Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 55–61

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

I. Labádi[1*], *G. Kenessey*[2] *and G. Liptay*[2]

[1]Department of Inorganic and Analytical Chemistry, University of Szeged, H-6720, Szeged, Dóm tér 7, Hungary
[2]Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest, Gellért tér 4, Hungary

Mixed ligand nickel(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 in the crystal state were observed. All complexes are sensitive for moisture. The bis complex proved to be the more stable complex.

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

Introduction

It is well known that the hydroxyl substituent (OH) in aliphatic organic compounds is a relatively weak donor group for the complexing 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]. The most important chemical factors in these processes are hydrogen-bonding and complexation, i.e. the formation of coordination bond(s) between the OH group and metal ions. For the characterization of these processes, IR spectroscopy and thermal analysis are often used [3–5].

To clarify the nature of the coordination bond between the OH group and metal ions, complexes of 1,2-ethanediol (glycol=Gl) with Cu(II), Fe(II), Zn(II), Ca(II), Mg(II), Cd(II) and Mn(II) ions were earlier prepared and investigated by thermoanalytical, magnetic susceptibility, IR spectroscopic and X-ray diffraction methods [6–11].

Nickel(II) complexes of 1,2-ethanediol have now been prepared and investigated by the above-mentioned methods. Besides the theoretical interest in the Ni(II) ion in coordination chemistry, its choice was supported by preliminary experiments. The Ni(II) ion forms many complexes with 1,2-ethanediol. As concerns the metal ions investigated to date, the number of complexes that can be reproducibly prepared is the largest for the Ni(II) ion. This gives a possibility for determination of the connection between the conditions of preparation and the compositions of the complexes. As earlier, the metal ion source was the sulfate ($NiSO_4 \cdot 7H_2O$) and the coordination abilities of 1,2-ethanediol, water and sulfate ion were studied [6–11].

Experimental

Preparation of complexes

$NiSO_4 \cdot 7H_2O$, 1,2-ethanediol and water were mixed to form solutions and different methods were used to obtain the solid complexes. As reference compound, commercial $NiSO_4 \cdot 7H_2O$ was used (Complex **0**). The latter were stored over $CaCl_2$ or P_2O_5 in desiccator. The preparation details are as follows:

Complexes **1** and **2**

20 g of $NiSO_4 \cdot 7H_2O$ was dissolved in a solution of 10 cm^3 of 1,2-ethanediol in 2 cm^3 of water (the ligand to metal ratio was approximately 1:2.25). The solution was stored under laboratory conditions at room temperature (complex **1**) or was heated to boiling and ethanol was added to the cooled solution (complex **2**). After some days (complex **1**) or after some hours (complex **2**), crystals precipitated from the solution; they were separated by filtration, washed by ethanol and stored over P_2O_5 in a desiccator.

Complexes **3** and **4**

5 g of $NiSO_4 \cdot 7H_2O$ and 5 cm^3 (complex **3**) or 10 cm^3 (complex **4**) of 1,2-ethanediol were mixed at room temperature (the ligand to metal ratio was approximately 1:9). The mixture was filtered to remove undissolved solid material, and 5 cm^3 of ethanol and 5 cm^3 of benzene were added to the filtrate during stirring. The precipitated solid compound was separated by filtration, washed by ethanol and dried and stored over P_2O_5 in desiccator.

---

[*] Author for correspondence: dome@chem.u-szeged.hu

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Complex **5** and **6**

10 g of $NiSO_4{\cdot}7H_2O$ was dissolved in 10 cm^3 of 1,2-ethanediol (the ligand to metal ratio was 1:4.5) by heating at 80–100°C and the solution was stored at room temperature under laboratory conditions (complex **5**) or over P_2O_5 in vacuum desiccator (complex **6**). After some days, solid compounds precipitated from the solutions; which were filtered off, washed by ethanol and dried.

Complexes **7** and **8**

5 g of $NiSO_4.7H_2O$ was dissolved in 5 cm^3 of 1,2-ethanediol by heating at 80–100°C. 5 cm^3 of ethanol and 5 cm^3 of benzene were added to the filtrate during stirring (the ligand to metal ratio was 1:4.5). The precipitated solid compound was separated by filtration, washed with ethanol, dried and stored under laboratory conditions or/and over $CaCl_2$ in a desiccator (complex **7**) or over P_2O_5 in a vacuum desiccator (complex **8**).

Complexes **9** and **10**

10 g of $NiSO_4{\cdot}7H_2O$ was dissolved in 15 cm^3 of 1,2-ethanediol by heating (70–80°C). (the ligand to metal ratio was 1:7). The solution was stored over P_2O_5 in a vacuum dessiccator. After several days, green crystals precipitated from the solution; they were separated by filtration and washed with ethanol and diethylether. The solid material was stored over $CaCl_2$ in a desiccator (complex **9**) or over P_2O_5 in a vacuum desiccator (complex **10**).

Determination of composition

The metal, 1,2-ethanediol and water contents of the complexes were determined by classical analytical methods (complexometry, The Malaprade reaction and the 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-Al_2O_3 was used as reference substance. Decomposition intermediates were obtained 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 the nujol method in the wavenumber range in 400–4000 cm^{-1}. The characteristic bands were followed to determine the co-ordination modes of the ligand and water molecules or the sulfate ion.

Magnetic susceptibility measurements

The magnetic susceptibilities of the complexes were measured by the Faraday method, using $CuSO_4{\cdot}5H_2O$ as reference compound. A Bruker M15 magnet and a Sartorius microbalance were used.

Results and discussion

Determination of the compositions of the complexes

The compositions of the complexes are presented in Table 1. The analyses relevant that two types of complexes, water-free and water-containing complexes, were prepared.

In the course of the preparative work, the metal ion to ligand ratio was varied, different solvents were used to change the dielectric constants of the solutions, and common desiccating agents ($CaCl_2$ or P_2O_5) were or were not applied. These changes in the preparation conditions had to aim of changing the co-ordination abilities of water, 1,2-ethanediol and sulfate ion and hence to obtain all of the possible complexes in this system. The following practical findings were observed.

- On increase of the ratio of 1,2-ethanediol to metal ion, the 1,2-ethanediol content of the complex increased and the water content decreased.
- On decrease of the dielectric constant of the solution by using ethanol or a mixture of ethanol and benzene, the complex formed had a lower with water content.
- When the solution or the solid complex was stored over $CaCl_2$ or P_2O_5 in a desiccator, complexes containing both water and 1,2-ethanediol molecules were formed. In the presence of P_2O_5, the water content of the complex formed decreased or disappeared.

Thermoanalytical behaviour of complexes

The complexes could be divided into three groups on the basis of their compositions and thermal behaviour. The first group comprises complexes **1, 2, 3** and **4,** which contain 1, 1, 1.5 and 1.5 mol of ethylene glycol and 5, 4, 4 and 3.5 mol of water, respectively. The second group comprises complexes **5, 6, 7** and **8**, which contain 2 mol of glycol and 0, 2, 3 or 4 mol of

Table 1 Suggested compositions of complexes with the theoretical and measured metal, glycol and water contents

Complex	Composition	% of metal		% of glycol		% of water	
		Theor.	Meas.	Theor.	Meas.	Theor.	Meas.
1	$Ni(Gl)(H_2O)_5SO_4$	19.14	18.94	20.23	21.00	29.34	28.00
2	$Ni(Gl)(H_2O)_4SO_4$	19.00	19.45	21.47	21.59	24.92	23.50
3	$Ni(Gl)_{1.5}(H_2O)_4SO_4$	18.36	18.25	29.10	29.25	22.50	21.50
4	$Ni(Gl)_{1.5}(H_2O)_{3.5}SO_4$	18.89	18.64	29.90	30.50	20.30	18.20
5	$Ni(Gl)_2(H_2O)_4SO_4$	16.72	16.53	35.37	34.78	20.53	19.40
6	$Ni(Gl)_2(H_2O)_3SO_4$	17.74	17.75	36.91	36.86	16.32	15.01
7	$Ni(Gl)_2(H_2O)_2SO_4$	18.64	18.47	39.42	40.19	11.43	9.01
8	$Ni(Gl)_2SO_4$	21.05	20.72	44.51	45.22	–	–
9	$Ni(Gl)_3(H_2O)_3SO_4$	14.87	14.97	47.10	47.59	13.67	–11.10
10	$Ni(Gl)_3SO_4$	17.22	17.31	54.61	53.63	–	–

water. Complexes **9** and **10**, containing 3 mol of glycol and 0 or 3 mol of water form the third group. These groups of complexes exhibit different types of thermoanalytical curves (type **A**, **B** or **C**).

Thermal behaviour of type A

The thermoanalytical curves of complexes **1** and **3** are shown in Fig. 1 and the suggested decomposition scheme is presented in Fig. 2. The TG curve could be divided into four parts; below 150°C, between 150–170 and 200°C, between 200 and 300°C, and above 300°C.

Below 150°C, 3 or 4 peaks could be observed in the DTG curves, which means that the water molecules in the complexes are bound with different strengths, that is they are located in different surroundings. The release of the water molecules is accompanied by an endothermic effect in the DTA curves. One water molecule is not released from the solid complexes up to 300°C.

Between 200 and 300°C all the glycol molecules are released from the solid compound, starting with an endothermic followed by an exothermic effect in air. In a nitrogen atmosphere, this process is accompanied by an endothermic effect.

Above 300°C, the last water molecule is released from the solid sample. This water molecule is the ‘sulfate’ water molecule, which is characteristic for many metal sulfates. We found that, the last water molecule in $NiSO_4{\cdot}7H_2O$ (complex **0**) is released from the solid matrices between 300 and 400°C.

In a nitrogen atmosphere, the same TG and DTG curves resulted with only an endothermic in the DTA curves.

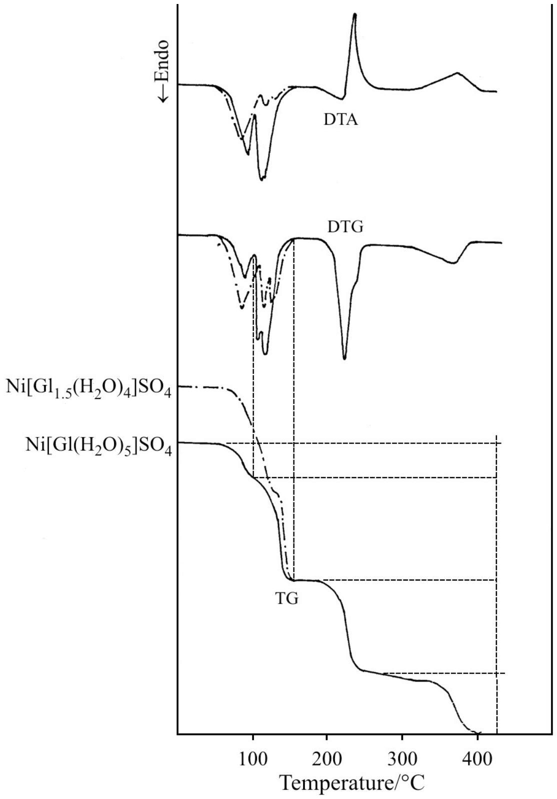

Fig. 1 Thermoanalytical curves of complexes of type **A**

Thermal behaviour of type B

The complexes in the second group (containing 2 glycol molecules) lose all their water molecules below 150°C in one, two or three steps, and the glycol molecules are released from the solid matrices between 200 and 300°C. The final decomposition product is $NiSO_4$. Typical thermoanalytical curves and the suggested decomposition scheme are shown in Figs 3 and 4, respectively.

$$\begin{array}{l} \mathrm{Ni(Gl)_{1–1.5}(H_2O)_{3–4}SO_4} \\ \downarrow \quad <170°\mathrm{C} \\ \mathrm{Ni(Gl)_{1–1.5}(H_2O)SO_4} \\ \downarrow \quad 200–300°\mathrm{C} \\ \mathrm{Ni(H_2O)SO_4} \\ \downarrow \quad >300°\mathrm{C} \\ \mathrm{NiSO_4} \end{array}$$

Fig. 2 Decomposition scheme of complexes **1, 2, 3** and **4**

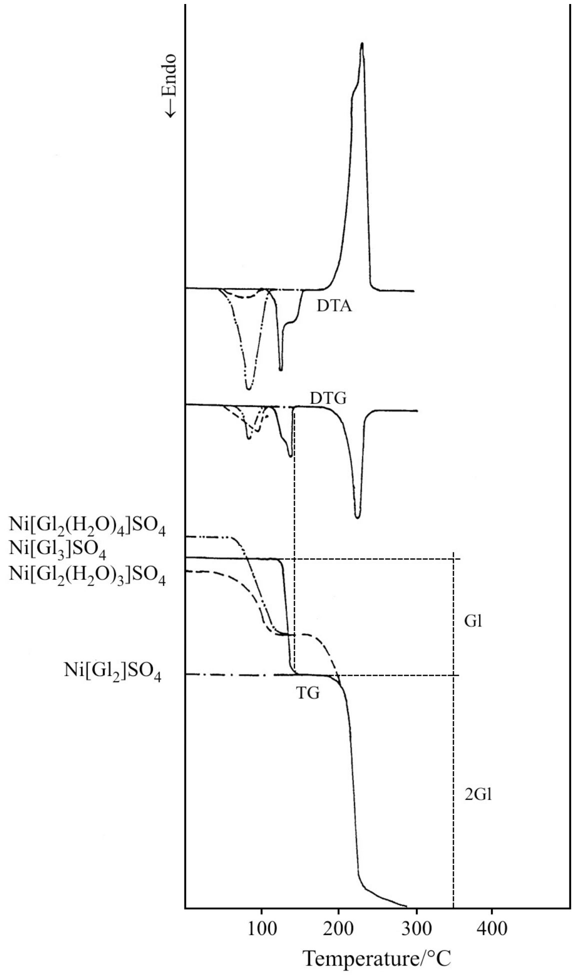

Fig. 3 Thermoanalytical curves of complexes of type **B** and **C**

$$\begin{array}{l} \mathrm{NiGl_2(H_2O)_{2–4}SO_4} \\ \downarrow \quad <150°\mathrm{C} \\ \mathrm{NiGl_2SO_4} \\ \downarrow \quad 200–300°\mathrm{C} \\ \mathrm{NiSO_4} \end{array}$$

Fig. 4 Decomposition scheme of complexes **5, 6, 7** and **8**

The release of the water molecules is accompanied by an endothermic effect, while the glycol molecules are released from the solid samples to the accompaniment of an exothermic effect in air. In nitrogen all the decomposition steps are accompanied by endothermic effects.

Thermal behavior of type **C**

The water-free and the water-containing tris-glycol complexes (complexes **9** and **10**) lose all their water and 1 mol of glycol below 150°C, with an endothermic effect (Fig. 3). The decomposition product is Ni(Gl)$_2$SO$_4$ (complex **8**), which decomposes to NiSO$_4$ between 200 and 300°C, as for the complexes of the second group. This process is exothermic in air and endothermic in nitrogen. The suggested decomposition scheme is shown in Fig. 5.

IR study

The characteristic stretching vibration of O–H (water and 1,2-ethanediol), C–O, the C–C of 1,2-ethanediol and sulfate ion, and deformation vibration of the water molecule were compared to the same bands of 1,2-ethanediol, water and NiSO$_4$·7H$_2$O. The observed IR bands are shown in Table 2.

$$\begin{array}{l} \mathrm{NiGl_3(H_2O)_{0\,or\,3}SO_4} \\ \downarrow \quad <150°\mathrm{C} \\ \mathrm{NiGl_2SO_4} \\ \downarrow \quad 200–300°\mathrm{C} \\ \mathrm{NiSO_4} \end{array}$$

Fig. 5 Decomposition scheme of complexes **9** and **10**

3000–4000 cm^{-1}

In this wavenumber range the stretching vibration of OH band of the water and 1,2-ethanediol molecules could be observed. In the case of liquid 1,2-ethanediol this band is broad (with maxima at 3200–3400 cm^{-1}) owing to the strong hydrogen-bond network.

In the spectra of the complexes, a very broad band with shoulders and many local maxima could be observed (Table 2), which point to the presence of OH groups located in different surroundings. Both the water molecules and the glycol OH groups form hydrogen-bonds and/or coordination bonds. The glycol molecules can coordinate to the nickel(II) ion by both monodentate and bidentate (chelate or bridging mode) binding modes. The large number of possible binding modes result in the local maxima.

1600–1800 cm^{-1}

The deformation vibration of coordinated and/or hydrogen-bonded water molecules could be observed in

Table 2 Characteristic IR bands of complexes and their assignments

Complex	ν(OH)	δ(OH)	ν(CO, CC)	$\nu_3(SO_4)$	$\nu_1(SO_4)$	$\nu_4(SO_4)$
$NiSO_4·7H_2O$	3340	1640		1100	985	630
	3280					(615)
	3200					
$Ni(Gl)(H_2O)_5SO_4$	3520	1640	1085	1150	985	630
	3410		1060	1110		615
	3320		1040			
	3220		1025			
	3200					
$Ni(Gl)(H_2O)_4SO_4$	3600sh	1640	1085	1110	990	630
	3410sh		1060		970	(615)
	3240br		1030			
$Ni(Gl)_{1.5}(H_2O)_4SO_4$	3400sh	(1740)	1085	1170	1000	645
	3260	1640	1070	1120	965	600
	3180		1050			
			1030			
$Ni(Gl)_{1.5}(H_2O)_{3.5}SO_4$	3400sh	(1740)	1085	1145	1000	630
	3320sh	1640	1070	1110	965	600
	3200br		1045			
			1030			
$Ni(Gl)_2(H_2O)_4SO_4$	3550sh	1640	1085	1145	985	630
	3410		1060	1110		615
	3320		1040			
	3220		1030			
$Ni(Gl)_2(H_2O)_3SO_4$	3550sh	(1735)	1085	1140	985	630
	3400sh	1640	1060	1110		615
	3250br	(1565)	1045			
	3180sh		1030			
$Ni(Gl)_2(H_2O)_2SO_4$	3540sh	1640	1085	1140	985	630
	3410sh		1060	1110		615
	3250		1045			
	3180sh		1030			
$Ni(Gl)_2SO_4$	3560sh		1080	1140	985	630
	3410sh		1040	1120		615
	3320br					
	3200br					
$Ni(Gl)_3(H_2O)_3SO_4$	3200br	1730	1085	1145	985	630
		1620	1055	1100	975	600
			1035			
			1020			
			1010			
$Ni(Gl)_3SO_4$	3580		1085br	1145	985	630
	3420		1050br	1100		615
	3340		1030br			
	3200br					

this wavenumber range. In the spectra of complexes **1–7** and **9**), (containing water molecules) and $NiSO_4{\cdot}7H_2O$ (complex **0**) the bands at 1740, 1640, 1620 cm^{-1} are assigned to this vibration. Since the band maxima are the same for the complexes and for $NiSO_4{\cdot}7H_2O$, it may be suggested that the water molecules in the investigated complexes are coordinated to the metal ion in a similar way as in $NiSO_4{\cdot}7H_2O$. The 1620 cm^{-1} band in the IR spectrum of complex **9** can be interpreted by the presence of a water molecule which is coordinated to the nickel(II) ion, forming a very strong hydrogen-bond.

1000–1200 cm^{-1}

The ν_3 vibration of the sulfate ion and the combined C–C and C–O stretching vibrations of 1,2-ethanediol result in an intense broad band with many shoulders and local peaks in this wave number range. The observed peaks could be interpreted by comparing this band and the bands at 600–700 cm^{-1} (the ν_4 vibration of the sulfate ion). In this way we can distinguish between the peaks of the combined vibrations of the C–C and C–O bonds and the peaks of the sulfate ion. This revealed that the 1,2-ethanediol molecules coordinated in the complexes demonstrate some changes as compared with the 1,2-ethanediol itself, which points to complex formation between the nickel(II) ion and the 1,2-ethanediol molecule.

Liquid 1,2-ethanediol has two bands in this wavenumber range, at 1085 and 1045 cm^{-1} [12, 13]. In the IR spectra of complexes **1–10,** 2–9 bands could be observed, assigned to the combined C–C and C–O bonds. They include the bands of the free (or hydrogen-bonded) OH bond (at 1085 and 1045 cm^{-1}). The bands at 1070, 1060, 1055, 1050, 1040, 1030, and 1025 cm^{-1} could be assigned to the vibration of the coordinated 1,2-ethanediol molecules. These changes are indicative of complexation and of the different modes and strengths of binding of 1,2-ethanediol to the nickel(II) ion.

900–1000 cm^{-1}

In this wavenumber range, the $\nu_1(SO_4)$ band could be observed. Complexes **1–4,** which exhibit thermoanalytical behaviour of type **A**, have 2–5 bands in this range (at 1000, 990, 985, 970, 975 and 965 cm^{-1}). Complexes **4–8** and **9** and **10** display only one or two bands in this wavenumber range (985 cm^{-1}), which indicates the unique role of the sulfate ion in the bis and tris (1,2-ethanediol) complexes. On the basis of the different $\nu_1(SO_4)$ values for the complexes, the presence of sulfate ion in different surroundings in the complexes could be suggested.

600–700 cm^{-1}

The ν_4 vibration of the sulfate ion could be observed in this wavenumber range. According to theoretical considerations [14], the binding mode of the sulfate ion (tridentate (or monodentate), bidentate or double bidentate, equally tetracoordinated or non-coordinated) may result in a doublet, a triplet or unsplit bands in the IR spectra. In the spectra of all the complexes, one or two bands were observed in this range, revealing that the sulfate ion is coordinated in a monodentate or tridentate way to the nickel(II) ion, or hydrogen-bonded to water or 1,2-ethanediol molecules.

Magnetic susceptibility measurements

The magnetic data on the complexes are shown in Table 3. The experimentally determined μ_{eff} values are close to the theoretical value for high-spin complexes of the nickel(II) ion(3.83) and an octahedral coordination sphere around the manganese ion may be suggested for all of the complexes [15].

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. According to this magnetic behaviour, a polymeric structure may be suggested for all the complexes.

Table 3 The magnetic data of complexes

Comp	Composition	Θ	C	μ_{eff}
0	$NiSO_4{\cdot}7H_2O$	–10.1	1.22	3.14
1	$Ni(Gl)(H_2O)_5SO_4$	–6.13	1.19	3.10
2	$Ni(Gl)(H_2O)_4SO_4$	–9.82	1.16	3.09
3	$Ni(Gl)_{1.5}(H_2O)_4SO_4$	–6.5	1.19	3.10
4	$Ni(Gl)_{1.5}(H_2O)_{3.5}SO_4$	–12.9	1.10	2.99
5	$Ni(Gl)_2(H_2O)_4SO_4$	–8.2	1.28	3.19
6	$Ni(Gl)_2(H_2O)_3SO_4$	–10.1	1.17	3.82
7	$Ni(Gl)_2(H_2O)_2SO_4$	–12.6	1.10	2.98
8	$Ni(Gl)_2SO_4$	–8.9	1.10	2.98
9	$Ni(Gl)_3(H_2O)_3SO_4$	–10.1	1.28	3.20
10	$Ni(Gl)_3SO_4$	–10.9	0.99	2.82

Conclusions

Six water molecules are coordinated to the nickel(II) ion in the $NiSO_4{\cdot}7H_2O$ molecule, while the 7th water is hydrogen-bonded between the sulfate ion and one of the coordinated water molecules [16]. The characteristic IR bands of the sulfate ion (Table 2) in all the complexes and in the $NiSO_4{\cdot}7H_2O$ molecule are similar, so the same role of the sulfate ion may be suggested in all the complexes and in the $NiSO_4{\cdot}7H_2O$

molecule. This role is participation in the formation of hydrogen-bonds. This leads to the conclusion that the sulfate ion is not coordinated in the investigated complexes, i.e. only water and 1,2-ethanediol molecules are present in the octahedral coordination sphere.

One 1,2-ethanediol molecule can replace one or two water molecules in the coordination sphere. In the latter case, the 1,2-ethanediol may replace water molecules in the coordination sphere of one (chelate) or two nickel(II) ions (bridging). In the wavenumber range 1000–1100 cm^{-1} in the IR spectra (combined C–C and C–O bonds, which change on coordination) besides the bands of the non-coordinated 1,2-ethanediol (1085 and 1045 cm^{-1}), 7 new bands could be observed. The presence of several different forms of coordinated 1,2-ethanediol could be suggested, as follows:

- Monodentate: one of the OH groups in 1,2-ethanediol is coordinated, while the other is not.
- Bidentate chelate mode: both OH groups are coordinated to the same nickel(II) ion.
- Bidentate bridging mode: the OH groups of the 1,2-ethanediol molecule are coordinated to two nickel(II) ions. Our earlier experience [8] and the magnetic susceptibilty measurements suggest that the bridging mode of 1,2-ethanediol is dominant.

Acknowledgements

Besides the formation of coordination bonds via O atoms, the OH groups of 1,2-ethanediol can form hydrogen-bonds with coordinated or non-coordinated water molecules, with the sulfate ion and with an other 1,2-ethanediol molecule. The variety of the possible modes of coordination and of hydrogen-bonding result in the presence of water molecules with different thermal behaviour and 1,2-ethanediol molecules with many IR bands in the wavenumber range 1000–1100 cm^{-1}.

References

1 P. Saltman, J. Chem. Ed., 42 (1965) 682.
2 B. Gyurcsik and L. Nagy, Coord. Chem. Rev., 203 (2000) 81.
3 Á. Gombás, P. Szabó-Révész, G. Regdon Jr. and I. Erős, J. Therm. Anal. Cal., 73 (2003) 615.
4 F. Taneri, T. Güneri, Z. Aigner, O. Berkesi and M. Kata, J. Therm. Anal. Cal., 73 (2003) 769.
5 D. Giron, J. Therm. Anal. Cal., 68 (2002) 335.
6 I. Labadi, K. Burger, G. Liptay, M. Czugler and A. Kalman, J. Thermal Anal., 31 (1986) 1171.
7 I. Labadi, G. Liptay, A. Horvath, L. Korecz, S. Papp and K. Burger, J. Thermal Anal., 32 (1987) 1575.
8 I. Labadi, G. Bernat, G. Kenessey, L. Parkanyi, J. Mink and G. Liptay, Polyhedron, 11 (1992) 2975.
9 I. Labadi, L. Parkanyi, G. Kenessey and G. Liptay, J. Cryst. Spectroscopic Res., 23 (1993) 333.
10 I. Labadi, G. Kenessey and G. Liptay, J. Therm. Anal. Cal., 69 (2002) 487.
11 I. Labadi, I. Lakos, G. Kenessey and G. Liptay, J. Therm. Anal. Cal., 76 (2004) 829.
12 P. Buckley and P. A. Giguere, Can. J. Chem., 45 (1967) 397.
13 H. Matsuura and T. Miyazawa, Bull. Chem. Soc. Japan, 40 (1967) 85.
14 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', Fifth Edition, John Wiley and Sons Inc., 1997.
15 B. N. Figgis, J. Lewis, 'The Magnetic Properties of Transition Metal Complexes' in 'Progress in Inorganic Chemistry', Ed. F. A. Cotton, Interscience, New York, Vol. 6. p. 179, (1964)
16 R. G. W. Wyckoff, Crystal Structures, 2nd ed., Interscience, Vol. 3. (1965)

Received: January 12, 2005
In revised form: Marc 8, 2005

DOI: 10.1007/s10973-005-6358-8