-3}	1.85×10^{-6}
$NiG . 3H_2O$	3.17	2.86×10^{-2}	1.72×10^{-6}
$CuG . H_2O$	2.10	2.26×10^{-3}	4.50×10^{-8}
Na_2CoG_2	5.07	[c]	[c]
Na_2NiG_2	3.18	[c]	[c]
Na_2CuG_2	2.11	[c]	[c]
$CrGOH . 2.5H_2O$	3.84	1.1×10^{-6}	
$FeGOH . 3H_2O$	3.32	3.01×10^{-5}	

[a] Molar susceptibility. [b] Grams of the compound per 100 grams of solution. [c] Decomposition.

Table III. Interplanar distances and relative intensities of the powder diagram lines

H_2G	$Na_2G .$ $3H_2O$	$NaHG .$ H_2O	$CrG .$ $1.5H_2O$	$MnG .$ H_2O	$FeG .$ H_2O	$CoG .$ H_2O	$NiG .$ $3H_2O$	$CuG .$ H_2O	Na_2-CoG_2	Na_2-NiG_2	Na_2-CuG_2
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
3.96 4	5.81 2	5.50 2	7.14 2	7.04 2	7.14 3	7.04 3	7.08 3	7.25 3	7.78 2	7.78 2	7.78 2
3.35 3	4.79 1	5.05 2	3.89 4	4.34 4	4.34 4	4.34 4	5.81 3	4.82 1	6.43 3	6.43 3	6.45 3
2.96 1	4.12 4	4.31 1	3.60 1	3.52 1	3.52 2	3.52 2	4.88 1	4.27 4	5.59 2	5.59 2	5.59 2
2.78 2	3.35 2	3.92 1	3.26 1	3.19 2	3.23 2	3.22 2	4.60 2	3.56 1	4.45 1	4.45 1	4.45 2
2.65 1	2.93 3	3.68 3	2.97 3	2.94 2	2.93 3	2.88 1	4.35 1	3.25 2	4.20 1		4.17 1
2.40 3	2.74 3	3.29 1	2.43 2	2.62 1	2.60 2	2.57 1	3.90 1	3.00 3	3.95 4	3.95 4	3.95 4
2.22 1	2.40 2	3.06 4	2.21 2	2.48 1	2.47 2		3.72 1	2.73 2	3.41 4	3.41 4	3.41 4
2.04 1	2.31 2	2.74 1	2.12 1		2.41 2	2.39 1	3.51 1	2.40 3	3.19 1	3.19 1	3.19 1
1.94 1	2.20 1	2.55 1	1.88 2	2.32 1	2.31 1		3.17 3	2.20 2	2.91 2	2.89 2	2.91 2
1.67 1	2.18 1	2.32 1		2.26 1	2.24 2	2.22 2	3.04 1	2.11 1	2.80 2	2.80 2	2.80 2
1.60 1	2.10 1	2.19 2		2.05 1	2.05 1	2.05 1	2.91 2	2.00 1	2.62 2	2.62 1	2.63 1
	1.97 1	1.98 1		1.92 2	1.90 2	1.90 1	2.63 2	1.92 1	2.52 1	2.52 1	
	1.92 2	1.84 1			1.70 1	1.70 1	2.36 1	1.86 2	2.41 2	2.39 1	2.43 1
	1.88 1	1.72 1			1.66 1	1.66 1	2.18 2	1.79 1	2.32 2	2.29 2	2.32 2
	1.79 1				1.60 1		2.03 1	1.73 1	2.18 2	2.19 2	2.18 2
	1.67 1				1.56 1		1.94 1	1.66 2	2.03 1	2.01 1	2.04 1
	1.61 1				1.50 2	1.50 2	1.87 1	1.56 1	1.96 3	1.96 3	1.96 3
					1.45 2	1.46 1	1.77 1	1.44 2	1.90 2	1.90 2	1.91 2
					1.37 1	1.36 1	1.69 1	1.40 1	1.84 2		1.85 1
					1.33 1			1.34 2	1.79 1	1.78 1	
								1.29 1	1.68 1	1.68 1	1.69 1
								1.25 2	1.62 1	1.60 1	
								1.15 1	1.48 2	1.47 2	1.47 2
								1.08 1		1.44 2	1.43 1
									1.42 1	1.42 1	
									1.20 1		

ling 0.5 *M* metal nitrate solution was added to 40 ml of boiling 0.5*M*—Na_2G solution. The precipitate formed instantaneously was separated by centrifugation, washed with hot water, ethanol, and ether, and air-dried. Yield, 90 to 95% of a grayish-blue (Cr) and ocre (Fe) amorphous powder. The identical products are also formed using other metal salts (sulphate, chloride, perchlorate).

$Na_2MeG_2 . 8H_2O$ (Me = Co, Ni, Cu): 20 milimoles of $MeG . nH_2O$ were finely ground and dissolved in a minimum amount of a suitable concentrated cold Na_2G solution (Co, 20 ml of 2 *M*, 30 ml of 1 *M*; Cu, 25 ml of 2 *M*). The filtered clear solutions were allowed to stand at 5°C, well-developed crystals so obtained were collected by suction and dried on the porous plate at 5°C. (Other methods of drying, as well as washing, caused dehydration and/or decomposition to MeG and Na_2G). Yield, 50 to 60% of deep red (Co), blue (Ni), and bluish-green (Cu) crystals, unstable towards dehydration even at room temperature. The complexes can be stored at −5°C without any loss of water. In solution, decomposition to Na_2G and slightly soluble MeG takes place within several minutes, especially on heating.

Analytical data of all compounds are given in Table I.

Properties of the compounds prepared.

The properties of solid salts and complexes of thiodiacetic acid are summarized in the following tables: magnetic and solubility data (Table II), powder diagrams data (Table III), thermal decomposition characteristics (Table IV), electronic spectra (Table V), and infra-red spectra (Table VI).

Discussion

The properties of solid thiodiacetate complexes clearly demonstrate the close similarity between the structure of these compounds in the solid state and in solution. Thiodiacetate anion seems also to be terdentate in solid complexes, the bonding being realized through two carboxyl oxygens and one sulphur atom. Consequently, the intense bands attributable to a sulphur-metal charge transfer occur in the U.V. spectra of the majority of complexes either as separate maxima (Cr^{2+}, Ni^{2+}, Cu^{2+}) or as shoulders lying on the border of the measurable range (Fe^{2+}, Co^{2+}).

Table IV. Thermal decomposition of the compounds prepared

	Dehydration			Decomposition of G			Other processes		
Compound	°C	DTA-effect	Product	°C	effect	Product	°C	DTA-effect	Product
H_2G				290	endo		130	endo	melt
$Na_2G . 3H_2O$	90	endo	Na_2G	390	exo	$Na_2CO_3+Na_2SO_4$			
$NaHG . H_2O$	80	endo	NaHG	310	exo	$Na_2CO_3+Na_2SO_4$			
$CrG . 1.5H_2O$	170	endo	CrG	250	exo	Cr^{III}sulphate+oxide	550	endo	Cr_2O_3
$MnG . H_2O$	240	endo	MnG	300	exo	$Mn_3O_4+MnSO_4$	800	endo	Mn_3O_4
$FeG . H_2O$	150	endo	FeG	280	exo	Fe^{III}sulphate+oxide	550	endo	Fe_2O_3
$CoG . H_2O$	240	endo	CoG	330	exo	$Co_3O_4+CoSO_4$	810	endo	Co_3O_4
				350	exo		890	endo	CoO
$NiG . 3H_2O$	190	endo	NiG	330	exo	$NiO+NiSO_4$	740	endo	NiO
				380	exo				
$CuG . H_2O$	110	endo	CuG	220	exo	Cu,Cu^I,Cu^{II}sulphate+oxide	730	endo	CuO
				270	exo				
$Na_2CoG_2 . 8H_2O$	20	endo	Na_2CoG_2	270	exo	$Co_3O_4+Na_2SO_4$	870	endo	$CoO+Na_2SO_4$
$Na_2NiG_2 . 8H_2O$	20	endo	Na_2NiG_2	320	exo	$NiO+Na_2SO_4+NiSO_4$	820	endo	$NiO+Na_2SO_4$
$Na_2CuG_2 . 8H_2O$	20	endo	Na_2CuG_2	210	exo	$CuO+Na_2SO_4+CuSO_4$	750	endo	$CuO+Na_2SO_4$
$CrGOH . 2.5H_2O$	30-160	endo	CrGOH	290	exo	Cr^{III}sulphate+oxide	550	endo	Cr_2O_3
$FeGOH . 3H_2O$	30-150	endo	FeGOH	230	exo	Fe^{III}sulphate+oxide	550	endo	Fe_2O_3

Table V. Diffuse reflectance spectra of the compounds prepared

Compound	cm^{-1}	Assignment	Compound	cm^{-1}
H_2G	42,500	CT		
	44,000	CT		
$Na_2G . 3H_2O$	44,000	CT		
$NaHG . H_2O$	44,000	CT		
$CrG . 1.5H_2O$	14,500	$^5T_{2g} \longleftarrow {}^5E_g$		
	34,500	CT		
$FeG . H_2O$	11,000	$^5E_g \longleftarrow {}^5T_{2g}$		
	42,200 sh	CT		
$CoG . H_2O$	15,800 sh	$^4A_{2g} \longleftarrow {}^4T_{1g}(F)$	16,000 sh	Na_2CoG_2
	18,200	$^2P,\ {}^2G,\ {}^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F)$	18,850	
	21,500		24,100	
	41,800 sh	CT	42,000 sh	
$NiG . 3H_2O$	14,300	$^3T_{1g}(F) \longleftarrow {}^3A_{2g}$	15,150	Na_2NiG_2
	25,600	$^3T_{1g}(P) \longleftarrow {}^3A_{2g}$	26,000	
	39,600	CT	40,400	
$CuG . H_2O$	12,700	$^2T_{2g} \longleftarrow {}^2E_g$	13,400	Na_2CuG_2
	31,200	CT	27,000	
		CT	35,100	
$CrGOH . 2.5H_2O$	17,000	$^4T_{2g} \longleftarrow {}^4A_{2g}$		
	23,300	$^4T_{1g}(F) \longleftarrow {}^4A_{2g}$		
$FeGOH . 3H_2O$	35,700	CT		

The co-ordination of sulphur is further supported by the fact that the C–S stretching frequency in the infra-red spectra of complexes is clearly shifted by some 20 cm^{-1} to lower wavenumbers comparing with free thiodiacetic acid and its sodium salts. The carboxyl-metal bonds appear to be essentially ionic in character as can be deduced from the difference betlween the symmetrical and antisymmetrical COO-stretch[14] in the infra-red spectra.

The main features of the electronic spectra are identical with those of solutions over whole the range measured taking no account of developing some shoulders in solutions to separate maxima in reflectance spectra. The only exception is the already mentioned appearance of far U.V. charge transfer maxima of Co^{2+} and Fe^{2+} complexes the presence of whose was not registered in solution because of an overlapping by intense bands of necessary ligand excess. In addition, data concerning chromous complex which could not be studied in solution owing to its very limited solubility were obtained from the reflectance spectrum. The parameter Dq = 1450 cm^{-1} found for CrG complex agrees quite well with the usual spectrochemical series of metals:[15] $Ni^{2+} < Co^{2+} < Fe^{2+} < Cu^{2+} < Cr^{2+} < Cr^{3+}$.

The similarity of the electronic spectra in the solid state and in solution as well as the application of Tanabe-Sugano diagrams[15] clearly shows that the

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

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

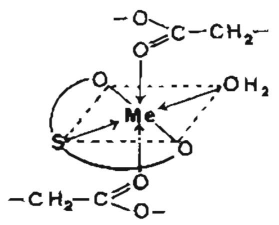
Table VI. Selected infra-red bands (cm^{-1}) of the compounds prepared

Compound	ν(C–S)	ν_s(COO)	ν_a(COO)	ν(OH)
H_2G	726 s	1380 vs	1742 vs	3080 vs, b
D_2G [a]	728 s	1380 vs	1738 vs	2280 s, b
$Na_2G \cdot 3H_2O$	721 s	1395 vs	1610 vs	3480 s, b
$NaHG \cdot H_2O$	724 m	1391 s	1602 vs 1735 s	3040 w, b 3440 s, b
$CrG \cdot 1.5H_2O$	697 s	1390 sh 1426 vs	1592 vs	3260 vs, b
$MnG \cdot H_2O$	693 s	1396 vs	1600 vs	3300 vs, vb
$FeG \cdot H_2O$	698 s	1402 vs	1593 vs	3230 s, b
$CoG \cdot H_2O$	703 s	1410 vs	1591 vs	3260 s, b
$NiG \cdot 3H_2O$	701 s	1387 vs 1405 vs	1605 vs	3200 vs, vb
$CuG \cdot H_2O$	692 s	1390 vs	1620 vs	3160 vs, vb
Na_2CoG_2	703 s	1380 vs 1411 vs	1601 vs	
Na_2NiG_2	702 s	1381 vs 1414 vs	1600 vs	
Na_2CuG_2	699 s	1389 s 1420 vs	1596 vs	
$CrGOH \cdot 2.5H_2O$	706 s	1395 vs	1595 sh 1622 vs	3200 s, b 3430 vs, vb
$FeGOH \cdot 3H_2O$	707 s	1408 vs	1610 vs	3200 sh 3450 vs, vb

[a] H_2G recrystallized repeatedly from D_2O

solid spectra can be reasonably interpreted in terms of a pseudo-octahedral crystal field surrounding the metal ion. Likewise, the magnetic moments are also consistent with an octahedral configuration of complexes. Despite the lack of spectral data, the manganous complex possesses evidently an analogous octahedral arrangement since the compounds $MnG \cdot H_2O$, $FeG \cdot H_2O$ and $CoG \cdot H_2O$ are isomorphous.

It should be pointed out that the number of water molecules in the complexes is not sufficient to complete the co-ordination sphere of metal in most cases. However, free oxygens of the carboxyl groups can contribute to the formation of an octahedral $[O_5S]$ chromophore leaving the type of electronic spectrum unchanged:

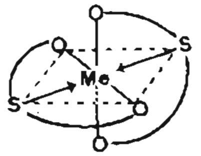


Of course, this proposed difference between the structure of complexes in solution and in solid state can be verified only by a crystal structure determination.

The foregoing molecular structure is further supported by the fact that one water molecule of 1:1 complexes is firmly co-ordinated being lost only at relatively high temperature.

Considering the stoichiometric composition only, a tetrahedral stereochemistry of the 1:1 complexes ought to be taken into account. However, such an arrangement can be excluded mainly on the basis of magnetic moments and electronic spectra. A trial calculation of tetrahedral crystal field parameters of Co and Ni complexes leads to abnormally low Dq values and unreal values of the nephelauxetic ratio ($\beta > 1$) in both cases.

The 1:2 complexes are isomorphous and their powder diagrams exhibit no lines of Na_2G and $MeG \cdot nH_2O$. The spectral and magnetic data of the nickel 1:2 complex agree well with those published[2] for $K_2NiG_2 \cdot 4H_2O$. Water is bound very weakly in the 1:2 complexes, the co-ordination sphere of metal being saturated with two thiodiacetate ligands. Of course, the proposed arrangement



must be considered as being only one of three possible isomeric forms, one of which should be optically active. Because of the limited stability of 1:2 complexes, any detailed study of this isomerism seems to be impossible.

The properties of the complexes of tervalent metals are quite different from those of bivalent ones indicating a polymeric structure of MeGOH complexes. The hydroxyl groups are bound very firmly in these substances showing no tendency of substitution by other anions. It seems very probable for these hydroxyls to act as bridges between metal atoms forming polymeric chains. Such a view is supported especially by the magnetic moment of the ferric complex which is typical of an oxo-bridged polymer, as well as by the slight solubility of MeGOH complexes and the type of water bonding: the loss of water is a continuous reversible process depending upon the humidity of air rather than the temperature, the relevant DTA-effect being only very indistinct. Such a behavior is typical of a substance containing water in gaps of a polymeric structure.