

PREPARATION, THERMOANALYTICAL AND IR STUDY OF MIXED-LIGAND COMPLEXES FORMED IN WATER-1,2-ETHANEDIOL-COBALT(II)SULFATE SYSTEMS

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Parent and mixed-ligand cobalt(II) complexes of different compositions were prepared with water, sulfate ion and 1,2-ethanediol as ligands. The magnetic susceptibility data, 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 were observed in the crystals plane.

Keywords: Co(II) complexes, 1,2-ethanediol, IR spectra, mixed-ligand complexes, thermoanalytical study

Introduction

It is well-known that a hydroxy (OH) group, in an aliphatic organic compound is a relatively weak donor group in respect of complexation of metal ions. However, some natural or artificial polyalcohols (e.g. sugars or cyclodextrins) can often absorb and transport metal ions in vivo [1, 2], which suggests the important coordinating ability of the OH groups. The most important chemical factor in these processes is complexation through the occurrence of coordination between OH groups and metal ions. To clarify the nature of the coordination between OH groups and metal ions, complexes of 1,2-ethanediol(Gl) with Cu(II), Fe(II), Zn(II), Ca(II), Mg(II), Cd(II), Mn(II) and Ni(II) ions were earlier prepared and investigated by thermoanalytical, magnetic susceptibility, IR spectroscopic and X-ray diffraction methods [3–9].

To complete this study from the aspect of theoretical considerations of the Irving-Williams series of metal ions [10], Co(II) complexes of 1,2-ethanediol have now been prepared and investigated by the above-mentioned methods. The metal ion source was $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, so that our earlier studies the coordination ability of 1,2-ethanediol, water and sulfate ion could be continued [3–9].

Experimental

Preparation of complexes

For the preparation of the complexes, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 1,2-ethanediol and water were mixed, the solid compound was dissolved, and different methods were

used to obtain solid complexes. The solid complexes were stored under CaCl_2 or P_2O_5 in a desiccator. The preparation was repeated several times to check the reproducibility. The details were as follows:

$\text{Co}(\text{Gl})_{1-1.5}(\text{H}_2\text{O})_{4-5}\text{SO}_4$ (complex 1)

20 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 10 cm³ of 1,2-ethanediol and 2 cm³ of water. In a refrigerator, solid crystals separated out during 1 day, the composition of which was close to that of the starting material, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, together with a small amount of 1,2-ethanediol. This solid was filtrated off and discarded. On the continued cooling, solid crystals precipitated out from the filtrate, these were separated by filtration, washed with ethanol and stored over CaCl_2 in a desiccator.

$\text{Co}(\text{Gl})_{1.5}(\text{H}_2\text{O})_4\text{SO}_4$ (complex 2)

5 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 5 cm³ of 1,2-ethanediol were mixed at room temperature. After some hours the mixture became a slurry. The precipitated solid compound was separated by filtration, washed with ethanol, dried and stored over CaCl_2 in a desiccator.

$\text{Co}(\text{Gl})_2(\text{H}_2\text{O})_{2-3}\text{SO}_4$ (complex 3)

5 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 10 cm³ of 1,2-ethanediol were mixed at room temperature. The mixture was filtered to remove the undissolved solid material. A mixture of ethanol (10 cm³) and benzene (20 cm³) was then added to the filtrate during stirring. The precipitated solid compound was separated by filtration, washed with ethanol, dried and stored over CaCl_2 or/and P_2O_5 in a desiccator.

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Co(Gl)₃(H₂O)₃SO₄ (complex 4)

5 g of CoSO₄·7H₂O was dissolved in 10 cm³ of 1,2-ethanediol by heating (70–80°C). The solution was stored over CaCl₂ in a vacuum desiccator. The pink crystals that precipitated from the solution after some days, were separated by filtration and washed with ethanol and ether. The solid material was stored over CaCl₂ in a desiccator.

Co(Gl)₃SO₄ (complex 5)

5 g of CoSO₄·7H₂O was dissolved in 10 cm³ of 1,2-ethanediol by heating (70–80°C). The solution was heated to evaporate the water content of the mixture, and then stored over P₂O₅ in a vacuum desiccator. Solid pink crystals precipitated from the solution after some days; they were separated by filtration and washed with ethanol and ether. The solid material was stored over P₂O₅ in a desiccator.

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 an air or nitrogen atmosphere and α-Al₂O₃ was used as 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 were taken in nujol in the interval 400–4000 cm⁻¹ with a DIGILAB instrument. The characteristic bands were utilized to

determine the coordination modes of the ligand, water molecules and sulfate ion.

Magnetic susceptibility measurements

The magnetic susceptibilities of the complexes were measured by the Faraday method, using CuSO₄ as a reference compound. A Bruker M15 magnet and a Sartorius microbalance were used.

Results and discussion*Preparation and compositions of complexes*

To prepare the cobalt – 1,2-ethanediol complexes, we primarily used the common methods, applied earlier to prepare other 1,2-ethanediol complexes [3–9]. The basic idea was to vary the temperature of the preparation, the ratio of the reactants, and the conditions of the storage of the prepared complexes. In contrast with the other 1,2-ethanediol metal complexes (e.g. those of Cu(II), Fe(II), Zn(II) and Ni(II) [3–6, 9]), these methods of preparation led to several complexes. Accordingly, we attempted a new way to obtain complexes: by adding an ethanol+benzene mixture (as a water-attractive agent) to a solution of cobalt sulfate and 1,2-ethanediol, the water content of the complexes could be decreased. This mode of preparation resulted in a complex with special thermal behaviour (complex 3).

The compositions of complexes 1 and 3 are uncertain, varying somewhat in the course of repeated experiments, and the composition was also strongly dependent on the condition of storage.

Magnetic susceptibility measurements

The magnetic data on the complexes are shown in Table 1. The experimentally determined μ_{eff} values are higher than the theoretical value for high-spin complexes of the cobalt(II) ion (3.83), and an octahedral coordination sphere around the cobalt(II) ion may be suggested for all of the complexes [11].

It was found that the magnetic susceptibility data followed the Curie–Weiss law. According to the Curie constant (Θ) values, all the complexes participate in antiferromagnetic interactions. This magnetic be-

Table 1 Magnetic data on the investigated complexes

Complex	Θ/°C	C	μ _{eff}	R
1	3.23	3.33	5.18	0.999
2	-10.82	3.24	5.11	0.997
3	-8.62	3.20	5.08	0.996
4	-17.85	3.30	5.17	0.997
CoSO ₄ ·7H ₂ O	-16.12	3.28	5.15	0.996

Table 2 Characteristic IR bands of complexes

Complex	Bands of SO_4^{2-}		Bands of CO bonds		Bands of H_2O	
	ν_4	ν_2	$\nu(\text{C}-\text{O})$		$\delta(\text{H}_2\text{O})$	
1,2-ethanediol	–	–	1085	1045	–	–
1	620	1150 1120	1085 1060	1040	1660	–
2	630 615	1170 1140 1110	1085 1070	1045 1030	1660	1730
3	630 610	1170 1110	1085 1070	1045 1030	1650	1730
4	630	1150 1110	1085 1080	1040	1650	–
5	630	1170 1130	1070	1030	–	–
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	610	1130	–	–	1650	–

haviour suggests a polymeric structure for all the complexes. Complex **5** is too sensitive to moisture for its magnetic behaviour to be determined.

IR spectroscopic measurements

In the IR spectra of the complexes, the bands of the water molecules, of the sulfate ion and the stretching vibration of the C–O bonds could be identified, the values of the band maxima are presented in Table 2. For comparison, the IR bands of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ are also listed.

Bands of the sulfate ion

A sulfate ion with T_d symmetry could be observed in $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, which correlates well with the structure of the molecule. In cobalt(II) sulfate heptahydrate, the sulfate ion is not coordinated to the cobalt(II) ions, it bound by hydrogen-bonds to water molecules [12]. In some 1,2-ethanediol complexes containing water molecules, the ν_2 and ν_4 stretching bands of the sulfate ion are split into two bands, indicating the C_{3v} symmetry of the sulfate ion. This means that the sulfate ion is coordinated by 1 oxygen atom to the metal ion in these complexes.

Bands of the water molecules

The coordinated water molecules in the hexa- and heptahydrate give a band with maximum at 1650 cm^{-1} (deformation vibration). This band could be observed in all off the water-containing complexes too, which show that coordinated water molecules are present in these complexes. The weak band at 1730 cm^{-1} indicates the presence of water bound by hydrogen-bonds (moisture water).

Bands of the 1,2-ethanediol molecule

1,2-Ethanediol gives 2 strong bands, with maxima at 1085 and 1045 cm^{-1} , assigned predominantly to the stretching vibration of the CO bond. Decreases in these band maxima are expected on coordination of the oxygen atom. This phenomenon can be observed in Table 2. In the IR spectra of complexes **1**, **2**, **3** and **4**, one or both of the CO bands of free 1,2-ethanediol are to be seen, with 2 other bands close each of these bands (1070 , 1060 , 1040 and 1030 cm^{-1}). These bands point to the presence of free and coordinated OH groups, i.e. the 1,2-ethanediol molecules act as monodentate and bidentate ligands.

The structure of the tris(1,2-ethanediol) complexes (like complex **5**) is known [13–15]: the 1,2-ethanediol molecules act as bidentate chelate ligands and the sulfate ion is located in the outer coordination sphere, bound by hydrogen-bonds. In accordance with this structure, the 1070 and 1030 cm^{-1} bands could be assigned to a bidentate 1,2-ethanediol.

Thermoanalytical behaviour of complexes

On the basis of the thermoanalytical behaviour, the investigated complexes can be divided into three groups (A, B and C).

Decomposition of type A

Complexes **1** and **2** lose most of their water and 1,2-ethanediol molecules below 100 and 150°C , respectively (Fig. 1). Analysis of the intermediates prepared at 200°C , showed that approximately 0.5 molecule of ethyleneglycol and 1 molecule of water remained in the solid compound. When the heating was stopped at 250°C , the product contained only 1 water molecule. The decomposition was accompa-

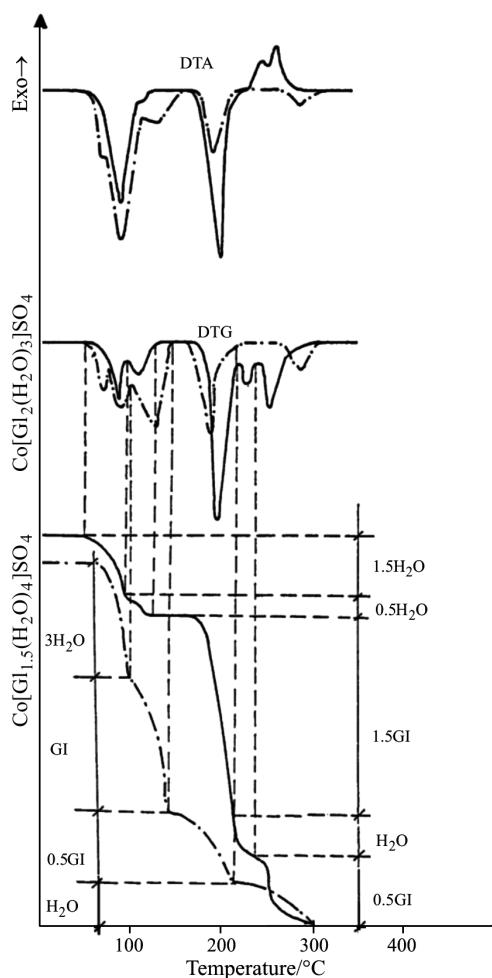
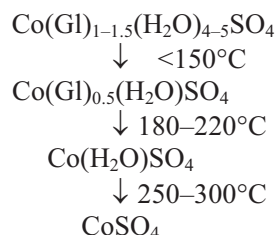


Fig. 1 Thermoanalytical curves of complexes of types --- A and — B

nied by endothermic effects and it was the same in air and in nitrogen atmosphere. The suggested decomposition scheme is as follows:



Decomposition of type B

Complexes **3** and **4** lose water molecules (two and three, respectively) and 1,2-ethanediol (one in the case of the complex **4**) molecules below 150°C and $\text{Co(Gl)}_2(\text{H}_2\text{O})_{0-1}\text{SO}_4$ bis complexes are formed. This step is endothermic. The bis complexes decompose between 180 and 250°C in endothermic process to give $\text{Co(Gl)}_x\text{SO}_4$ ($x=0.5$ and 0.66) and between 250 and 300°C in exothermic process to give CoSO_4 . The ratio of losses of masses is 2 to 1 in the case of the

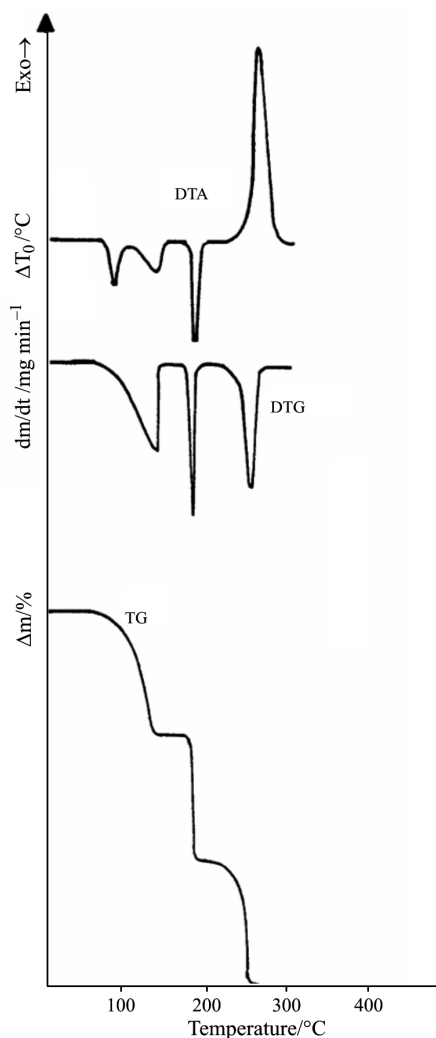
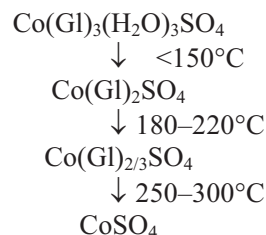


Fig. 2 Thermoanalytical curves of complexes of type C

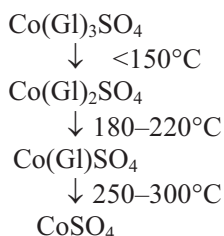
complex **4**. The decomposition scheme for complex **3** is shown on Fig. 1 and for complex **4** is as follows:



In a nitrogen atmosphere, the decomposition is the same as in air, but the exothermic effect is then not observed. This points to the oxidation of 1,2-ethanediol in air at this temperature.

Decomposition of type C

The tris(1,2-ethanediol) cobalt complex (**5**) decomposes in 3 steps: one molecule of the 1,2-ethanediol leaves the solid phase in each step. The third step is exothermic (Fig. 2). The decomposition scheme is as follows:



Conclusions

The magnetic and IR data indicate that in all the investigated cobalt complexes the sulfate ion, the water and the 1,2-ethanediol molecules form an octahedral coordination sphere around the cobalt(II) ion. The water and the sulfate ion are coordinated as monodentate ligands, while in the case of 1,2-ethanediol there are several possibilities. The 1,2-ethanediol molecule may coordinate to a metal ion through 1 or 2 oxygen atoms (as a mono- or bidentate ligand). In the latter case, bridging or chelating binding occurs. Earlier studies found that, in the presence of water, 1,2-ethanediol always acts as a bridging ligand: chelation exists only in the water-free complexes [3–7]. The suggested polymeric structure for the mixed-ligand complexes (complexes 1–4) could be explained by the bridging coordination. This was also observed in other mixed-ligand metal complexes of 1,2-ethanediol ($M=\text{Mn}$, Zn , Cu and Ni) [3, 5–9]. In the tris(1,2-ethanediol) complex, the molecule forms a chelate and the structure is not polymeric [13–15].

It is known that cobalt sulfate heptahydrate loses 6 water molecules at approximately 100°C (depending on the heating rate). Only 1 water molecule can bind to metal sulfates above 150°C ; the water oxygen atom and the sulfate oxygen atoms complete the octahedral coordination sphere. In the mixed-ligand complexes, besides the water, the 1,2-ethanediol molecules can compete with the sulfate oxygen atoms for the coordination sites. This competition depends on the amounts of water and 1,2-ethanediol, and on the binding modes of water and 1,2-ethanediol in the complex.

From the aspect of thermal behaviour, complex 4 seems to be characteristic. On heating, this complex loses all its water below 150°C and a bis(1,2-ethanediol) complex is formed, which decomposes in 2 steps between 180 and 250°C . In the first step, 4/3 molecules of 1,2-ethanediol are released from the solid phase. Similar behaviour was observed in the case of $\text{Zn}(\text{1,2-ethanediol})\text{SO}_4$ [4] and pyridine or picoline complexes of nickel, cobalt, zinc and cadmium halides [16]. Such compositions of the intermediate were interpreted in terms of a polymeric and layered structure.

In complexes 1 and 2, there is not enough 1,2-ethanediol to form a bis complex on heating, so the intermediate (above 150°C) contains both water

and 1,2-ethanediol, in approximately the same ratio as present in the complexes (0.5–1).

In complex 4, there are more than 2 molecules 1,2-ethanediol, and thus the bis(1,2-ethanediol) intermediate complex is formed on heating above 150°C . On further heating, this intermediate decomposes in a similar way as complex 3.

In complex 5, there is no water and the 1,2-ethanediol molecules are bound via chelation. On heating, the bis(1,2-ethanediol) complex also forms as an intermediate, which decomposes in a different way from the intermediates of complexes 3 and 4. Because of the chelation of 1,2-ethanediol, there is no possibility for the formation of polymeric structure, which was suggested for the decomposition products of complexes 3 and 4.

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Received: March 30, 2005

In revised form: May 20, 2005

DOI: 10.1007/s10973-005-7011-2