

PREPARATION AND CHARACTERIZATION OF IRON(II) COMPLEXES OF ETHYLENE GLYCOL

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Nine iron(II) ethylene glycol sulphate complexes were prepared. Their compositions were determined by standard analytical methods. They were characterized by means of temperature-dependent magnetic susceptibility and Mössbauer spectroscopic measurements. On the basis of the patterns of their thermal decompositions, the complexes could be classified into three groups.

The absorption and transport of vital metal ions such as iron in vivo are possible only if these ions are complexed. Sugar-type compounds may serve as ligands in these processes [1]. In a series of former investigations [2], it was shown that even simple monosaccharides form complexes with rather complicated compositions and structures. A better insight into such complex systems may be obtained from an analogous study of simple model compounds. Ethylene glycol may serve as the simplest model of polyols and sugars. We have therefore started coordination chemical studies of its transition metal complexes. Preparative, thermoanalytical and X-ray structural investigations of the copper(II)-ethylene glycol-sulphate-water system showed that, depending on the preparation mode, eleven complexes with different compositions could be prepared from the four basic components of this system [3]. Because of the Mössbauer activity of iron and the sensitivity of the quadrupole splitting of iron(II), this series of investigations has been continued with a study of the analogous iron(II)-ethylene glycol-sulphate-water system.

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Ethylene glycol complexes of iron(II) were first prepared by Romer and Tyson [4], but they were not characterized by adequate methods. Knetsch and Groeneweld [5, 6] later questioned the possibility of the preparation of well-defined iron(II) ethylene glycol complexes.

On the basis of our experience during the work with copper(II)-ethylene glycol complexes, we were able to prepare and characterize nine different complexes containing only iron(II) and sulphate ions with ethylene glycol and water molecules (Table 1). The results of thermoanalytical studies and Mössbauer and magnetic susceptibility measurements on these complexes are presented in this paper.

Table 1 Compositions and analysis data on investigated compounds

Com- pound	Composition	Iron content, %		Water content, %		Ethylene glycol content, %	
		calc.	exp.	calc.	exp.	calc.	exp.
I	Fe(Gl)(H ₂ O)SO ₄	24.1	24.3	7.8	7.1	26.8	24.6
II	Fe(Gl) _{1.5} (H ₂ O) _{1.5} SO ₄	20.5	21.0	9.9	11.0	34.2	34.6
III	Fe(Gl) _{2.5} (H ₂ O) _{2.5} SO ₄	15.9	15.2	12.8	13.5	44.1	44.5
IV	Fe(Gl) ₃ (H ₂ O) ₃ SO ₄	14.2	14.3	13.8	14.1	47.5	46.9
V	Fe(Gl) _{3.5} (H ₂ O) _{3.5} SO ₄	12.9	13.2	14.6	16.8	50.3	50.6
VI	Fe(Gl)(H ₂ O) ₃ SO ₄	20.8	21.3	20.2	22.6	23.2	23.6
VII	Fe(Gl) ₂ (H ₂ O) ₂ SO ₄	17.8	18.5	11.5	12.1	39.8	38.8
VIII	Fe(Gl) _{2.25} (H ₂ O) ₂ SO ₄	17.1	17.4	11.0	12.4	42.6	42.5
IX	Fe(Gl) ₄ (H ₂ O) ₄ SO ₄	11.8	12.0	15.3	14.1	52.6	52.4

Experimental

Ethylene glycol (Reanal p.a.) was purified by vacuum distillation, and was freed from dissolved oxygen by bubbling oxygen-free nitrogen through the liquid. Crystalline FeSO₄·7H₂O (Reanal p.a.) was dissolved in the purified ethylene glycol. The molar ratio of the organic ligand (also acting as solvent) to the iron(II) salt was ~6.5 in the preparation of compound **VI**, ~19.5 in that of **VIII**, and ~13 in all other bases. Differences in treatment and temperature led to different compounds. Complexes **I** and **IX** were prepared in the presence of elemental iron; **III** and **IV** were made to crystallize at room temperature in a closed system, **V** and **IX** at room temperature in an open system, and **I** and **II** at the temperature of a boiling water-bath in an open system under a nitrogen atmosphere.

In most of the cases, the compound to be prepared precipitated in about 1 hour.

The precipitates were collected on a glass filter and washed free of sulphate ion with diethyl ether. Compounds VI, VII and VIII were also washed with water-free ethanol. The solid samples were kept in a desiccator over anhydrous calcium chloride.

Analytical control methods

The iron(II) content was determined by chromatometric titration, with diphenylamine as indicator, in sulphuric acid medium.

The ethylene glycol content was determined by oxidation with periodate according to the Malaprade method.

The water content was measured by K. Fischer titration, with dead-stop end-point detection.

The thermoanalytical curves were recorded with a MOM-OD2 (Hungarian Optical Works) derivatograph using 200 mg samples in platinum crucibles and a heating rate of 2 deg min^{-1} as described previously [3], but in a nitrogen atmosphere. These contributed to the determination of the compositions of the

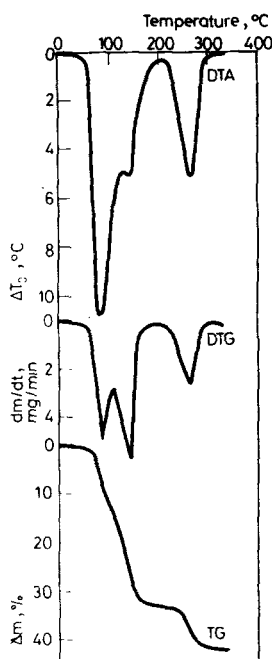


Fig. 1 Thermoanalytical (TG, DTG, DTA) curves of $\text{FeGl}(\text{H}_2\text{O})_3\text{SO}_4$ classified in group A

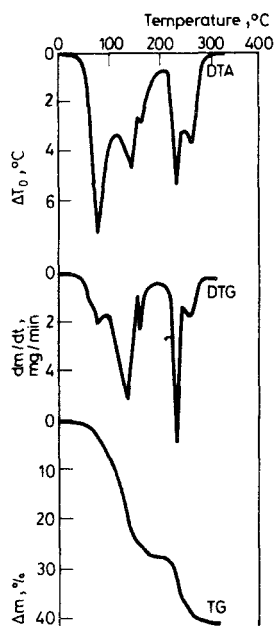


Fig. 2 Thermoanalytical (TG, DTG, DTA) curves of $\text{FeGl}_{1.5}(\text{H}_2\text{O})_{1.5}\text{SO}_4$ classified in group B

Table 2 Results of magnetic susceptibility measurements

Compound	μ_{eff}	θ	C	R
I	5.62 ± 0.03	21.5 ± 1.6	3.92 ± 0.04	0.9984
II	5.44 ± 0.03	34.8 ± 1.8	3.67 ± 0.03	0.9986
III	5.53 ± 0.03	22.3 ± 1.8	3.79 ± 0.04	0.9980
IV	5.33 ± 0.02	20.9 ± 1.7	3.52 ± 0.03	0.9983
V	5.67 ± 0.04	22.6 ± 2.4	3.98 ± 0.05	0.9958
VI	5.28 ± 0.03	3.5 ± 1.6	3.45 ± 0.04	0.9988
VII	5.35 ± 0.02	17.4 ± 1.2	3.55 ± 0.02	0.9988
VIII	5.64 ± 0.03	15.4 ± 1.7	3.95 ± 0.04	0.9984
IX	5.18 ± 0.02	4.2 ± 1.6	3.32 ± 0.03	0.9983

compounds. Typical thermoanalytical curves for three compounds are shown in Figs 1–3.

The results of the analytical investigations, together with the corresponding calculated values (the latter based on the assumed chemical compositions) are presented in Table 1.

The magnetic susceptibility data on the compounds were determined with a

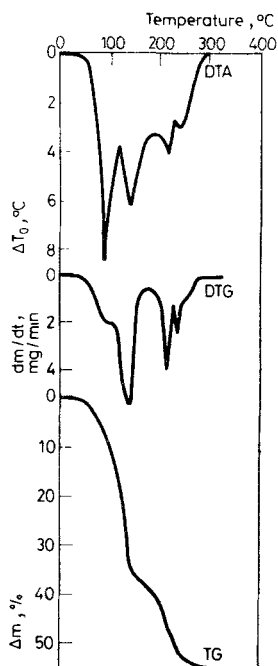


Fig. 3 Thermoanalytical (TG, DTG, DTA) curves of $\text{FeGl}_2(\text{H}_2\text{O})_2\text{SO}_4$ classified in group C

Bruker SU device in the temperature interval 85–290 K. The experimental data were evaluated with a computer program, leading to effective magnetic moments (μ_{eff}), Curie constants (C) and Weiss constants (θ). The reliability of evaluation is reflected by the regression coefficients (R). The results are presented in Table 2.

The Mössbauer spectra were recorded as described previously [2], at room and liquid nitrogen temperatures. The Mössbauer parameters were derived from a computer evaluation of the spectra. The isomer shift (IS) values are referred to that of metallic iron at room temperature. IS and quadrupole splitting (QS) values are presented in Table 3.

The Mössbauer spectra reflected the uniform compositions of the samples, i.e. the equivalence of the iron(II) atoms in each complex (Fig. 4).

Results and discussion

The formal compositions per iron(II) atom of the new compounds, calculated from the analytical data, are presented in the first column of Table 1. The fractional numbers of the ethylene glycol and/or water molecules indicate that **II**, **III**, **V** and

Table 3 Mössbauer parameters* of investigated complexes

Compounds	IS	QS	IS	QS
	at room temperature		at liquid N ₂ temperature	
I	1.26	2.73	1.38	3.19
II	1.26	2.78	1.38	3.19
III	1.26	2.82	1.39	3.24
IV	1.30	2.81	1.38	3.23
V	1.30	2.80	1.39	3.26
VI	1.29	3.06	1.38	3.41
VII	1.29	2.80	1.38	3.23
VIII	1.29	2.82	1.39	3.24
IX	1.29	2.80	1.39	3.25

* Given in mm s⁻¹; reproducibility ± 0.01 mm s⁻¹

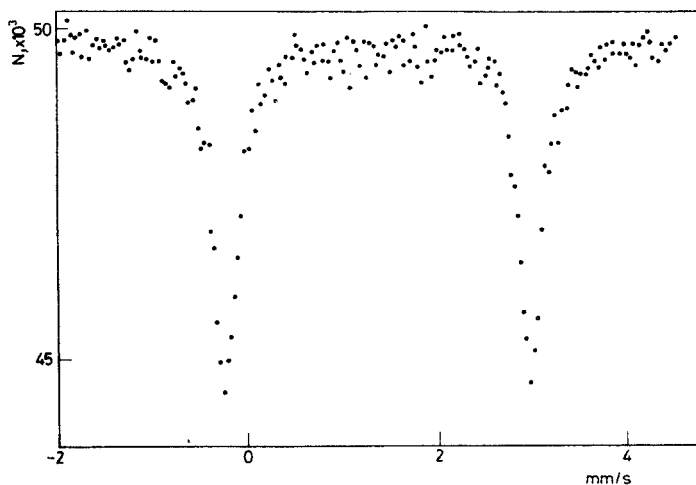


Fig. 4 The Mössbauer spectrum of FeGl_{2.5}(H₂O)_{2.5}SO₄ recorded at liquid nitrogen temperature

VIII must be dimeric or oligomeric compounds containing ethylene glycol or sulphate bridges.

The Θ values calculated from the temperature-dependence of the magnetic susceptibilities (Table 2) clearly show that the investigated compounds (except **VI** and **IX**) are antiferromagnetic, due to the presence of bridging ligands. The magnetic moments (μ_{eff} between 5.18 and 5.67) indicate a distorted octahedral coordination sphere of the iron(II) in all these complexes. This symmetry is attained through ligand bridges in compounds **I–V** and **VII–VIII**.

The Mössbauer parameters reflected a high-spin iron(II) ($t_{2g}^4 e_g^2$) electron structure for all complexes. The isomer shifts are not sensitive to changes in composition of the complexes. They are equal within experimental error. The quadrupole splitting values are significantly lower ($2.73\text{--}3.06\text{ mm s}^{-1}$ at room temperature and $3.19\text{--}3.41\text{ mm s}^{-1}$ at liquid N_2 temperature) than those for $\text{Fe}(\text{OH}_2)_6^{2+}$ (3.20 and 3.60 mm s^{-1} , respectively), indicating a higher covalency of the ethylene glycol-containing coordination spheres than that of the aquo complex. Higher quadrupole splitting values probably indicate higher water contents in the inner coordination sphere of the iron(II). The water molecules can be bound directly to the iron(II) through coordination of the oxygen donor atom, or to ethylene glycol via hydrogen-bonds. Water molecules bound in this way to ethylene glycol are presumed not to influence the Mössbauer parameters. Similarly, the ethylene glycol can be coordinated to the iron(II) in various ways through its oxygen atoms: monofunctionally, as a chelating ligand, or as a bridge-forming ligand. It may also be bound by hydrogen-bonds to water or sulphate ions in the compound.

Both the magnetic data and the Mössbauer parameters indicate that the coordination spheres of the iron(II) differ in the complexes with different compositions. We therefore assumed that the differences in the coordination spheres would be reflected in the thermal decompositions of the complexes.

Depending on their thermal decomposition patterns, the nine investigated complexes could be divided into three groups (A, B and C).

For the assignment of the different DTG peaks to the corresponding thermal decomposition processes, the decomposition intermediates were prepared by stopping the heating process with the derivatograph at 180° (in some cases also at 140°), and were analysed for ethylene glycol and water contents. From the analytical results, the individual DTG peaks could be assigned to the individual processes. This permitted characterization of the three groups.

Compounds **I**, **IV**, **V**, **VI** and **IX** belong in group A. These compounds release the total ethylene glycol content and all but one water molecule below 180° *. These two types of ligands are released in successive, well-separated processes only for **VI** and **IX**. **VI** loses 2 water molecules just below 110° and 1 ethylene glycol molecule between 110 and 160° . **IX** releases 3 water molecules and 1 ethylene glycol together in one step below 145° , and the remaining ethylene glycol content (3 molecules) between 145 and 180° .

The low temperature of the release of ethylene glycol (for **VI**, below 160° ; for **IX**, 1 below 145° and 3 below 180°) is noteworthy, since the boiling point of pure ethylene glycol is 197° . Thus, the glycol molecules are less strongly bound in the

* This process is similar to the thermal decomposition of crystalline $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, which releases only 6 water molecules below 180° [7].

iron(II) complexes than in the pure liquid bulk, where they are connected by hydrogen-bonds to their neighbours.

The magnetic susceptibility measurements indicate that **VI** and **IX** are monomeric species not exhibiting antiferromagnetic behaviour. With regard to their compositions and the Mössbauer quadrupole splitting values, it may be assumed that the ethylene glycol is coordinated monofunctionally through one of its oxygens to the iron(II) in both compounds; in spite of the higher water content of **IX**, the inner coordination sphere in **IX** contains fewer water molecules than that in **VI**.

For the other compounds in group **A** (**I**, **IV**, **V**), the two types of ligands are released in overlapping processes below 180°. This may indicate the interaction (probably hydrogen-bonding) between ethylene glycol and water molecules in these complexes.

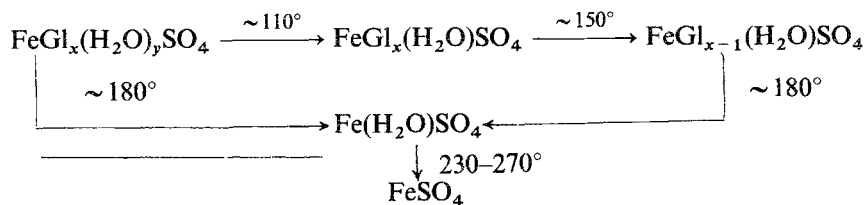
Compounds **II** and **III** are classified in group **B** on the basis of their thermal decompositions. Both release the last ~0.5 molecule of ethylene glycol and the last ~0.5 molecule of water in separate steps above 180° (ethylene glycol at 235° and water at 260°). This behaviour may indicate that one ethylene glycol bridge and one water bridge were formed during the thermal process up to 180°, or that they were still present from among the original bridges in the complexes.

Compound **II** loses water and ethylene glycol below 180°, also in two steps: water at 110°, and ethylene glycol at 130–160°. The processes of release of the two types of ligands from **III** below 180° overlap. This suggests that the ethylene glycol and water interact more strongly in **III** than in **II**.

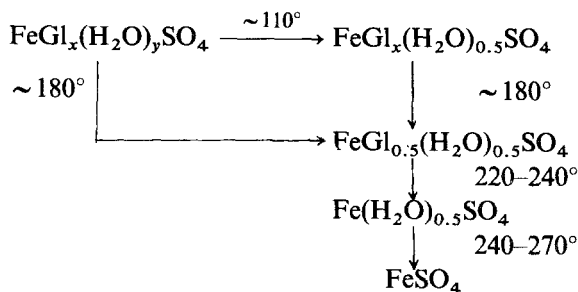
Compounds **VII** and **VIII** belong in group **C**. Their thermal behaviour is similar to that of the compounds in group **B**, with the difference that at 180° they contain ~0.6 mol of ethylene glycol, which is released in two steps, at 225° and 235°. The ratio of the released quantities was found to be different for **VII** and **VIII**.

On the basis of the observed thermal behaviour, the following 3 decomposition schemes are postulated:

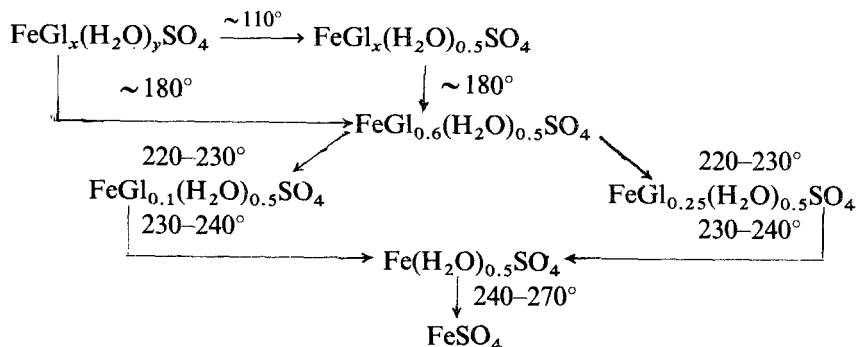
A



B



C



Gl = denotes ethylene glycol.

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Zusammenfassung — Neun Eisen(II)-ethylenglykol-sulfat-Komplexe wurden dargestellt. Die Zusammensetzung dieser Komplexe wurde nach analytischen Standardmethoden bestimmt. Die Verbindun-

gen wurden durch Messungen der temperaturabhängigen magnetischen Suszeptibilität sowie mittels Mössbauer-Spektroskopie charakterisiert. Nach dem Verhalten bei der thermischen Zersetzung konnten diese Komplexe in drei Gruppen klassifiziert werden.

Резюме — Получено девять комплексов сульфате двухвалентного железа с этиленгликолем, состав которых определен обычными аналитическими методами. Комплексы были изучены измерением температурной зависимости магнитной восприимчивости и мёсбауэровской спектроскопией. Комплексы разделены на три группы, исходя из подобия их термического разложения.