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PREPARATION, THERMOANALYTICAL AND STRUCTURAL STUDY OF COMPLEXES OF 1,2-ETHANEDIOL AND MANGANESE(II) SULFATE

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Abstract

Parent and mixed ligand complexes of manganese(II) ion were prepared with water, sulfate ion and 1,2-ethanediol as ligands. The IR spectra and the thermoanalytical curves of the complexes were recorded. Oxygen atoms bound by one or two coordinate bonds to the metal ion, or by hydrogen-bonds in the crystal, were observed. As for the water molecule, 'crystal' and 'monohydrate' type of 1,2-ethanediol molecules were found, depending on the type of binding of the oxygen atoms.

Keywords: 1,2-ethanediol, IR spectra, mixed ligand complexes, Mn(II) complexes, TA studies

Introduction

To compare the coordination abilities of water and 1,2-ethanediol (*Gl*=glycol), some parent and mixed ligand complexes of water, 1,2-ethanediol and divalent metal sulfates (Cu(II), Zn(II), Fe(II), Ca(II), Mg(II) and Cd(II)) were earlier prepared and their thermochemical behaviour (<600°C) and IR spectra were investigated in our laboratories [1–5]. It was suggested, that in aqueous solution the 1,2-ethanediol molecule can partly, but never completely displace all of the water molecules and sulfate ion in the coordination spheres of metal ions. The experience attained with the preparation of the complexes showed that, in the absence of water, the 1,2-ethanediol molecule can displace the sulfate ions from the coordination sphere, but the complex compounds formed are sensitive to moisture and heating. This observation supports our earlier finding that water and 1,2-ethanediol molecules have similar coordination abilities and/or form strong hydrogen-bonds with the oxygen atoms of water and the sulfate ion, thereby making the mixed coordination sphere more stable than the coordination sphere containing water or 1,2-ethanediol alone.

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To follow this study, the manganese complexes of 1,2-ethanediol, water and sulfate ion were prepared and investigated by thermoanalytical and IR spectroscopic methods, and the magnetic susceptibility data were recorded. The manganese(II) ion was chosen because of its ability to coordinate water and sulfate ion. This knowledge may help in the understanding of coordination properties of manganese(II) ion *vs*. other organic compounds, which thermal behaviour was investigated last years [6–7].

Manganese(II) sulfates exist as pentahydrate or tetrahydrate, dihydrate or monohydrate forms at room temperature and above [8]. The heptahydrate form ($MnSO_4 \cdot 7H_2O$), which is common for the Fe(II)-, Zn(II)-, Co(II)- and Ni(II) ions, exists only below 5°C [8]. Qualitatively, this phenomenon demonstrates the high coordination ability of the manganese(II) ion towards the sulfate ion. This gives another possibility for comparison of the coordination abilities of the sulfate ion and the water and 1,2-ethanediol molecules.

Experimental

Preparation of complexes

In the course of the preparation, $MnSO_4 \cdot 7H_2O$, 1,2-ethanediol and water were mixed in solution and different methods were used to obtain solid complexes. The solid complexes were stored in a desiccator under $CaCl_2$ or P_2O_5. The details are as follows:

$MnSO_4 \cdot 7H_2O$ [8]

70 g of commercial $MnSO_4 \cdot xH_2O$ (x=1–4) was dissolved in 100 g of water and the solution was stored in a refrigerator at 5°C. The precipitated crystals were collected, washed with cold water and dried in the air. The solid material was used immediately for the preparation of 1,2-ethanediol complexes.

Complex **1**

4 g $MnSO_4 \cdot 7H_2O$ was dissolved in 20 mL of 1,2-ethanediol during stirring and 30 mL of ethanol was added to the solution. After some minutes, a white precipitate was formed, which was separated by filtration and washed with ethanol.

Complex **2**

10 g of $MnSO_4 \cdot 7H_2O$ was dissolved in 25 mL of cold 1,2-ethanediol and the solution was stored in a refrigerator at 5°C. After one night, solid crystals were precipitated; they were filtered off and washed with methanol.

Complex **3**

Cold $MnSO_4 \cdot 7H_2O$ (5 g) and 1,2-ethanediol (25 mL), which had been stored in refrigerator, were mixed and stirred at room temperature. The solid manganese sulfate dissolved, and after some minutes a solid material precipitated from the solution. The complex was separated by filtration and washed with diethylether. The water content of the complex was sensitive to conditions of storage.

Complex **4**

- Cold $MnSO_4 \cdot 7H_2O$ (5 g), 1,2-ethanediol (25 mL) and diethylether (20 mL) were mixed and stirred at room temperature. After some minutes, a solid compound separated out from the aqueous phase; it was separated by filtration and washed with cold water and methanol.
- Cold $MnSO_4 \cdot 7H_2O$ (3 g) and 1,2-ethanediol (3 mL) were mixed and stored at room temperature in a desiccator under P_2O_5. The solid was filtered off and washed with ethanol and diethylether.

Complex **5**

5 g of cold $MnSO_4 \cdot 7H_2O$ and 40 mL of cold 1,2-ethanediol were mixed and the solid compound was dissolved. The solution was kept in a refrigerator at –5°C and after one day a solid compound separated out from the solution. The complex was very sensitive to water and this prevented measurement of the magnetic susceptibility.

Determination of composition

The metal, 1,2-ethanediol and water contents of the complexes were determined by classical analytical methods (complexometry, Malaprade reaction and Karl Fischer method). The analytically determined compositions were checked thermoanalytically.

Thermoanalytical studies

The thermal decompositions of the complexes were investigated with a MOM OD-2 derivatograph at a heating rate of 2°C min^{-1}. The mass of the investigated samples was 100–200 mg. The measurements were carried out in Pt crucibles in air or nitrogen atmosphere. α-Al_2O_3 was used as a reference substance. Decomposition intermediates were prepared by stopping the heating process at appropriate temperatures and their compositions were determined by analytical methods.

IR study

The IR spectra of the complexes in KBr tablets were taken in the wave number range 400–4000 cm^{-1}. The characteristic bands were followed to determine the coordination modes of the ligand and water molecules or sulfate ion.

Magnetic susceptibility measurements

The magnetic susceptibility of each complexes was measured between 100 and 300 K by the Faraday method, with $CuSO_4$ as reference compound. A Bruker M15 magnet and Sartorius microbalance were used. The gram and mole susceptibility values (taking into consideration the Pascal constants) were calculated.

From the mole magnetic susceptibility values, the effective magnetic moments were calculated and compared with theoretical values and other data.

Results and discussion

Preparation and compositions of complexes

The suggested compositions of the complexes suggested on the basis of the analytical measurements are presented in Table 1. The analysis indicates that two types of complexes, water-free and water-containing complexes were prepared.

Table 1 Compositions of complexes

Complex	Composition	Metal content/%		*Gl* content/%		Water content/%	
		theor.	found.	theor.	found.	theor.	found
1	$MnGlSO_4$	25.79	25.59	29.12	29.70	–	–
2	$MnGl_{1.5}(H_2O)_{1.5}SO_4$	20.26	19.94	34.34	35.21	9.96	9.55
3	$MnGl_2(H_2O)SO_4$	18.74	18.30	42.34	44.90	6.14	5.90
4	$MnGl_2(H_2O)_2SO_4$	17.65	17.44	39.89	40.42	11.59	11.25
5	$MnGl_{3.5}SO_4$	14.92	15.11	58.99	58.19	–	–

Gl=glycol=1,2-ethanediol

In the course of the preparative work, the metal ion to ligand ratio was changed, different solvents were used to vary the dielectric constants of solution, and common desiccating agents ($CaCl_2$ and P_2O_5) were used. These variations in the circumstances of the preparation had to aim of changing the coordination ability of water, 1,2-ethanediol and sulfate ion and hence to produce all possible complexes in this system. The following practical findings were made:

1. With increasing ratio of 1,2-ethanediol to metal ion, the 1,2-ethanediol content of the product increased and the water content decreased (complexes **2**, **3** and **5**).
2. Decrease of the dielectric constant of the solution by using ethanol resulted in the formation of a water-free complex (complex **1**).
3. When the solution was stored in a desiccator under P_2O_5 or when water and an organic phase system was used (the organic phase is a solvent which is strongly water attractive), complexes containing both water and 1,2-ethanediol molecules were formed.

Thermoanalytical behaviour of complexes

The thermoanalytical curves of the decomposition of the investigated complexes are shown in Fig. 1. When the complexes containing water molecules (complexes **2**, **3** and **4**) were heated, the water molecules were released firstly in the solid phase below 80°C. This step was accompanied by an endothermic heat effect (DTA curve). On increase of the temperature to 180°C, the complexes lost half (complex **2**) or one mole of 1,2-ethanediol (complexes **3** and **4**) and the mono-1,2-ethanediol manganese sulfate complex was formed as an intermediate decomposition product (the same in a stoichiometric sense as complex **1**). Similarly to the first step, this process was accompanied by an endothermic heat effect. The last step was the decomposition of $MnGlSO_4$ (*Gl*=glycol=1,2-ethanediol), which produced $MnSO_4$ as end-product. This process was accompanied by an exothermic heat effect.

There was no change in mass below 180°C in the course of the decomposition of complex **1**. Above 180°C, complex **1** decomposed similarly to the other complexes in this temperature range. Between 100 and 180°C, the water-free complex (**5**) gave the same decomposition product as complex **1** ($MnGlSO_4$). The composition of this decomposition product was the same as in the case of complex **1**.

The calculated and the found Δ*m*% values are presented in Table 2.

Table 2 Calculated and found Δ*m* % values for complexes **1–5**

Composition of complex	Δ*m*/%<100°C		Δ*m*/% 100–180°C		Δ*m*/% 180–400°C	
	meas.	calc.	meas.	calc.	meas.	calc.
$MnSO_4 \cdot H_2O$	–	–	–	–	12.0	10.7
$MnGlSO_4$	–	–	–	–	27.9	29.1
$MnGl_{1.5}(H_2O)1.5SO_4$	6.0	6.6	14.0	14.8	23.0	22.9
$MnGl_2(H_2O)SO_4$	6.0	6.1	23.3	21.1	20.0	21.1
$MnGl_2(H_2O)SO_4$	10.0	11.7	22.0	20.0	19.3	20.0
$MnGl_{3.5}SO_4$	–	–	38.0	42.1	16.6	16.7

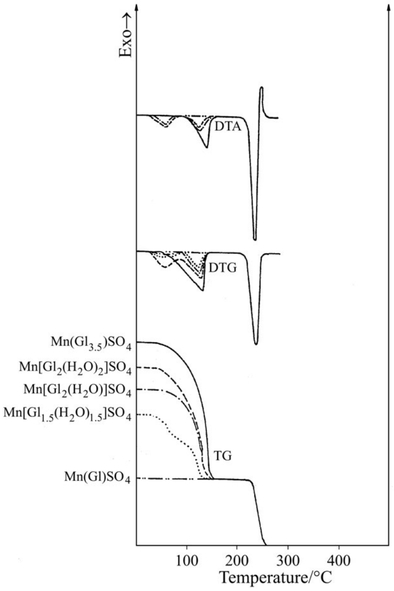

Fig. 1 Thermoanalytical curves of the decomposition of the investigated complexes

IR study

The characteristic stretching vibrations of OH (water and 1,2-ethanediol), of CO, of CC bonds of the 1,2-ethanediol and of the sulfate ion, and the deformation vibration of water molecule, were followed and compared with the corresponding bands of 1,2-ethanediol, water and $MnSO_4 \cdot 4H_2O$. They are shown in Table 3.

Table 3 Characteristic IR bands of complexes and their assignment

Band maxima of complexes and reference compounds							Assignment
1	**2**	**3**	**4**	**5**	Gl [10]	$MnSO_4 \cdot 4H_2O$	
			3540	3540			
	3450		3430	3430		3340	ν(OH) water
3330	3330	3300	3330	3400	3340		ν(OH) 1,2-ethanediol
			3200	3200		3200	
	1650	1650	1650			1620	δ(OH) water
1085	1085	1080	1085	1080	1087		
	1060	1060	1070	1070			
1040	1040	1040	1040	1040	1043		ν(CO and CC)
		1030					
1130	1150	1165	1180	1180		1180	$\nu_3(SO_4)$
1090	1130	1140	1130	1145		1130	
	1090	1090	1090	1130		1090	
1010	1010	1002	1010	990		1015	$\nu_1(SO_4)$
642	642	640	642	640		650	$\nu_4(SO_4)$
615	620	620	620	620		625	
	615	615	615	615		605	

3000–4000 cm^{-1}

In this wavenumber range, the stretching vibration of the OH band in water and 1,2-ethanediol could be observed. For liquid 1,2-ethanediol, this band is broad (3200–3400 cm^{-1}) because of the strong hydrogen-bond network.

1600–1700 cm^{-1}

The deformation vibration of coordinated water molecules could be observed in this wavenumber range. In the spectra of complexes **2**, **3** and **4** (containing water molecules) and $MnSO_4 \cdot 4H_2O$ the bands at 1650 and 1620 cm^{-1} are assigned to this vibration. Since the band maximum was higher for the complexes, it could be suggested that the water molecules in the investigated complexes are coordinated to the metal ion, but the strength of the bonding is weaker than in $MnSO_4 \cdot 4H_2O$.

1000–1200 cm^{-1}

The ν_3 vibration of the sulfate ion and the combined CC and CO stretching vibrations resulted in an intensive broad band with many shoulders and local peaks in this wavenumber range. The observed peaks could be interpretated by comparing this band and the bands in the 600–700 cm^{-1} range (4 vibration of sulfate ion). In this way, we could determine the peaks of the combined vibrations of the CC and CO bonds and hence determine the effect of coordination by 1,2-ethanediol. It could be stated that the coordinated 1,2-ethanediol molecules in the complexes show some changes in the bands of the complexes as compared with those of 1,2-ethanediol itself, which points to complex formation between the manganese ion and the 1,2-ethanediol molecule.

600–700 cm^{-1}

The ν_4 vibration of the sulfate ion could be observed in this wavenumber range. In accordance with theoretical considerations, 3, 2 or 1 bands could be observed in this range (similarly as in the 1000–1200 cm^{-1} range) if the binding mode of the sulfate ion was tridentate (or/and monodentate), bidentate or double bidentate, or tetracoordinated or non-coordinated, respectively.

In the spectrum of complex **1**, **2** bands were observed in this range, which indicates that the sulfate ion is bound in a monodentate or tridentate way, or in both tridentate (3 oxygen atoms) and monodentate (1 oxygen atom) ways. In the spectra of all the other complexes, **3** peaks could be observed, which points to the bidentate or double bidentate binding mode of the sulfate ion.

Magnetic susceptibility measurements

The magnetic data on the complexes are shown in Table 4. The experimentally determined μ_{eff} values were close to the theoretical value for high-spin complexes of the manganese(II) ion (5.92), and an octahedral coordination sphere around the manganese ion may be suggested in all of the complexes [9].

Table 4 Measured magnetic susceptibility data on complexes

Complex	**1**	**2**	**3**	**4**
μ_{eff}	5.71	5.99	5.72	5.76
Θ	5.91	–46.21	–47.76	–46.21
C	4.082	4.486	4.093	4.147
R	0.9834	0.9975	0.9978	0.9978

It was found that the magnetic susceptibility data followed the Curie–Weiss law. The Curie constants (Θ) indicated the presence of ferromagnetic (complex **1**) and antiferromagnetic (complexes **2**, **3** and **4**) interactions in the solid materials. In accordance with this magnetic behaviour, polymeric structures may be suggested for all of the complexes.

Conclusions

Both the preparative work and the thermoanalytical study demonstrated that the most characteristic compound among the investigated complexes is the complex **1**. It may be produced by a preparative route (using ethanol as dielectric constant-decreasing agent) or by heating the other complexes. In the IR spectra of all the complexes, some bands were observed around 3330, 1085 and 1040 cm^{-1}.

The IR study and the magnetic data on the investigated complexes suggest the composition of the coordination sphere around the manganese(II) ion, which is shown in Table 5. The suggested number of coordination sites (6) fits the IR data and the magnetic data.

Table 5 Suggested compositions of coordination spheres around the manganese(II) ion in the investigated complexes

Complex	Number of coordination sites		
	1,2-ethanediol	water	sulfate ion
1	2	–	3+1
2	2.5	1.5	2
3	3	1	2
4	2	2	2
5	4	–	2

A polymeric structure formed by sulfate ions and 1,2-ethanediol molecules (as bridging ligands) may be suggested for all of the investigated complexes.

As regards the manganese(II) ion, it may be concluded that it coordinates the sulfate ion relatively strongly; the water and 1,2-ethanediol molecules can not replace the sulfate ion in the coordination sphere of the manganese(II) ion. The water can be removed from the coordination sphere with a large excess of 1,2-ethanediol, by heating or with a water-attractive solvent (such as ethanol).

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