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Synthesis and thermal behaviour of some oxalate complexes of bivalent metals Mn, Co, Ni, Cu, Zn and Cd

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Abstract

The reaction of M(II) oxalate (M = Mn, Co, Ni, Zn or Cd) with monomethylammonium oxalate in the presence of monomethylamine gives different compounds, depending on the metal atom. For M = Ni, Co or Zn double oxalates with the general empirical formula $(CH_3NH_3)_4M(C_2O_4)_3 \cdot nH_2O$ (where $n = 2$ for Zn and Co, and $n = 1$ for Ni) are obtained, whilst for M = Cd or Mn the monomethylamine complexes $(CH_3NH_3)_2Cd(C_2O_4)_2 \cdot (CH_3NH_2) \cdot H_2O$ and $(CH_3NH_3)_2Mn(C_2O_4)_3 \cdot (CH_3NH_2)_2 \cdot H_2O$, respectively, are obtained. Dissolution of Cu(II) oxalate in concentrated ammonia gives diammine Cu(II) oxalate dihydrate. X-ray powder-diffraction patterns show that the complexes have different structures, except for the complexes of Co and Zn which are isostructural. Differential thermal analysis and thermogravimetry show that the compounds obtained undergo different modes of thermal decomposition.

INTRODUCTION

In this paper we present the results of an investigation of the products obtained by the reaction between M(II) oxalate (M = Mn, Ni, Co, Zn or Cd) and monomethylammonium oxalate in the presence of monomethylamine, as well as the product obtained by the reaction between Cu(II) oxalate and a concentrated ammonia solution. The identification of the products obtained was done by means of X-ray powder diffraction, infra-red (IR) spectroscopy, elemental and static thermogravimetry (TG) and differential thermal analysis (DTA).

A survey of the literature shows that a number of amine complexes of bivalent metals have been investigated in detail. The reaction of Co(II) oxalate with primary aliphatic amines has been studied and compounds having the general formula $CoC_2O_4RNH_2$ (R = H, CH_3, C_2H_5, C_3H_7, C_4H_9 or C_5H_{11}) have been obtained [1].

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The thermal decomposition of Cu(II) oxalate hemihydrate and its compounds with different amines or functional groups containing nitrogen, have been studied using TG and DTA with nitrogen and air atmospheres [2]. It was found that $CuC_2O_4(CH_3NH_2)_2$ gives Cu(II) oxide as a final product, whereas $CuC_2O_4(NH_3)_2$ and $CuC_2O_4(py)$ give Cu(I) oxide. Bisethylenediamine nickel(II), diethylenetriamine nickel(II) and triethylenetetramine nickel(II) complexes have been prepared with different anions (NO_3^- and CLO_4^-) and studied using IR spectroscopy [3]. Preliminary investigations on and the IR spectra of some complexes of Co(II) oxalate with functional groups containing nitrogen, such as $CoC_2O_4(Am)_2$ (where Am = pyridine, aniline or piperidine) have been described [4]. The thermal decomposition of M(II) oxalates has also been reported [5]. The synthesis and thermal decomposition of pyridine oxalate complexes of Fe(II), Ni(II), Co(II) and Zn(II) have recently been reported [6].

The present investigations were carried out in order to establish the formation of complexes of M(II) with monomethylammonium oxalate and monomethylamine, and the formation of diammine Cu(II) oxalate dihydrate and to study their thermal behaviour under constant conditions over the temperature range 20–800°C. This study is a continuation of our work on the oxalate complexes of bivalent metals with different amines.

EXPERIMENTAL

Chemicals

The starting compounds were the M(II) sulphates crystallohydrates (p.a.), a 25–30% (w/v) aqueous solution of monomethylamine (BDH analytical reagent), oxalic acid (p.a.) and a 25% aqueous solution of ammonia (p.a.)

The M(II) oxalates were obtained by treating an aqueous solution of the M(II) sulphate with an aqueous solution of oxalic acid. A concentrated solution of monomethylammonium oxalate was obtained by neutralizing a suspension of oxalic acid with monomethylamine to pH 4.

Procedures and methods

The monomethylammonium double oxalates of Co(II), Ni(II) and Zn(II) and the monomethylamine complexes of Cd(II) and Mn(II) were obtained by treating a mixture of an aqueous suspension of M(II) oxalate (0.002 mol) with an aqueous solution of oxalic acid (0.004 mol) in a molar ratio of 1 : 2 with monomethylamine (0.05 mol). The reaction mixture was heated gently in order to dissolve the M(II) oxalate and kept at room temperature until crystallization occurred. The crystalline products were filtered off, washed in ethanol and dried in air. The monomethylamine complex of Mn(II) was obtained by the same procedure except that monomethylamine was added until pH 7 was reached.

The ammine complex of Cu(II) was obtained by treating Cu(II) oxalate with 25% aqueous NH_3 in order to dissolve the copper oxalate. Dark-blue crystals were obtained after leaving the reaction mixture at room temperature for a few days. The crystals were filtered off and dried in air.

Elemental analyses for carbon and hydrogen were done using Liebig's method and a carbon–hydrogen analyser (Coleman Model 33) and analysis for nitrogen was done using the Dumas method. In addition, the oxalate anion was titrated against a standardized solution of potassium permanganate.

X-ray powder-diffraction patterns were recorded on a Philips PW 1050 vertical goniometer with a proportional counter using graphite monochromatized Cu Kα radiation.

Infra-red (IR) spectra were recorded on a Perkin-Elmer M 580 spectrophotometer using KBr pellets.

The TGAs were done using a Cahn RG Electrobalance in air atmosphere at a heating rate of 5°C min^{-1} over the range 20–800°C, and using 7–8 mg of sample in a quartz crucible. The DTA was done using a Netzsch differential thermal analyser. DTA curves were obtained in static air atmosphere, with sample masses of 70–100 mg, at a heating rate of 5°C min^{-1} from ambient temperature to 850°C. The reference compound was pure alumina.

RESULTS AND DISCUSSION

The X-ray powder-diffraction patterns (Figs. 1–3), the IR spectra (Figs. 4 and 5), and the DTA and TG curves (Table 1) for the compounds obtained point to their different structures and to the isostructural aspect of Co(II) and Zn(II). The compounds are of different stoichiometry but related to the compound of Cu(II) obtained previously under the same experimental conditions as used in the preparation of the Co, Ni, Zn and Cd complexes; i.e. an anhydrous double oxalate with the empirical formula $(CH_3NH_3)_2Cu(C_2O_4)_2$. The crystal structure and thermal behaviour of this complex will be described in a forthcoming publication. In comparing the thermal behaviour of the compounds obtained (Figs. 6–8) great differences are observed. For this reason it is more practical to present the thermal decomposition of each compound separately.

M = Mn

The thermal decomposition of $(CH_3NH_3)_2Mn_2(C_2O_4)_3(CH_3NH_2)_2 \cdot H_2O$ ($M_r = 518.19$) takes place in three steps (Fig. 7(b)). Due to the mass

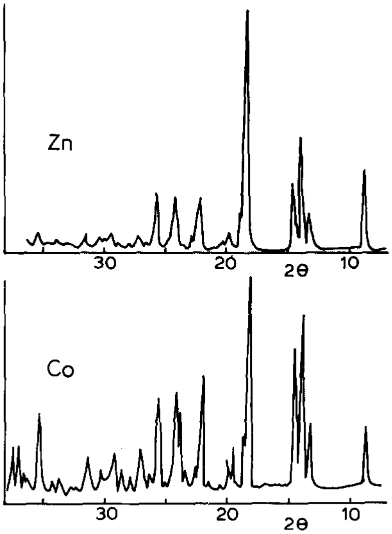

Fig. 1. X-ray powder diffraction patterns of the compounds having the empirical formula $(CH_3NH_3)_4M(C_2O_4)_3 \cdot 2H_2O$.

losses observed the thermal decomposition is assumed to occur in the way described below.

Step 1 (35–114°C)

$$(RH)_2Mn_2(C_2O_4)_3 \cdot R_2 \cdot H_2O \rightarrow H_2O + (RH)_2Mn_2(C_2O_4)_3 \cdot R_2$$

Observed mass loss 3.42%°C; calculated mass loss 3.48%; $R = CH_3NH_2$; $RH = CH_3NH_3^+$.

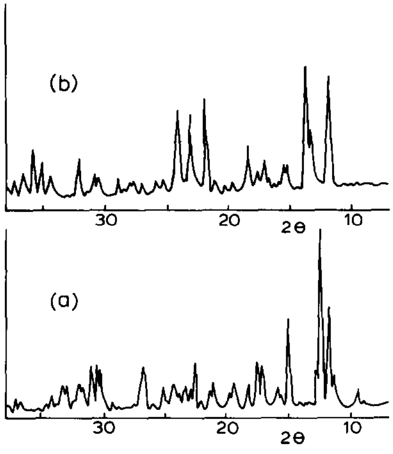

Fig. 2. X-ray powder diffraction patterns of (a) $(CH_3NH_3)_2Cd(C_2O_4)_2(CH_3NH_2) \cdot H_2O$; and (b) $(CH_3NH_3)_2Mn_2(C_2O_4)_3(CH_3NH_2)_2 \cdot H_2O$.

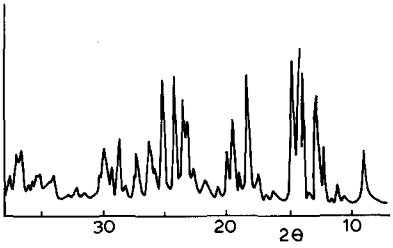

Fig. 3. X-ray powder diffraction pattern of $(CH_3NH_3)_4Ni(C_2O_4)_3 \cdot H_2O$.

Step 2 (114–208°C)

$$(RH)_2Mn_2(C_2O_4)_3 \cdot R_2 \rightarrow (RH)_2Mn_2(C_2O_4)_3 + 2R$$

Observed mass loss 12.40%; calculated mass loss 11.98%.

Step 3 (208–783°C)

$$(RH)_2Mn_2(C_2O_4)_3 \rightarrow Mn_2O_3 + 2R + 2CO_2 + 4CO + H_2O$$

Observed mass loss 51.52%; calculated mass loss 54.06%.

The DTA curve shows only two exothermic maxima (at 290 and 310°C). The final product was confirmed as α-Mn_2O_3 by comparing its X-ray powder diffraction pattern with Powder Diffraction File No. 24-508 [7]. It can be seen from the thermal decomposition presented here that the double oxalate of Mn(II) is more stable than the corresponding methylamine complex because the latter decomposes at a lower temperature.

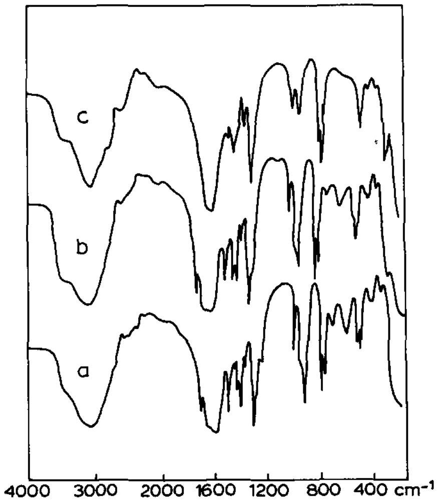

Fig. 4. IR spectra of (a) $(CH_3NH_3)_4Zn(C_2O_4)_3 \cdot 2H_2O$; (b) $(CH_3NH_3)_4Co(C_2O_4)_3 \cdot 2H_2O$; and (c) $(CH_3NH_3)_4Ni(C_2O_4)_3 \cdot H_2O$.

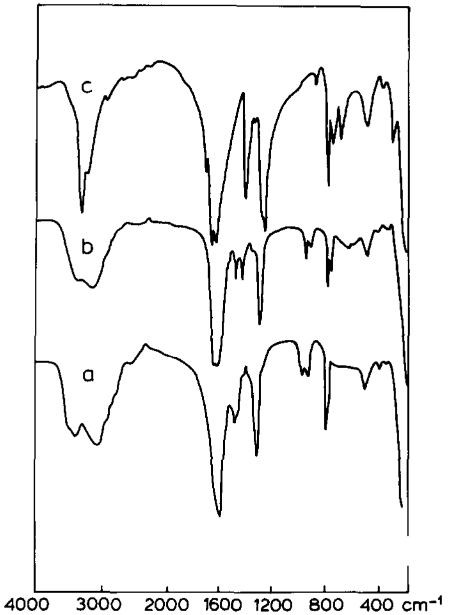

Fig. 5. IR spectra of (a) $(CH_3NH_3)_2Cd(C_2O_4)_2(CH_3NH_3)\cdot H_2O$; (b) $(CH_3NH_3)_2Mn_2(C_2O_4)_3(CH_3NH_2)\cdot H_2O$; and (c) $Cu(C_2O_4)(NH_3)_2\cdot 2H_2O$.

M = Ni

The thermal decomposition of $(CH_3NH_3)_4Ni(C_2O_4)_3\cdot H_2O$ (M_r = 469.04) takes place in three steps (Fig. 8(a)). On the basis of the mass

TABLE 1

Results of elemental and thermal analyses of the oxalate complexes

Compound	Mass (%)				
	C	H	N	Ox	M_xO_y
$(RH)_4Co(Ox)_3\cdot 2H_2O$	Obs. 25.20	5.45	11.92	54.19	19.32
(M_r = 487.28)	Calc. 24.65	5.79	11.50	54.55	16.47
$(RH)_4Zn(Ox)_3\cdot 2H_2O$	Obs. 24.61	5.36	11.67	53.70	17.08
(M_r = 493.74)	Calc. 24.32	5.72	11.35	53.48	16.48
$(RH)_4Ni(Ox)_3\cdot H_2O$	Obs. 25.38	5.26	11.93	56.80	18.48
(M_r = 469.04)	Calc. 25.61	5.59	11.95	56.30	15.93
$(RH)_2Cd(Ox)_2R\cdot H_2O$	Obs. 20.64	4.24	9.50	44.50	32.20
(M_r = 401.63)	Calc. 20.93	4.17	10.46	43.83	31.97
$(RH)_2Mn_2(Ox)_3R_2\cdot H_2O$	Obs. 24.10	4.89	11.50	51.70	32.20
(M_r = 518.19)	Calc. 23.18	4.28	10.81	50.96	30.47
$CuC_2O_4(NH_3)_2\cdot 2H_2O$	Obs. 10.20	4.57	12.21		36.17
(M_r = 221.59)	Calc. 10.80	4.56	12.60		35.90

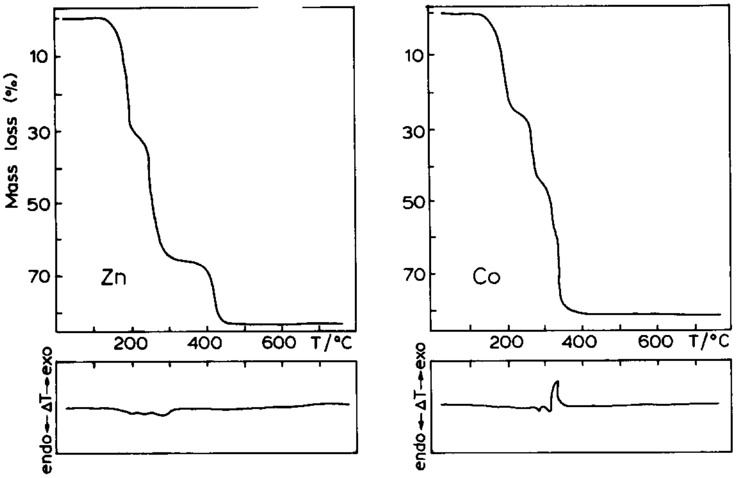

Fig. 6. TG and DTG curves of compounds having the empirical formula $(CH_3NH_3)_4M(C_2O_4)_3 \cdot 2H_2O$.

losses, the following manner of thermal decomposition is proposed.

Step 1 (134–237°C)

$$(RH)_4Ni(C_2O_4)_3 \cdot H_2O \rightarrow (RH)_2Ni(C_2O_4)_2 \cdot R \cdot H_2O + H_2O + CO_2 + CO + R$$

Observed mass loss 24.59%; calculated mass loss 25.81%.

Step 2 (237–326°C)

$$(RH)_2Ni(C_2O_4)_2 \cdot R \cdot H_2O \rightarrow NiC_2O_4 \cdot R_3 + CO_2 + CO + 2H_2O$$

Observed mass loss 22.20%; calculated mass loss 23.03%.

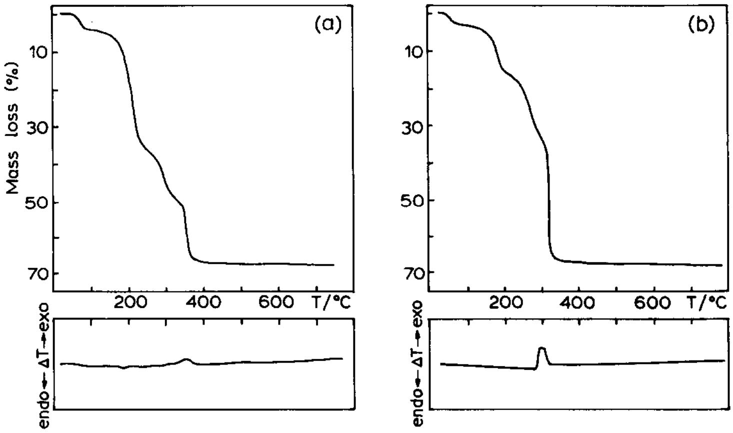

Fig. 7. TG and DTG curves of (a) $(CH_3NH_3)_2Cd(C_2O_4)_2(CH_3NH_2) \cdot H_2O$; and (b) $(CH_3NH_3)_2Mn_2(C_2O_4)_3(CH_3NH_2)_2 \cdot H_2O$.

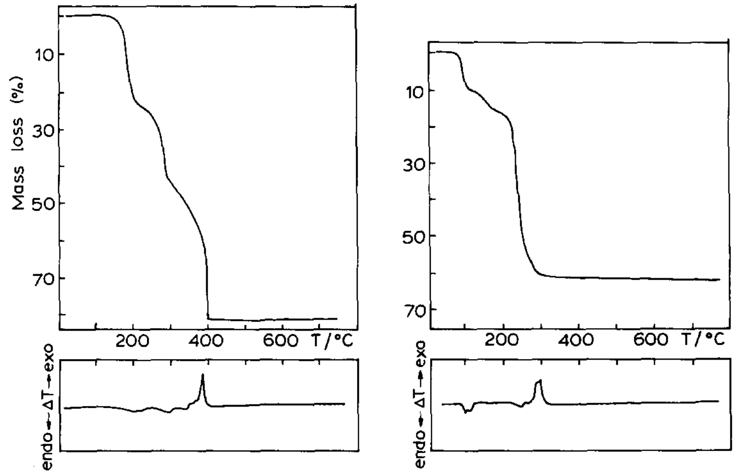

Fig. 8. TG and DTG curves of (a) $(CH_3NH_3)_4Ni(C_2O_4)_3 \cdot H_2O$; and (b) $CuC_2O_4(NH_3)_2 \cdot 2H_2O$.

Step 3 (326–760°C)

$NiC_2O_4 \cdot R_3 \rightarrow NiO + 3R + CO_2 + CO$

Observed mass loss 34.94%; calculated mass loss 34.83%.

The final product was confirmed as NiO by the X-ray powder diffraction pattern of the residue (Powder Diffraction File No. 4-835 [7]).

M = Zn

It can be seen from Figs. 1 and 4 that the complexes of Co(II) and Zn(II) are isostructural. However, the two complexes decompose in different ways, as it can be seen from Fig. 6. The thermal decomposition of $(CH_3NH_3)_4Zn(C_2O_4)_3 \cdot 2H_2O$ ($M_r = 493.74$) takes place in three steps.

Step 1 (128–225°C)

$(RH)_4Zn(C_2O_4)_3 \cdot 2H_2O \rightarrow (RH)_2Zn(C_2O_4)_2 \cdot R + R + CO_2 + CO + 3H_2O$

Observed mass loss 31.27%; calculated mass loss 31.82%.

Step 2 (225–374°C)

$(RH)_2Zn(C_2O_4)_2 \cdot R \rightarrow ZnC_2O_4 + 3R + H_2O + CO_2 + CO$

Observed mass loss 34.98%; calculated mass loss 37.10%.

Step 3 (374–774°C)

$ZnC_2O_4 \rightarrow ZnO + CO_2 + CO$

Observed mass loss 16.67%; calculated mass loss 14.58%.

The X-ray powder diffraction pattern of the residue confirms it as ZnO (Powder Diffraction File No. 36-1451 [7]). The DTA curve shows endothermic maxima only at 190 and 280°C. The mass of the residue is 17.08% (from DTA 16.98%), the calculated value 16.48%.

M = *Co*

Like its isostructural Zn(II) complex the thermal decomposition of $(CH_3NH_3)_4Co(C_2O_4)_3 \cdot 2H_2O$ ($M_r = 487.28$) (Fig. 6) takes place in three steps, but in a different way, as can be seen from the proposed equations.

Step 1 (128–237°C)

$$(CH_3NH_3)_4Co(C_2O_4)_3 \cdot 2H_2O \rightarrow (RH)_2Co(C_2O_4)_2 \cdot R_2 + 3H_2O + CO_2 + CO$$

Observed mass loss 26.30%; calculated mass loss 25.88%.

Step 2 (293–352°C)

$$3(RH)_2Co(C_2O_4)_2 \cdot R_2 \rightarrow Co_3(C_2O_4)_4 \cdot R_9 + 3H_2O + CO_2 + 3CO + 3R$$

Observed mass loss 19.04%; calculated mass loss 18.83%. The DTA curve shows two endothermic maxima at 190 and 285°C, as for the isostructural Zn(II) complex. Two exothermic maxima at 325 and 335°C point to the possible partial oxidation of Co(II) to Co(III).

Step 3 (352–774°C)

$$Co_3(C_2O_4)_4 \cdot R_9 \rightarrow Co_3O_4 + 9R + 4CO_2 + 4CO$$

observed mass loss 35.34%; calculated mass loss 38.82%. The mass of the residue is 19.32% (calculated value 16.47%). The X-ray powder diffraction pattern of the residue confirmed it as Co_3O_4 (Powder Diffraction File No. 4-418 [7]).

M = *Cd*

The monomethylamine oxalate complex of Cd(II) has the empirical formula $(CH_3NH_3)_2Cd(C_2O_4)_2 \cdot (CH_3NH_2) \cdot H_2O$ ($M_r = 401.63$) and decomposes in four steps (Fig. 7(a)) as follows.

Step 1 (50–80°C)

$$(RH)_2Cd(C_2O_4)_2 \cdot R \cdot H_2O \rightarrow (RH)_2Cd(C_2O_4)_2 \cdot R + H_2O$$

Observed mass loss 4.04%; calculated mass loss 4.48%.

Step 2 (80–265°C)

$2(RH)_2Cd(C_2O_4)_2 \cdot R \rightarrow Cd_2(C_2O_4)_2 \cdot R_3 + 3R + 2H_2O + 2CO_2 + 2CO$

Observed mass loss 33.37%; calculated mass loss 34.00%.

Step 3 (265–336°C)

$Cd_2(C_2O_4)_2 \cdot R_3 \rightarrow 2CdC_2O_4 + 3R$

Observed mass loss 12.24%; calculated mass loss 11.60%.

Step 4 (336–779°C)

$CdC_2O_4 \rightarrow CdO + CO_2 + CO$

Observed mass loss 17.97%; calculated mass loss 17.93%. The mass of the residue is 32.42% (from DTA 30.87%); the calculated value is 31.97%. The X-ray powder diffraction pattern of the residue confirmed it as CdO (Powder Diffraction File No. 5-640 [7]). It is worth noting that the thermal decomposition in Step 2 goes through the formation of a monomethylamine complex with a stoichiometry different from the monomethylamine complexes of the other M(II) complexes. The thermal decomposition in Steps 1 to 3 is related to endothermic maxima at 95, 180, 230 and 280°C; step 4 is associated with an exothermic maximum at 340°C. It can be seen from the proposed equations that the thermal decomposition of the cadmium complexes is very complex and is related to the formation of many intermediate products.

M = Cu

The thermal decomposition of $CuC_2O_4 \cdot (NH_3)_2 \cdot 2H_2O$ ($M_r = 221.59$) (Fig. 8(b)) takes place in two stages:

Stage 1

Step 1 (60–114°C)

$CuC_2O_4 \cdot (NH_3)_2 \cdot 2H_2O \rightarrow 1.5H_2O + CuC_2O_4 \cdot (NH_3)_2 \cdot 0.5H_2O$

Observed mass loss 10.83%; calculated mass loss 12.2%.

Step 2 (114–190°C)

$CuC_2O_4 \cdot (NH_3)_2 \cdot 0.5H_2O \rightarrow 0.5H_2O + CuC_2O_4 \cdot (NH_3)_2$

Observed mass loss 5.19%; calculated mass loss 4.07%. The total mass loss in Stage 1 is 16.06% (calculated value 16.27%).

Stage 2

Step 1 (190–237°C)

$CuC_2O_4 \cdot (NH_3)_2 \rightarrow CuCO_3 + 2NH_3 + CO$

Observed mass loss 28.36%; calculated mass loss 28.02%.

Step 2 (237–788°C)

$CuCO_3 \rightarrow CuO + CO_2$

Observed mass loss 18.38%; calculated mass loss 19.86%. The mass of the residue is 36.17% (calculated value 35.90%). The formation of CuO as a final product is confirmed by comparison of its X-ray powder diffraction pattern with Powder Diffraction File No. 5-661 [7]. It can be seen from the proposed manner of thermal decomposition of the anhydrous Cu(II) complex that the decomposition takes place in two very closed steps. It seems that diammine Cu(II) oxalate dihydrate loses water at a low temperature (60°C) and is unstable in air.

SUMMARY

The oxalate complexes of Mn, Ni, Co, Zn and Cd decompose via different intermediate compounds. In the case of the Mn(II) complex, the double oxalate is more stable than the amine complex. Between 114 and 208°C the Mn(II) amine complex loses two moles of amine and to form the double oxalate which decomposes above 208°C. Conversely, the Ni(II) double oxalate forms an amine complex and, finally above 326°C the amine complex decomposes to NiO. In a similar way, the Zn(II) double oxalate decomposes in two steps: in the first step an amine complex of the double oxalate is formed and in the second step a Zn(II) oxalate is produced. The isostructural Co(II) complex transforms to an amine complex in step 2 and, finally, decomposes to Co_3O_4 in the third step. Like the Co(II) complex, the Cd(II) complex transforms into an amine in Step 2 and then decomposes to the oxalate in Step 3.

The characteristic bands observed in the IR spectra of the obtained complexes ($\nu_{as}(COO^-)$ 1670–1570, $\delta_{as}(NH_3^+)$ 1530–1485, $\delta_{as}(CH_3)$ 1468–1448, ν(M–O) 520–500 and ν(M–N) 410–390 cm^{-1}) are in agreement with those reported previously [3,8–10]. The lower value of ν(M–N) compared to ν(M–O) indicates the weaker M–N bonding. This is in agreement with the thermal decomposition of the complexes of M(II) where the amine complex decomposes before the M(II) oxalate.

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