Journal of Thermal Analysis and Calorimetry, Vol. 69 (2002) 487–497

PREPARATION AND CHARACTERIZATION OF Mg(II)-, Ca(II) AND Cd(II) COMPLEXES OF 1,2-ETHANEDIOL AND WATER

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, Budapest University of Technology and Economics, H-1521 Budapest, Gellért tér 4, Hungary

(Received December 3, 2001; in revised form January 18, 2002)

Abstract

Mixed ligand complexes of different compositions were prepared with water, sulfate ion and 1,2-ethanediol as ligand. 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, 1,2-ethanediol molecules of ‘crystal’ and ‘monohydrate’ type were found, depending on the type of binding of the oxygen atoms.

Keywords: 1,2-ethanediol, IR spectra, Mg(II), Ca(II) and Cd(II) complexes, mixed ligand complexes, thermoanalytical study

Introduction

To compare the coordination abilities of water and 1,2-ethanediol (*L*), some parent and mixed ligand complexes of water, 1,2-ethanediol and divalent metal sulfates (of Cu(II), Zn(II) and Fe(II) were earlier prepared and their thermochemical behaviour (<400°C) was investigated in our laboratory [1–4]. It was observed that the Cu(II), Fe(II) and some Zn(II) complexes (similarly to the metal sulfate hydrates) decompose in two endothermic steps. Most of the water and 1,2-ethanediol molecules are released from the solid phases between 100 and 200°C. The intermediate products ($MLSO_4$, $M(H_2O)SO_4$ or $ML_x(H_2O)_ySO_4$, x=0.25, y=0.5) decompose between 200 and 300°C to give MSO_4 as final product. On the basis of this observation, the coordination abilities of water and 1,2-ethanediol were considered to be similar.

The exceptional Zn(II) complexes decompose between 100 and 200°C in the same manner as the Cu(II) and Fe(II) complexes. An endothermic process could be observed with $ZnLSO_4$ as intermediate, which decomposes in two exothermic steps between 200 and 300°C to give $ZnL_{1/3}SO_3$ and $ZnSO_4$ as a final products in air. In nitrogen atmosphere, the decomposition was not accompanied by heat evolution.

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

To interpret this phenomenon, a strong bond (existing in the complexes originally or formed on heating) was suggested, which prevents release of the 1,2-ethanediol molecules without chemical decomposition [4]. This chemical decomposition proceeds with combustion in air and causes heat evolution. In nitrogen atmosphere, the combustion, and consequently the heat evolution, is absent.

In order to identify this strong bond, it was decided to prepare and study complexes of water and 1,2-ethanediol with other metal ions. The Mg(II), Ca(II) and Cd(II) ions were chosen, which coordinate water and 1,2-ethanediol differently in solution [5] and in the solid phase with chloride as anion [6, 7]. Derivatography and IR spectroscopy were chosen as experimental methods.

Experimental

Preparation of complexes

Reproducible procedures for the preparation of the complexes were decided by mixing metal sulfate hydrate, water and 1,2-ethanediol in different molar ratios and by using different methods (heating, and mixing with organic solvents) for dissolution of the metal sulfate and producing the solid complexes. The compositions of the solid complexes were determined. In spite of many attempts, we were not able to prepare anhydrous parent 1,2-ethanediol complexes.

The reproducibility of the procedure was accepted if the composition of the solid material was reproducible within 1% relative error. The following procedures were accepted:

$MgL(H_2O)_2SO_4$ (**1**): 5 g $MgSO_4\cdot7H_2O$ was dissolved in a mixture of 1,2-ethanediol (10.0 cm^3) and water (2.0 cm^3) by heating to 60°C. The solution was left to stand at room temperature. After 1–2 days, a white solid compound was formed. This was collected by filtration, washed with ethanol and stored in a desiccator over $CaCl_2$.

$MgL_2(H_2O)_2SO_4$ (**2**): 5 g $MgSO_4\cdot7H_2O$ was dissolved in 10 cm^3 1,2-ethanediol by heating to 100–110°C. In the course of heating, the $MgSO_4\cdot7H_2O$ dissolved at 50–60°C, a suspension was formed at higher temperature. The solid complex was collected by filtration, washed with diethyl ether and stored in a desiccator over P_2O_5.

$MgL_3(H_2O)_2SO_4$ (**3**): 5 g $MgSO_4\cdot7H_2O$ was dissolved in 20 cm^3 1,2-ethanediol by heating to 50°C. A small amount of solid material was formed at room temperature after 1–2 days. This was collected by filtration, washed with diethyl ether and stored in a desiccator over P_2O_5.

$CdL_{2/3}(H_2O)SO_4$ (**4**): 5 g $CdSO_4\cdot8/3H_2O$ and 10 cm^3 1,2-ethanediol were heated together at 100–120°C for 10–20 min. The solid compound was separated by filtration, washed with diethyl ether and stored in a desiccator over $CaCl_2$.

$CdL(H_2O)SO_4$ (**5**): Mixture of 2 g $CdSO_4\cdot8/3H_2O$ and 20 cm^3 1,2-ethanediol was refluxed for 1 h. A pale-yellow solid was formed. It was collected by filtration, washed with ethanol and diethyl ether and stored in a desiccator over $CaCl_2$.

$CaL_3(H_2O)_2SO_4$ (**6**): a mixture of 5 g $CaSO_4 \cdot 2H_2O$ and 20 cm^3 1,2-ethanediol was heated to 100–110°C. At 70–80°C, a gel-like suspension was formed. The solid compound was filtered off, washed with diethyl ether and stored in a desiccator over $CaCl_2$.

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.

Results and discussion

Compositions of complexes

The compositions of the complexes are presented in Table 1.

Table 1 Composition of complexes

Complex	Metal/m/m%		1,2-ethanediol/m/m%		Water/m/m%	
	calc.	found	calc.	found	calc.	found
1	10.52	–	28.42	27.34	16.48	16.00
2	9.62	9.50	44.25	44.48	12.84	13.20
3	7.88	8.00	54.35	53.90	10.51	11.10
4	41.11	41.03	15.10	14.72	8.77	8.15
5	38.95	39.08	21.51	21.16	6.25	6.10
6	10.91	11.18	52.77	52.16	10.94	10.05

Thermoanalytical behaviour of complexes

No melting of the investigated complexes was observed. On the basis of their thermal decomposition patterns, the complexes could be divided into two groups (A and B), depending on the number of decomposition steps. The complexes decomposed in one (group B) or more than one (group A) steps. The thermoanalytical curves and the decomposition schemes of the complexes are shown in Fig. 1 (group A), Fig. 2 (group B) and Fig. 3 (decomposition schemes).

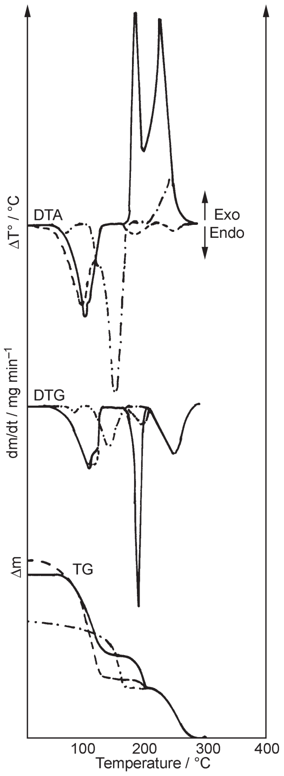

Fig. 1 Thermoanalytical curves of complexes of type A

Magnesium complexes

The Mg(II) complexes (type A) decompose in two (**1**) or three steps (**2** and **3**) (Figs 1 and 3a). A double and a single peak were observed in the differential thermogravimetric (DTG) curve of complex **1** (Fig. 1) between 120 and 180°C and between 220 and 400°C, respectively. These were accompanied by endothermic and exothermic peaks in the differential temperature analysis (DTA) curve. 1 mole water and 0.5 mole 1,2-ethanediol were released together in both steps (Fig. 3a).

Complexes **2** and **3** decomposed to $MgL(H_2O)SO_4$ below 150°C, the process was endothermic. The decomposition proceeded in two steps to $MgSO_4$ between 160 and 220°C and between 220 and 400°C. 0.5 mole 1,2-ethanediol and 0.5 mole water molecules were released together in both steps (Fig. 3a). These decomposition steps were accompanied by exothermic peaks in the DTA curves. When the experiment was performed in nitrogen atmosphere, a similar decomposition route was observed, but without heat evolution. The final mass of the decomposition product was a little larger, than in the course of decomposition in air.

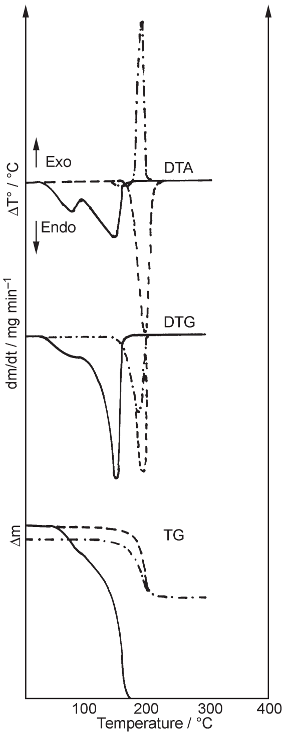

Fig. 2 Thermoanalytical curves of complexes of type B

On the basis of the thermal behaviour, it could be suggested that the Mg(II) complexes and/or the decomposition products ($MgL_{1/2}(H_2O)SO_4$, $MgL(H_2O)SO_4$ and $MgL_{1/2}(H_2O)_{1/2}SO_4$) contain strongly bound water and 1,2-ethanediol molecules. This strongly bound water molecule is probably bound by two coordination bonds and two hydrogen-bonds (a sulfate water molecule); it released from the solid phase between 200 and 300°C, as in $MgSO_4{\cdot}H_2O$ [8, 9]. Analogously, it can be suggested that one or both oxygen atoms are involved in two coordination bonds in the strongly bound 1,2-ethanediol molecules, which are released from the solid phase at higher temperature.

The absence of an anhydrous intermediate means that the coordination ability of 1,2-ethanediol towards Mg(II) is less than that of water, or that there is a strong intramolecular interaction between the water and 1,2-ethanediol molecules.

Cadmium complexes

$CdSO_4{\cdot}8/3H_2O$ decomposes between 40 and 69°C [10] with loss of most of the water, and giving $CdSO_4{\cdot}H_2O$ as intermediate. The one water molecule is released between 120 and 320°C. This behaviour is similar to that in the decomposition of other metal sulfate monohydrates. Consequently, it could be concluded that this water molecule forms two coordination bonds and two hydrogen-bonds [8, 9].

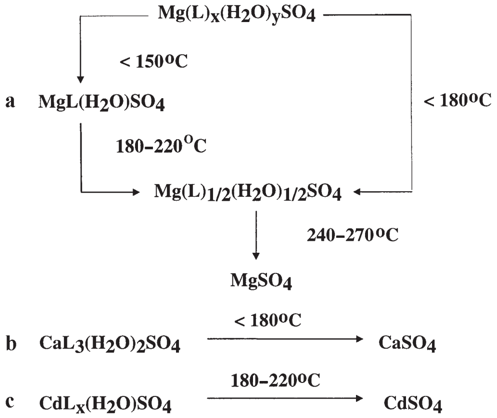

Fig. 3 Decomposition schemes of complexes

In contrast with $CdSO_4 \cdot 8/3H_2O$, the Cd(II) complexes of 1,2-ethanediol decompose in one step between 180 and 220°C (Figs 2 and 3b). The water and 1,2-ethanediol are released simultaneously and $CdSO_4$ is the final product. Decomposition of complex **4**, prepared at lower temperature, was accompanied by heat evolution in air. In nitrogen atmosphere, and endothermic process was observed. Complex **5**, prepared at the *b.p.* of 1,2-ethanediol (197°C), decomposed in the same temperature range by an endothermic reaction. A strong interaction is presumed between the water and 1,2-ethanediol molecules, coordinated to the Cd(II)ion, which prevents water and 1,2-ethanediol molecules from leaving the solid phase under 200°C temperature and separately.

Calcium complex

Ca(II) complex (**6**) decomposes in a simple way (Fig. 2). An overlapping double peak was observed in the DTG and the DTA curves of the Ca(II) complex below 180°C and $CaSO_4$ was the decomposition product. The ratio of the mass losses below and above 100°C suggests that the water molecules are released first. This thermal behaviour is similar to that of $CaSO_4 \cdot 2H_2O$ [10], which loses its water molecules below 100°C. This reflects to the similar binding of the water molecules in the two compounds.

IR spectra of complexes

The compositions and thermal behaviour of the investigated complexes might suggest that water, and 1,2-ethanediol and sulfate ion may all coordinate to the metal ion in the complexes. To determine whether they are coordinated or not, the IR spectra of the complexes may serve as a powerful tool. Coordinated water and sulfate ion are known to have different IR bands, depending on the type of binding, and the ν(CO) band of 1,2-ethanediol will also shift on coordination. In our analysis of the IR spectra of the complexes, the water deformation bands between 1500 and 1800 cm^{-1}, and the splitting of the ν_3 and ν_4 bands of the sulfate ion were followed. The water and sulfate bands of the complexes were compared with the spectra of the parent metal sulfate hydrates. Liquid 1,2-ethanediol has two intense bonds in the range 1000–1100 cm^{-1} at 1088 and 1045 cm^{-1}, which were assigned to a combination of the ν(CO) and ν(CC) bands, the former being the dominant. An analysis of these bands will therefore reflect the coordination of 1,2-ethanediol.

Magnesium complexes

The thermal behaviour of Mg(II) complexes suggest the presence of water and 1,2-ethanediol molecules bound with different strengths. This is supported by the IR spectra of the complexes (Table 2).

Two intense bands were observed in the range 1500–1700 cm^{-1} (water bending vibrations), with maxima at 1600 and 1650 cm^{-1}. The band at higher frequency is present in the spectrum of $MgSO_4·7H_2O$ and could be assigned to a single coordinated water molecule. The other band, in the lower frequency range, could be assigned to the water molecule bound by two coordinate bonds to Mg(II) [8], or coordinated by one bond, but involved in a strong hydrogen-bond. The latter case is more probable because $MgSO_4·H_2O$ has a band at 1525 cm^{-1} [8, 9].

Table 2 Characteristic IR bands (cm^{-1}) of magnesium complexes

Assignments		**1**	**2**	**3**	$MgSO_4·7H_2O$
Water		1600 1650	1600 1650	1600 1650	1660
Sulfate ion	ν_3	1170 1140 1110	1150 1110	1140 1110	1150 1105
	ν_4	640 615 595	615 585	620 590	640 615
ν(CO)		1085 1040	1065 1040 1085 1030	1085 1070 1062 1045 1040 1030	

ν(CO) bands (1088 and 1045 cm^{-1}) of the 1,2-ethanediol molecule are shifted (by 3 and 5 cm^{-1}) in complex **1** (Table 2), which points to differently coordinated oxygen atoms in the 1,2-ethanediol molecule. In complexes **2** and **3**, four and six bands were observed in the 1000–1100 cm^{-1} range, which means that all the 1,2-ethanediol molecules in the complexes are in different surroundings. One band (1045 cm^{-1}) indicate the presence of an uncoordinated OH group in the complexes. The different values of shifts (3–15 cm^{-1}) suggest that the oxygen atoms of the 1,2-ethanediol molecules are coordinated with different strengths. One or both oxygen atoms in the 1,2-ethanediol molecule may be involved in hydrogen-bonds only, or in one or two coordination bonds (3–5 or 5–10 cm^{-1} shift of ν(CO) bands).

The symmetry of the sulfate ion was C_{2v} in complex **1** and C_{3v} in $MgSO_4 \cdot 7H_2O$ and in complexes **2** and **3**. It may be postulated that two of the sulfate oxygen atoms are bound to the Mg^{2+} in complex **1**. The C_{3v} symmetry of the sulfate ion in complexes **2** and **3** means that one oxygen atom is coordinated to the Mg^{2+}, or the oxygen atoms in the sulfate ion form hydrogen-bonds of different strengths, as in $MgSO_4 \cdot 7H_2O$.

Cadmium complexes

In the IR spectra of $CdSO_4 \cdot 8/3H_2O$ and of complexes **4** and **5** (Table 3), three (1550, 1620 and 1740 cm^{-1}) bands, respectively, were observed in the range 1500–1700 cm^{-1}. The literature data [11] indicate that three types of water molecules are present in $CdSO_4 \cdot 8/3H_2O$. One of them is coordinated to the Cd^{2+} ion and forms three hydrogen-bonds, with one oxygen atom of the sulfate ion, with one oxygen atom of one water molecule and with a hydrogen atom of the other water molecule. The water molecule of the second type is coordinated to Cd^{2+} and its hydrogen atoms form two hydrogen-bonds with one water and one sulfate oxygen atom. The third one is uncoordinated to Cd^{2+}, but forms four hydrogen-bonds, with two oxygen atoms of the sulfate ions and with two hydrogen atoms of the other water molecules. The bands at 1550, 1620 and 1740 cm^{-1} are attributed to the first, second ant third types of water molecules in $CdSO_4 \cdot 8/3H_2O$. In complex **5**, the band at 1550 cm^{-1} was not observed. It can be concluded that in this complex the 1,2-ethanediol molecule replaces the first type of water molecule in the coordination sphere around Cd^{2+}.

Table 3 Characteristic IR bands (cm^{-1}) of cadmium and calcium complexes

Assignments		**4**	**5**	$CdSO_4 \cdot 8/3H_2O$	**6**	$CaSO_4 \cdot 2H_2O$
Water		1740 1620 1550	1740, 1620	1740 1620 1550	1650	1680 1620
Sulfate ion	ν_3	110, 1110	1150 1110	1175 1110 1080	1210 1150 1100	1150 1100
	ν_4	650 610 592	615 585	655 615 595	680 620 592	605 580
ν(CO)		1085 1040	1090 1075 1035		1085 1045	

This supported by the changes in the bands involving the ν(CO) frequency. The shifts in this point to the presence of a weakly (Δν=3 cm^{-1}) and a strongly bound (Δν=15 cm^{-1}) oxygen atom for the 1,2-ethanediol molecules in the Cd^{2+} complexes [4].

A difference was observed between the IR spectra of the sulfate ion in $CdSO_4{\cdot}8/3H_2O$ and 1,2-ethanediol complexes. The symmetry of the sulfate ion in the hydrate and in complexes **4** and **5** is C_{2v}, C_{2v} and C_{3v}, respectively. In $CdSO_4{\cdot}8/3H_2O$, the oxygen atoms of the sulfate ion are coordinated to the Cd^{2+} in different ways. The inclusion of 1,2-ethanediol in the coordination sphere of Cd^{2+} changes the binding mode of the sulfate ion and consequently the symmetry of the sulfate ion in the complexes is changes.

Calcium complex

Two and one absorption bands were observed in the IR spectra of $CaSO_4{\cdot}2H_2O$ and the Ca(II) complex (**6**) in the range 1600–1700 cm^{-1} (Table 3). In the structure of $CaSO_4{\cdot}2H_2O$ [11], the water molecules are coordinated to the Ca(II) ion and hydrogen-bonded to the oxygen atoms of two different sulfate ions, forming two sheets. In complex **6**, both water molecules are in the same surrounding, while in $CasSO_4{\cdot}2H_2O$ the water molecules have different geometries.

IR spectra in the range 1000–1100 cm^{-1} (ν(CO) group frequency, Table 3) suggest that the 1,2-ethanediol molecules in the Ca(II) complex are weakly bound by coordinate bonds via one of the oxygen atoms or hydrogen-bonded via both oxygen atoms.

The absorption bands characteristic of the sulfate ion in $CaSO_4{\cdot}2H_2O$ and in Ca(II) complex of 1,2-ethanediol reveal a change in the symmetry of the sulfate ion, which has C_{3v} and C_{2v} symmetry in $CaSO_4{\cdot}2H_2O$ and in the 1,2-ethanediol complex, respectively.

Conclusions

The role of the water molecules in the investigated complexes was the same as in the metal sulfate hydrates. Three types of bound-water were observed. The 'lattice' water molecule forms hydrogen-bonds only and has an absorption band in the range 1700–1800 cm^{-1} (e.g. 1740 cm^{-1} in Cd(II) compounds). The 'coordinated' water molecule forms one coordination bond and one or two hydrogen-bonds, it has an absorption band in the range 1600–1700 cm^{-1} (e.g. 1660 and 1650 cm^{-1} (Mg(II) compounds, 1640 cm^{-1} (Cd(II) compounds and 1680, 1650 and 1620 cm^{-1} in Ca(II) compounds). The third type of water molecule in the complexes is bound more strongly. It forms two coordination bonds and two hydrogen-bonds, as for the water molecule in the metal sulfate monohydrates, or it forms one coordination bond and three hydrogen-bonds to oxygen atoms of the sulfate ion and oxygen and hydrogen atoms of the other water molecules, as in $CdSO_4{\cdot}8/3H_2O$ [10] (e.g. 1600 and 1550 cm^{-1} in the Mg(II) and Cd(II) compound, respectively).

The 1,2-ethanediol molecule can partly replace, but never displaces all the water molecules and sulfate ion in the coordination spheres of metal ions. This leads support to our carlier statement that the water and 1,2-ethanediol molecules have similar coordination ability 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 only.

Both the thermal behaviour and the IR spectra of the complexes led to the conclusion that the oxygen atoms in 1,2-ethanediol may form similar bonds to that of the water oxygen: hydrogen-bonds and one or two coordination bonds. The main difference between the water and 1,2-ethanediol molecules is that the latter contains two oxygen atoms. As one oxygen atom may form one or two hydrogen-bonds, one or two coordination bonds, or a hydrogen-bond and coordination bond together, 1,2-ethanediol may be involved in more types of binding. It may act for instance as a monodentate or bidentate ligand via one oxygen a atom, bidentate chelating ligand, a bidentate bridging ligand or a tridentate or terdentate bridging ligand.

To find the type of binding responsible for the chemical decomposition of 1,2-ethanediol complexes on heating, the thermal behaviour of metal alkoxides, was analysed. Maleki and Schwing–Well [12–15] prepared and studied the thermal stabilities and IR spectra of Al(III) and Mg(II) alkoxides formed with different diols, among them 1,2-ethanediol. The Mg(II) and Al(III) and 1,2-ethanediol form polymeric alkoxides with 1:1 ($Mg(OCH_2CH_2O)$) or 4:7 stoichiometry ($Al_4(OCH_2CH_2O)_5(OCH_2CH_2OH)_2$). In the latter compound, four 1,2-ethanediol residues form bidentate chelate bonds, one forms terdentate bonding with oxygen atoms and two molecules form bidentate bonds to Al(III) ion via one oxygen atom.

The thermal behaviour of these alkoxides was similar to our experimental observations. They lost some 1,2-ethanediol between 100 and 200°C, which the authors attributed to diol bound via hydrogen-bonds. The polymeric alkoxides structure decomposed between 200 and 400°C, giving MgO or Al_2O_3 as final product in air atmosphere. This decomposition step was accompanied by an exothermic heat effect in the case of the aluminium alkoxides, in which free non-ionic OH groups were present, and the formation of acetaldehyde was observed. For the alkoxides, shifts of 10 and 15 cm^{-1} in the $\nu(CO)$ frequency were observed.

A comparison of the thermal behaviour and the IR spectra of the alkoxides (formed from 1,2-ethanediol) and our complexes demonstrated that the presence of specifically bound 1,2-ethanediol is necessary to explain the decomposition of 1,2-ethanediol on heating. One oxygen atom is bound by two coordination bonds and the second oxygen atom is not bound. In this case there is possibility for the formation of acetaldehyde. At and above 200°C, acetaldehyde induces some oxidation process, which is accompanied by heat evolution in the presence of dioxygen. The total organic parts of the complexes will form gaseous products in this combustion process and the final decomposition product is the metal oxide. In the absence of dioxygen, the decomposition of complexes containing the OH group, the acetaldehyde will not give gaseous product, but it results carbon. That is why the TG and DTG curves of some investigated complexes are differentate in air and nitrogen atmosphere.

References

1 I. Labádi, K. Burger, G. Liptay, M. Czugler and A. Kálmán, J. Thermal Anal., 31 (1986) 1171.

2 I. Labádi, G. Liptay, A. Horváth, L. Korecz, S. Papp and K. Burger, J. Thermal Anal., 32 (1987) 1575.

3 I. Labádi, G. Bernát, G. Kenessey, L. Párkányi, J. Mink and G. Liptay, Polyhedron, 11 (1992) 2975.

4 I. Labádi, L. Párkányi, G. Kenessey and G. Liptay, J. Cryst. Spectroscopic Res., 23 (1993) 333.

5 R. M. Williams and R. H. Atalla, J. Chem. Soc. Perkin Trans II, (1975) 1155.

6 D. Knetsch and W. L. Groeneveld, Recl. Trav. Chim., 92 (1973) 855.

7 D. Knetsch and W. L. Groeneveld, Inorg. Nucl. Chem. Lett., 12 (1976) 27.

8 H. R. Oswald, Helv. Chim. Acta, 48 (1965) 590.

9 H. R. Oswald, Helv. Chim. Acta, 48 (1965) 600.

10 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, Houston, New York, London, 1953.

11 a. R. W. G. Wyckow, Crystal Structures Interscience, 1951. Vol. II. Ch. 10., p. 52.
b. H. Lipson, Proc. Roy Soc. (London), A156 (1936) 462.

12 P. Maleki and M. J. Schwing-Well, J. Inorg. Nucl. Chem., 37 (1975) 435.

13 P. Maleki and M. J. Schwing-Well, J. Inorg. Nucl. Chem., 38 (1976) 1787.

14 P. Maleki and M. J. Schwing-Well, J. Inorg. Nucl. Chem., 38 (1976) 1783.

15 P. Maleki, Ann. Chim., 2 (1977) 167.