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Synthesis, characterization and mode of thermal decomposition of oxalate complexes of cadmium(II) and zinc(II) with hydrazine, and cobalt(II), nickel(II) and copper(II) with hydrazinium cation

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Abstract

The reaction of $CdSO_4$ with hydrazine and hydrazinium oxalate in aqueous solution at several pH values leads to the formation of various complexes. Only three complexes were successfully isolated: $Cd_2(C_2O_4)_2 \cdot N_2H_4$, $CdC_2O_4 \cdot N_2H_4 \cdot 0.5H_2O$ and $CdC_2O_4 \cdot 1.5N_2H_4$.

The reaction of $ZnSO_4$ with hydrazine and hydrazinium oxalate produces only the complex $ZnC_2O_4 \cdot 2N_2H_4$.

On reaction of MSO_4 with hydrazinium oxalate, double oxalates of Co, Ni and Co of general formulae $Co(NH_3NH_3)(C_2O_4)_2 \cdot 2H_2O$, $Ni_2(NH_3NH_3)(C_2O_4)_3 \cdot 4H_2O$, and $Cu(NH_2NH_3)_2(C_2O_4)_2 \cdot H_2O$ were obtained.

The complexes obtained were characterized by elemental analysis, X-ray powder patterns, IR spectroscopy, and TG and DTA techniques.

Keywords: IR spectra; Synthesis; Thermal studies

1. Introduction

Numerous data are available in the literature on hydrazine complexes of bivalent transition metal ions. Complexes with a general empirical formula $MX_2(N_2H_4)_n$ (where X is Hal^-, NO_3^-) have been prepared. Also, complexes with a general empirical

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formula $MC_2O_4(N_2H_4)n \cdot xH_2O$, where n varies from 1 to 4 and x from 0 to 2, have been the subject of many investigations [1–12]. It was found that the molar ratio of hydrazine: M(II) observed in the complexes is related to the capability of the hydrazine of behaving as a monodentate, bidentate or bridging ligand [13]. In the case of Ni(II) oxalate complexes with hydrazine, it was found that the molar ratio of hydrazine: M(II) is up to 4:1 [1, 4, 8]. The conditions of their synthesis, some structural investigations by means of their infrared spectra and X-ray powder diffraction patterns, as well as their thermal decomposition, are also reported.

The coordinating properties of neutral hydrazine acting as mono- or bidentate ligand to M(II) transition metal ions are well established in the literature. However, there are only a few data for complexes for these ions with monovalent hydrazinium cation. Complexes with the general formula $M(N_2H_5)_2(SO_4)_2$ (where M(II) is Mn, Fe, Co, Ni, Cu, Zn, Cd) have been studied. Magnetic and spectroscopic properties [16], as well as the crystal structure [17] of $Zn(N_2H_5)_2(SO_4)_2$, have been reported. The X-ray powder diffraction patterns of these complexes showed that all are isomorphous. It was found that M(II) ions are pseudo-octahedrally surrounded by two $N_2H_5^+$ ions, trans to each other, and two bidentate sulfate ions. A few double oxalate compounds of M(II) transition metal ions with alkylammonium cations are also mentioned in the literature. The synthesis and characterization of some compounds with methylammonium ions have been reported [18, 19]. The crystal structure of $Cu(CH_3NH_3)_2(C_2O_4)_2$ has been determined [20]. It was found that this compound crystallizes in the triclinic space group $P_{\bar{1}}$ (No. 2) with the oxalic anion acting as a bidentate ligand. The Cu–O distances are between 1.951(4) and 1.914(4) Å and the Cu(II) ion is in the center of a square plane, surrounded by four oxygen atoms from two oxalic groups at the corners of this square.

Continuing our work on the amine complexes and double salts of M(II) transition metal ions, we present here the results of the synthesis and characterization of oxalate complexes of Cd(II) and Zn(II) with hydrazine, and of the double oxalates of Co(II), Ni(II) and Cu(II) with hydrazinium ion, for which we have not found any data presented in the literature. Our investigations mainly consider the conditions of synthesis, the thermal behavior in static air atmosphere and some structural investigations of the isolated complexes by means of their X-ray powder diffraction patterns and IR spectra.

2. Experimental

2.1. Chemicals

$MSO_4 \cdot xH_2O$ p.a., $H_2C_2O_4 \cdot 2H_2O$ p.a., and 100% N_2H_5OH (Merck) were used for the synthesis of the compounds, without further purification.

2.2. Complex syntheses

Hydrazinium oxalate aqueous solution (1.1 mol dm^{-3}) was prepared by a dropwise neutralization to pH 5 of an aqueous solution of oxalic acid with hydrazine hydroxide. The mixture was stirred under permanent freezing using an external ice bath.

2.2.1. $Cd_2(C_2O_4)_2 \cdot N_2H_4$

This compound was obtained by adding an aqueous solution of hydrazinium oxalate (0.008 mol, pH 5) to a hot aqueous solution of cadmium sulfate (0.004 mol in about 20 ml of water). After cooling, a solid product was obtained which was filtered off, washed with several portions of water and ethanol, and dried in air.

2.2.2. $CdC_2O_4 \cdot N_2H_4 \cdot 0.5H_2O$

This compound was obtained by heating a mixture of 0.004 mol of $CdSO_4 \cdot H_2O$ and 0.008 mol of oxalic acid in about 30 ml of water. Hydrazine hydroxide was added dropwise with stirring to pH 6.5. After cooling, the solid product obtained was filtered, washed with several portions of water and ethanol, and dried in air.

2.2.3. $CdC_2O_4 \cdot 1.5N_2H_4$ and $ZnC_2O_4 \cdot 2N_2H_4$

These compounds were prepared from a hot mixture containing 0.004 mol of M(II) sulfate and 0.008 mol of hydrazinium oxalate in about 20 ml of water. The dropwise addition with stirring of hydrazine hydroxide to pH 9 yielded a solid product which was filtered, washed with several portions of about 5 ml of water and ethanol, and dried in air.

2.2.4. $Co(NH_3NH_3)(C_2O_4)_2 \cdot 2H_2O$ and $Ni_2(NH_3NH_3)(C_2O_4)_3 \cdot 4H_2O$

These compounds were prepared from a hot aqueous solution of 0.004 mol of M(II) sulfate and 0.008 mol of hydrazinium oxalate by addition of an aqueous solution of oxalic acid until pH 3. The crystals formed were filtered, washed with several portions of 5 ml of water and ethanol, and dried in air.

2.2.5. $Cu(NH_2NH_3)_2(C_2O_4)_2 \cdot H_2O$

This compound was obtained as crystals from a hot aqueous solution of 0.004 mol of Cu(II) sulphate hydrate and 0.008 mol of hydrazinium oxalate. The crystals formed were treated as in Section 2.2.4.

2.3. Analytical

Carbon and hydrogen contents were determined by Liebig's method using a C/H analyzer (Coleman Model 33). Nitrogen content was determined by Dumaś method.

Infrared spectra were obtained with samples of the compounds in a KBr matrix using a Perkin-Elmer M 520 spectrophotometer.

Thermal studies were made using a Cahn RG Electrobalance in air atmosphere at a heating rate of 5 K min^{-1}, with samples of 7–8 mg in weight in a quartz crucible. The differential thermal analysis (DTA) curves were made using a Netzsch differential thermal analyzer in static air atmosphere, with sample masses of 70–100 mg, at a heating rate of 5 K min^{-1} in the temperature range 293–850 K. The reference compound was pure α-Al_2O_3.

3. Results and discussion

3.1. Hydrazine oxalate complexes of Cd and Zn

The reaction of Cd(II) sulfate with hydrazine in the presence of hydrazinium oxalate at several pH values led to the formation of different complexes depending on the pH values. The elemental analyses of the complexes (Table 1) support the different attributed stoichiometries. Their X-ray patterns and IR spectra (Fig. 1) also support the conclusion that different compounds were obtained. It can be seen that the hydrazine complexes of cadmium are not isomorphous. This suggests that the presence of hydrazine in the complexes changes the crystal structure of cadmium oxalate. Because the complexes were obtained at pH values of 5, 6.5 or 9, it is concluded that the hydrazine content of the complexes increases with increasing pH value. However, although the formation of the hydrazine complexes at pH 6.5 or 9 can be explained, the formation of the hydrazine complex at pH 5 is strange: the formation of a double oxalate of Cd(II) with hydrazinium cation was expected, analogous with the formation of copper(II) hydrazinium oxalate at pH 5. The formation of this complex may be described by the equations

$$CdSO_4 + (NH_2NH_3)_2C_2O_4 \rightarrow CdC_2O_4 + (NH_2NH_3)_2SO_4$$

$$2CdC_2O_4 + (NH_2NH_3)_2C_2O_4 \rightarrow Cd_2(C_2O_4)_2NH_2NH_2 + NH_3NH_3C_2O_4$$

The difference in the crystal structures of the obtained complexes can be observed in their IR spectra in the regions of the ν(COO), ν(N–N) and ν(OH) stretching vibration modes. A band at 3250 cm^{-1} is observed in the IR spectrum of $CdC_2O_4 \cdot N_2H_4 \cdot 0.5H_2O$ (Fig. 1(b)), attributed to coordinated water and due to ν(OH). Other bands are observed in the same region of the spectrum and are attributed to $\nu(NH_2)$ stretching modes. The bands observed at 965 and 967 cm^{-1} (Fig. 1(a), (b), (c)) are attributed to bidentate hydrazine and are observed in all the complexes [13].

Table 1
Results of elemental analyses of Cd(II) and Zn(II) oxalate hydrazine complexes

Compound (Mr) $M(C_2O_4) \cdot nN_2H_4 \cdot mH_2O$	C	H	N
	% observed (calculated)		
M is Cd, $n = 0.5$, $m = 0$	11.25 (11.09)	1.32 (0.90)	5.85 (6.47)
M is Cd, $n = 1$, $m = 0.5$	10.52 (9.95)	1.48 (2.09)	10.80 (11.60)
M is Cd, $n = 1.5$, $m = 0$	10.32 (9.66)	2.96 (2.43)	16.28 (16.91)
M is Zn, $n = 2$, $m = 0$	11.50 (11.05)	4.30 (3.71)	25.54 (25.78)

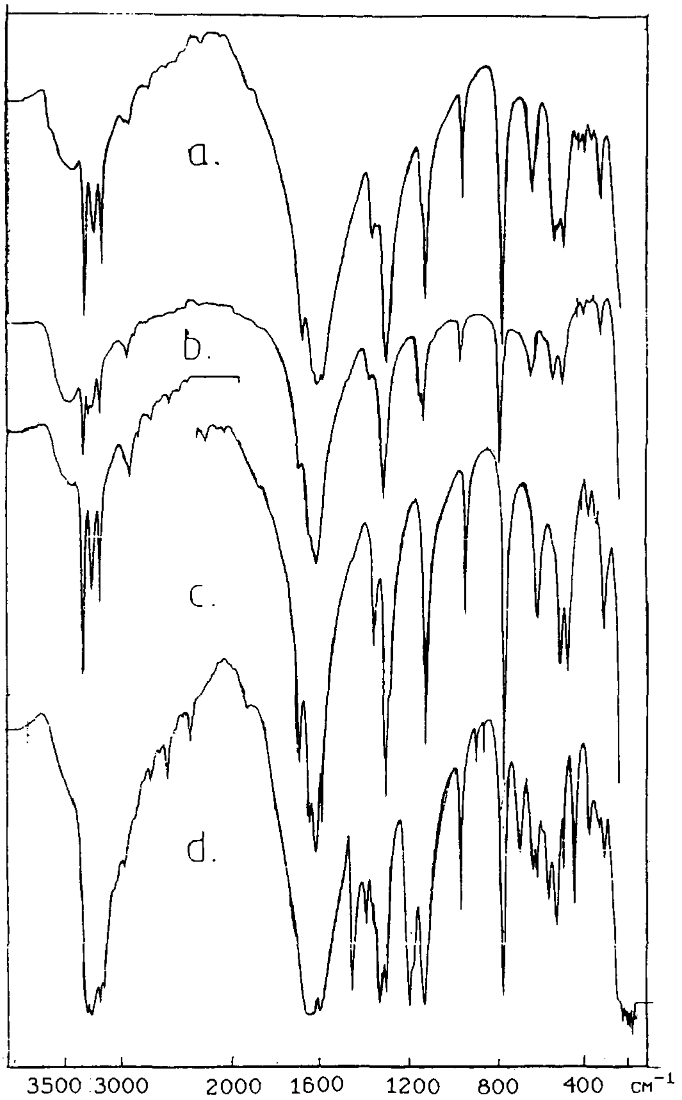

Fig. 1. IR spectra of: (a) $Cd_2(C_2O_4)_2 \cdot N_2H_4$; (b) $CdC_2O_4 \cdot N_2H_4 \cdot 0.5H_2O$; (c) $CdC_2O_4 \cdot 1.5N_2H_4$; (d) $ZnC_2O_4 \cdot 2N_2H_4$.

Bands at 400 and 410 cm^{-1} (Fig. 1(a), (b), (c)) are attributed to the ν(Cd–N) stretching mode. The bands at 500 and 510 cm^{-1} (Fig. 1(a), (b), (c)) are attributed to the ν(Cd–O) stretching mode. The attributions were made by comparing IR spectra of the complexes with those of free ligand and M(II) oxalate dihydrates (M is Mn, Ni or Zn) [15]. The band attributed to ν(M–N) is absent in the IR spectra of the latter two. It is also absent in IR spectra of hydrazinium(II) complexes of Co and Ni oxalates, as may be seen in Fig. 3.

The IR spectrum of the Zn(II) complex (Fig. 1(d)) shows bands that are attributed to stretching vibration modes of the following groups: ν_{as}(COO) at 1660–1620 cm^{-1}; ν_s(COO) at 1300 and 1330 cm^{-1}; ν(N–N) at 970 cm^{-1}; ν(Zn–O) at 480 cm^{-1} and ν(Zn–N) at 440 cm^{-1}. They are in agreement with previous observations made on the IR spectrum of the hydrazine complex of Ni(II) oxalate [14].

The thermal decompositions of the hydrazine complexes of Cd show different patterns. They are explained individually as follows.

3.1.1. $Cd_2(C_2O_4)_2 \cdot N_2H_4$

The general decomposition of this compound (Fig. 2(a)) takes place in two steps, as explained in the following equations

$$Cd_2(C_2O_4)_2N_2H_4 \xrightarrow[-(N_2H_4, 2CO)]{577\text{–}657\,K} 2CdCO_3$$

Observed mass loss 20.54%; calculated value 20.34%.

$$2CdCO_3 \xrightarrow[-2CO_2]{657\text{–}1093\,K} 2CdO$$

Observed mass loss 20.17%; calculated value 20.33%.

On the DTA curve, three exothermic peaks in the region from 573 to 700 K can be observed.

3.1.2. $CdC_2O_4 \cdot N_2H_4 \cdot 0.5H_2O$

The thermal decomposition of this compound (Fig. 2(b)) also occurs in two steps. In the first, the compound loses water and in the second, it decomposes as explained in the following equations.

$$CdC_2O_4 \cdot N_2H_4 \cdot 0.5H_2O \xrightarrow[-0.5H_2O]{331\text{–}492\,K} CdC_2O_4 \cdot N_2H_4$$

Observed mass loss 4.04%; calculated value 3.70%.

$$CdC_2O_4 \cdot N_2H_4 \xrightarrow[-(CO_2, CO, N_2H_4)]{492\text{–}967\,K} CdO$$

Observed mass loss 42.51%; calculated value 43.10%.

In the temperature range of the second step, three exothermic peaks are observed in the DTA curves, as was the case for the previous complex. A low-temperature endothermic peak is observed for dehydration in the first step of decomposition. This suggests that water is weakly bound. The high temperature observed for the decomposition shows that monohydrazine complex is more stable than those with a higher content of hydrazine. $CdC_2O_4 \cdot 1.5N_2H_4$ and $ZnC_2O_4 \cdot 2N_2H_4$ decompose to give the monohydrazine complexes (see below), which decompose at higher temperatures.

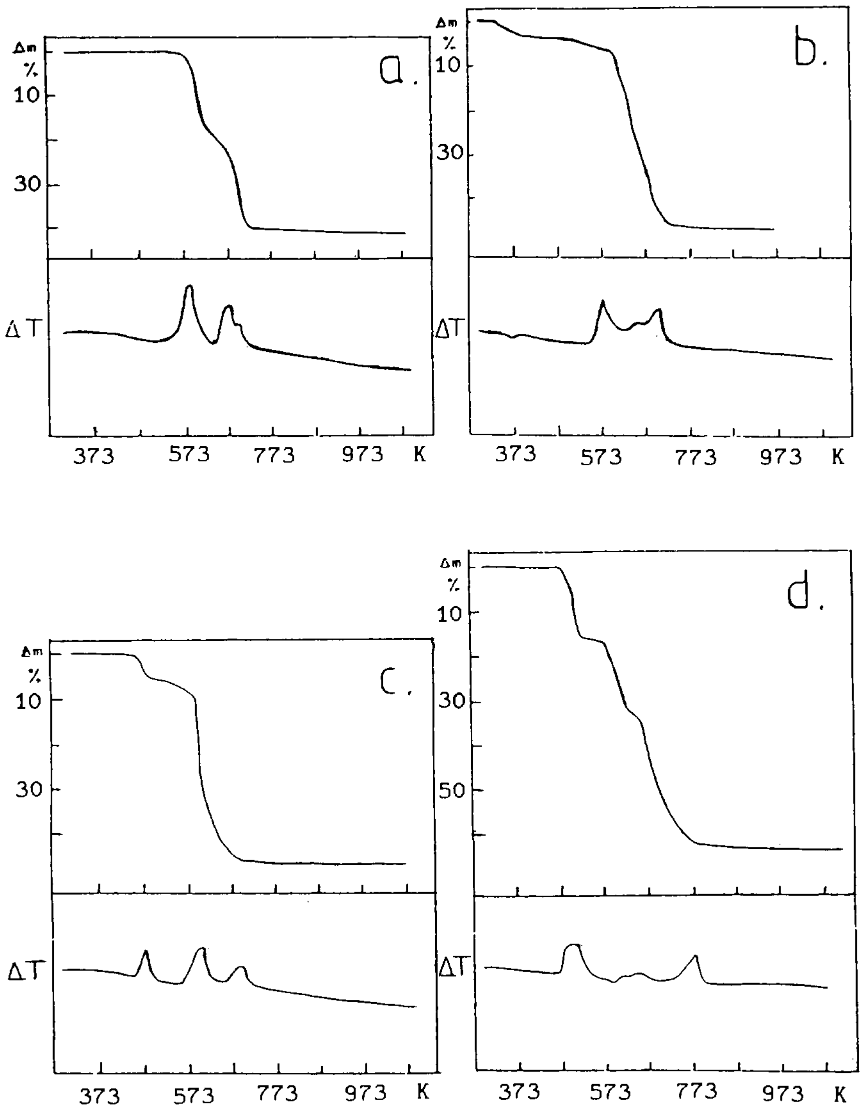

Fig. 2. TG and TAD curves of the thermal decomposition of: (a) $Cd_2(C_2O_4)_2 \cdot N_2H_4$; (b) $CdC_2O_4 \cdot N_2H_4 \cdot 0.5H_2O$; (c) $CdC_2O_4 \cdot 1.5N_2H_4$; (d) $ZnC_2O_4 \cdot 2N_2H_4$.

3.1.3. $CdC_2O_4 \cdot 1.5N_2H_4$

The thermal decomposition of this compound (Fig. 2(c)) takes place in two steps. The following decomposition sequence is proposed

$$CdC_2O_4 \cdot 1.5N_2H_4 \xrightarrow[-0.5N_2H_4]{451-549\,K} CdC_2O_4 \cdot N_2H_4$$

Observed mass loss 6.47%; calculated value 6.45%.

$$CdC_2O_4{\cdot}N_2H_4 \xrightarrow[-(N_2H_4, CO_2, CO)]{549\text{–}1092\,\mathrm{K}} CdO$$

Observed mass loss 40.54%; calculated value 41.88%.

On the DTA curve, three exothermic peaks are apparent.

3.1.4. $ZnC_2O_4{\cdot}2N_2H_4$

This compound has the same stoichiometry as the hydrazine complexes of Fe(II) and Co(II) oxalates previously synthesized [14]. Its TG curve (Fig. 2(d)) shows three well-resolved decomposition steps, related to the three exothermic peaks observed in the DTA curve. The thermal decomposition of the compound can be represented by the following equations

$$ZnC_2O_4{\cdot}2N_2H_4 \xrightarrow[-N_2H_4]{475\text{–}521\,\mathrm{K}} ZnC_2O_4{\cdot}N_2H_4$$

Observed mass loss 15.10%; calculated value 14.74%.

$$ZnC_2O_4{\cdot}N_2H_4 \xrightarrow[-N_2H_4]{521\text{–}615\,\mathrm{K}} ZnC_2O_4$$

Observed mass loss 14.57%; calculated value 14.74%.

$$ZnC_2O_4 \xrightarrow[-(CO_2, CO)]{615\text{–}1107\,\mathrm{K}} ZnO$$

Observed mass loss 33.11%; calculated value 33.13%.

The thermal study shows that the monohydrazine complex of Zn(II) is more stable than the bishydrazine complex. This behavior is also observed for the bishydrazine complex of Co(II) oxalate [9].

3.2. Hydrazinium double oxalate complexes of M(II) transition metals

The X-ray powder patterns and IR spectra of the compounds of bivalent Co, Ni and Cu (Fig. 3) show the differences in their crystal structure. The elemental analyses (Table 2) and TG curves of the compounds show that they have the following general formulae: $Co(NH_3NH_3)(C_2O_4)_2{\cdot}2H_2O$; $Ni_2(NH_3NH_3)(C_2O_4)_3{\cdot}4H_2O$; and $Cu(NH_2NH_3)_2(C_2O_4)_2{\cdot}H_2O$.

Some information about the bonding in these complexes can be obtained from their IR spectra. The stretching vibration of the N–N group, ν(N–N), is found at 975 cm^{-1} in the Cu(II) complex (Fig. 3(c)). This is characteristic of $NH_2{-}NH_3^+$ acting as a monodentate ligand. In the Ni(II) complex, it is observed at 1000 cm^{-1}. The higher value can be attributed to a shorter N–N bonding distance in $NH_3^+{-}NH_3^+$. This is in agreement with previous observations and its relation with the spectroscopic results [14, 16]. It is not quite clear why ν(N–N) is observed at 970 cm^{-1} in the case of the Co(II) complex. The stretching vibration of the Cu–N group, ν(Cu–N), is observed at

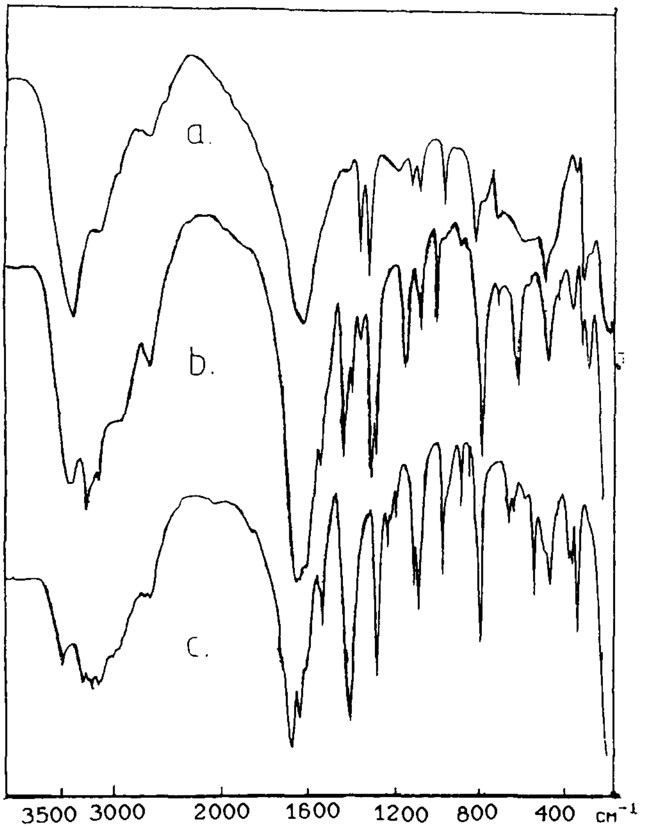

Fig. 3. IR spectra of: (a) $Co(NH_3NH_3)(C_2O_4)_2 \cdot 2H_2O$; (b) $Ni_2(NH_3NH_3)(C_2O_4)_3 \cdot 4H_2O$; (c) $Cu(NH_2NH_3)(C_2O_4)_2 \cdot H_2O$.

Table 2
Results of elemental analyses of the double oxalate hydrazinium complexes

Compound	C	H	N
	% observed (calculated)		
$Co(NH_3NH_3)(C_2O_4)_2 \cdot 2H_2O$	16.06	3.73	8.40
	(15.75)	(3.30)	(9.18)
$Ni_2(NH_3NH_3)(C_2O_4)_3 \cdot 4H_2O$	14.10	3.54	5.54
	(14.78)	(2.89)	(5.75)
$Cu(NH_2NH_3)_2(C_2O_4)_2 \cdot H_2O$	14.25	3.40	17.28
	(14.84)	(3.74)	(17.31)

410 cm^{-1}, which agrees with the position of this band in $[Cu(NH_3)_4]^+$ [22]. For the complexes of Co(II) and Ni(II), the band attributed to the stretching vibration of the M–N group, ν(M–N), at 409 cm^{-1} in hydrazine complexes of Ni(II) [14] is not observed. A band at 1710 cm^{-1} attributed to the stretching vibration of the N–H

group, $\nu(NH_2)$, is observed for the Cu(II) complex but not for the Ni(II) and Co(II) complexes. Bands attributed to the stretching vibration of the M–O group, ν(M–O), at about 490 cm^{-1} are found in all the spectra of the complexes. This is in agreement with previous observations for complexes of M(II) oxalates [14].

The thermal decompositions of the double oxalates show different patterns. Each of them is described below.

3.2.1. $Co(NH_3NH_3)(C_2O_4)_2 \cdot 2H_2O$

The thermal decomposition of this compound takes place in two well-resolved steps. The first step (Fig. 2(a)) is observed in the temperature range 326–555 K and is related to the loss of part of the oxalate ions as oxalic acid. This suggests that the double oxalate is less stable than the hydrazine complex. The latter decomposes at a higher temperature, 573 K, according to the second step of the TG curve. It is strange that the evolution of water takes place in the second stage. This could be attributed to the fact that the water molecules are strongly bonded to Co(II), as is the bidentate bonded hydrazine. The thermal decomposition is related to the thermal effect peaks observed in the DTA curves: the endothermic peak is related to the first step of the TG curve and the two exothermic peaks are related to the second step of the TG curve. The thermal decomposition of the above compound can be described with the following equations

$$Co(NH_3NH_3)(C_2O_4)_2 \cdot 2H_2O \xrightarrow[-H_2C_2O_4]{326\text{–}555\,K} CoC_2O_4 \cdot N_2H_4 \cdot 2H_2O$$

Observed mass loss 28.98%; calculated value 29.51%.

$$3(CoC_2O_4 \cdot N_2H_4 \cdot 2H_2O) \xrightarrow[-(6H_2O,\,3N_2H_4,\,4CO,\,2CO_2)]{555\text{–}1098\,K} Co_3O_4$$

Observed mass loss 44.90%; calculated value 44.17%.

3.2.2. $Ni_2(NH_3NH_3)(C_2O_4)_3 \cdot 4H_2O$

The thermal decomposition (Fig. 4(b)) of the double oxalate of Ni(II) with bivalent hydrazinium cation takes place in one step over a large temperature range, 473–643 K. On the DTA curve, two endothermic peaks and then one exothermic can be observed.

It is difficult to distinguish between decomposition steps of the complex, but the following steps can be assumed

$$Ni_2(NH_3NH_3)(C_2O_4)_3 \cdot 4H_2O \xrightarrow[-3H_2O]{315\text{–}492\,K} Ni_2(NH_3NH_3)(C_2O_4)_3 \cdot H_2O$$

Observed mass loss 10.67%; calculated value 11.02%.

$$Ni_2(NH_3NH_3)(C_2O_4)_3 \cdot H_2O \xrightarrow[-(H_2C_2O_4,\,H_2O)]{492\text{–}615\,K} Ni_2(C_2O_4)_2 \cdot N_2H_4$$

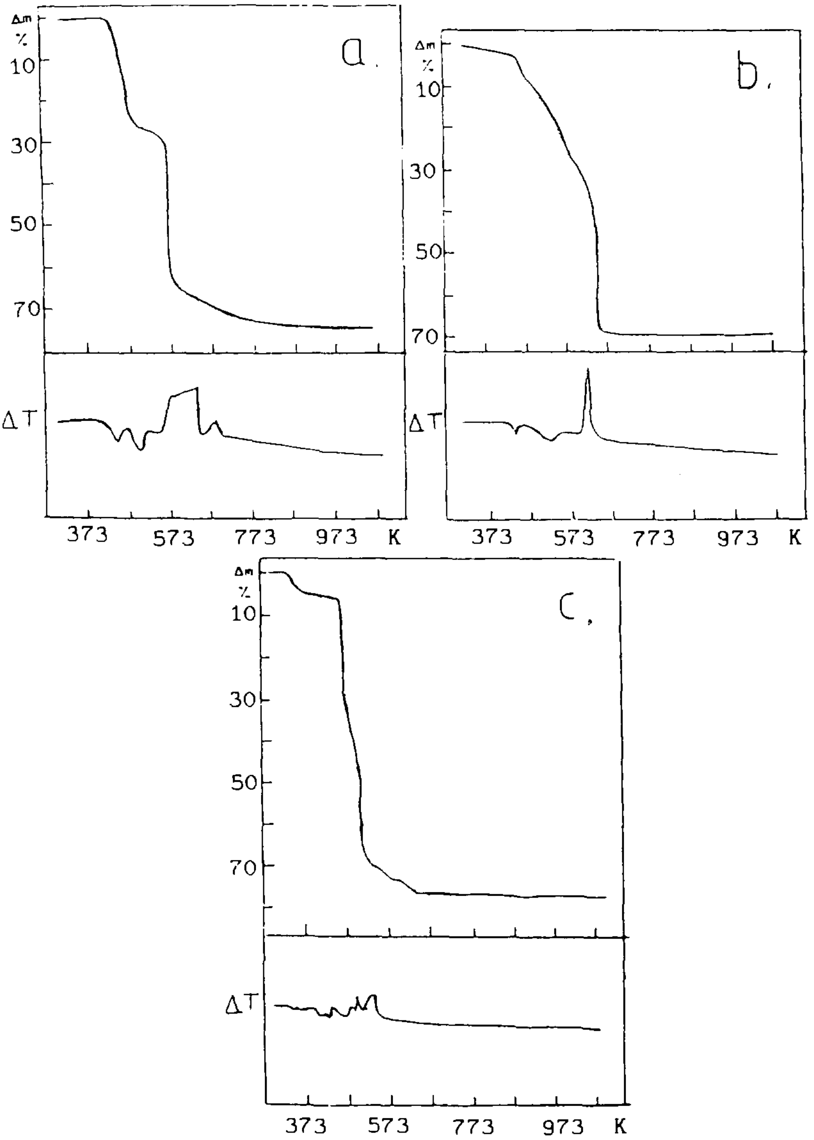

Fig. 4. TG and DTA curves of the thermal decomposition of: (a) $Co(NH_3NH_3)(C_2O_4)_2\cdot 2H_2O$; (b) $Ni_2(NH_3NH_3)(C_2O_4)_3\cdot 4H_2O$; (c) $Cu(NH_2NH_3)_2(C_2O_4)_2\cdot H_2O$.

Observed mass loss 21.60%; calculated value 22.22%.

$$Ni_2(C_2O_4)_2\cdot N_2H_4 \xrightarrow[-(N_2H_4, 2CO_2, 2CO)]{615-1102\,K} 2NiO$$

Observed mass loss 36.09%; calculated value 36.03%.

3.2.3. $Cu(NH_2NH_3)_2(C_2O_4)_2 \cdot H_2O$

The TG curve (Fig. 4(c)) shows three mass loss steps. In the first step, the complex evolves water. In the second, oxalic acid is given off, and in the third, CuO is obtained as a residue. These processes can be described by the following equations

$$\mathrm{Cu(NH_2NH_3)_2(C_2O_4)_2 \cdot H_2O} \xrightarrow[-\mathrm{H_2O}]{323\text{–}457\,\mathrm{K}} \mathrm{Cu(NH_2NH_3)_2(C_2O_4)_2}$$

Observed mass loss 5.44%; calculated value 5.57%.

$$\mathrm{Cu(NH_2NH_3)_2(C_2O_4)_2} \xrightarrow[-\mathrm{H_2C_2O_4}]{457\text{–}481\,\mathrm{K}} \mathrm{CuC_2O_4 \cdot 2N_2H_4}$$

Observed mass loss 27.73%; calculated value 27.81%.

$$\mathrm{CuC_2O_4 \cdot 2N_2H_4} \xrightarrow[-(\mathrm{2N_2H_4, CO_2, CO})]{481\text{–}1098\,\mathrm{K}} \mathrm{CuO}$$

Observed mass loss 43.31%; calculated value 42.04%.

It is usual for double oxalates to decompose with loss of oxalic acid (related to the endothermic DTA peak). An oxalatehydrazine complex is formed which decomposes at higher temperatures. This is related to the exothermic DTA peaks. It can be concluded that hydrazine oxalate complexes are more stable than the hydrazinium double oxalate complexes. This is in agreement with the results of the thermal decomposition of methylammonium M(II) oxalates [18]. Attempts to obtain double oxalates with other bivalent metal ions, such as Zn, Cd, and Mn, were unsuccessful. The compounds obtained have indefinite stoichiometries. The attributions of the residue to MO (for Ni and Cu) and Co_3O_4 (for Co) for the TG analysis of the compounds, are supported by observations made by other authors in related complexes [2, 8, 21].

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