

OXALATE-2-ETHANOLAMINE COMPLEXES OF SOME BIVALENT CATIONS (Mn, Co, Ni, Cu, Zn and Cd)

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Abstract

On the refluxing of $M(\text{II})$ oxalate ($M = \text{Mn, Co, Ni, Cu, Zn}$ or Cd) and 2-ethanolamine in chloroform, the following complexes were obtained: $\text{MnC}_2\text{O}_4 \cdot \text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, $\text{CoC}_2\text{O}_4 \cdot 2\text{HOCH}_2\text{CH}_2\text{NH}_2$, $\text{Ni}_2(\text{C}_2\text{O}_4)_2 \cdot 5\text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}_2(\text{C}_2\text{O}_4)_2 \cdot 5\text{HOCH}_2\text{CH}_2\text{NH}_2$, $\text{Zn}_2(\text{C}_2\text{O}_4)_2 \cdot 5\text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cd}_2(\text{C}_2\text{O}_4)_2 \cdot \text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{H}_2\text{O}$.

Following the reaction of $M(\text{II})$ oxalate with 2-ethanolamine in the presence of ethanolammonium oxalate, a compound with the empirical formula $\text{ZnC}_2\text{O}_4 \cdot \text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{H}_2\text{O}^1$ was isolated. The complexes were identified by using elemental analysis, X-ray powder diffraction patterns, IR spectra, and thermogravimetric and differential thermal analysis. The IR spectra and X-ray powder diffraction patterns showed that the complexes obtained were not isostructural. Their thermal decompositions, in the temperature interval between 20 and about 900°C, also take place in different ways, mainly through the formation of different amine complexes. The DTA curves exhibit a number of thermal effects.

Keywords: ethanolamine complexes, $M(\text{II})$ oxalates

Introduction

This paper presents the results of an investigation of the compounds obtained in the reaction of $M(\text{II})$ oxalate and 2-ethanolamine. The products obtained were identified by using X-ray powder diffraction, infrared (IR) spectroscopy, elemental analysis, static thermogravimetry (TG) and differential thermal analysis (DTA).

A survey of the literature reveals that a number of amine complexes of bivalent metals have been investigated in detail. The reaction of $\text{Co}(\text{II})$ oxalate with primary aliphatic amines has been studied and compounds of general formula $\text{CoC}_2\text{O}_4\text{RNH}_2$ ($R = \text{H, CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$ or C_5H_{11}) have been obtained [1]. The thermal decompositions of $\text{Cu}(\text{II})$ oxalate hemihydrate and its compounds with different amines or with compounds containing nitrogen (such as monoethylamine and pyridine) have been studied by using TG and DTA in ni-

trogen and air atmospheres [2]. Preliminary investigations and the IR spectra of complexes of Co(II) oxalate with pyridine, aniline or piperidine have been described [3]. The thermal decompositions of $M(\text{II})$ oxalates have also been reported [4]. The syntheses and thermal decompositions of some $M(\text{II})$ pyridine oxalate complexes were recently reported [5]. Data are also available on the synthesis, identification and thermal behavior of $M(\text{II})$ monomethylammonium oxalate and monomethylamine oxalate complexes [6].

In a continuation of our work on the oxalate complexes of $M(\text{II})$ with different amines, the present investigations were carried out in order to establish the possibility of the formation of complexes of $M(\text{II})$ oxalates with 2-ethanolamine, to study their thermal behavior under constant conditions over the temperature range between 20 and about 900°C, and to acquire structural information from their X-ray powder diffraction patterns and IR spectra.

Experimental

Chemicals

The starting compounds were $M(\text{II})$ sulfate crystallohydrates (p.a.), 2-ethanolamine (purum, Merck), oxalic acid (p.a.) and CHCl_3 (p.a.) as solvent.

The $M(\text{II})$ oxalates were obtained by treating an aqueous solution of $M(\text{II})$ sulfate with an aqueous solution of oxalic acid.

Procedure and methods

The 2-ethanolamine oxalate complexes of $M(\text{II})$ ($M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ and Cd) were obtained by treating a mixture of a suspension of $M(\text{II})$ oxalate (0.002 mole) with 1 cm³ (0.016 mole) of 2-ethanolamine in CHCl_3 and refluxing for 1 h. After cooling, the solid product was filtered off, washed with ethanol and dried in air. Another complex of Zn(II) was obtained by treating Zn(II) oxalate (0.002 mole) with ethanlammonium oxalate ($\text{pH} = 4$) up to a molar ratio of 1:4 with heating, and treating this reaction mixture with 2-ethanolamine (1 cm³). The reaction mixture was kept at room temperature and the solid product obtained was filtered off, washed with ethanol and dried in air at room temperature.

Elemental analyses for carbon and hydrogen were performed by using Liebig's method and a carbon-hydrogen analyser (Coleman Model 33), and nitrogen was analysed by using the Dumas method.

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

IR spectra were recorded on a Perkin-Elmer M 580 spectrophotometer, using KBr pellets.

Table 1 Results of elemental and thermal analyses

Compound of*	1. Mn	2. Co	3. Ni	4. Cu	5. Zn	6. Zn	7. Cd
M_r	222.06	269.01	652.91	608.52	648.21	250.50	497.15
	found/calcd., %						
C	20.77/21.63	26.26/26.79	26.24/25.75	27.18/27.63	25.40/25.94	20.04/19.18	14.85/14.49
H	3.85/4.09	4.83/5.20	6.88/7.1	6.60/5.80	3.03/2.78	5.01/4.40	2.45/2.23
N	5.60/6.31	11.35/10.42	11.31/10.73	11.51/11.51	10.15/10.81	5.82/5.50	3.36/2.82
H ₂ O	/4.58	—	8.85/8.28	—	6.65/5.56	14.66/14.38	7.22/7.25
MO	34.37/35.56 ^{2*}	28.21/29.84 ^{3*}	22.89/22.72	26.97/26.14	25.17/26.03	31.14/32.48	51.66/51.65

1. $Mn(C_2O_4)_2 \cdot HOCH_2CH_2NH_2 \cdot H_2O$; 2. $Co(C_2O_4)_2 \cdot 2HOCH_2CH_2NH_2 \cdot H_2O$; 3. $Ni_2(C_2O_4)_3 \cdot 5HOCH_2CH_2NH_2 \cdot 3H_2O$; 4. $Cu_2(C_2O_4)_2 \cdot 5HOCH_2CH_2NH_2$; 5. $Zn_2(C_2O_4)_2 \cdot 5HOCH_2CH_2NH_2 \cdot 2H_2O$; 6. $Zn(C_2O_4) \cdot HOCH_2CH_2NH_2 \cdot H_2O$; 7. $Cd_2(C_2O_4)_2 \cdot HOCH_2CH_2NH_2 \cdot 2H_2O$; ^{2} Mn_2O_3 ; ^{3*} Co_3O_4

TG was carried out with a Cahn RG electrobalance in an air atmosphere at a heating rate of $5 \text{ deg}\cdot\text{min}^{-1}$ over the range from 20 to 900°C , on a 10–12 mg sample in a quartz crucible.

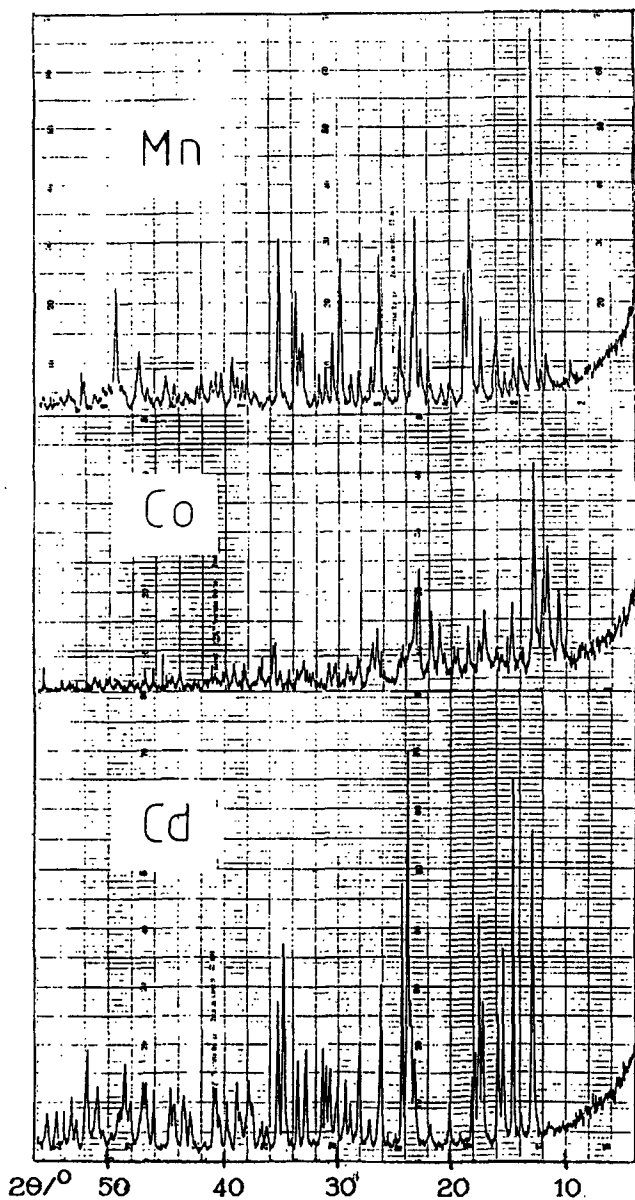


Fig. 1 X-ray powder diffraction patterns of oxalate-2-ethanolamine complexes of Mn, Co and Cd

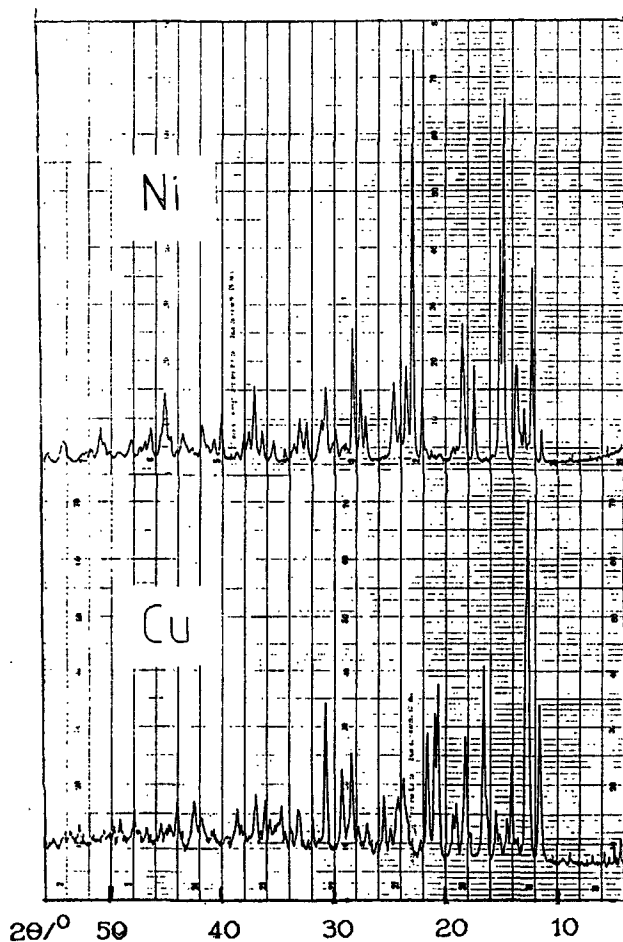


Fig. 2 X-ray powder diffraction patterns of oxalate-2-ethanolamine complexes of Ni and Cu

The total mass loss for all samples was calculated at the final temperature.

DTA was performed with a Netzsch differential thermal analyser. DTA curves were obtained in a static air atmosphere, with sample masses of 70–100 mg, at a heating rate of $5 \text{ deg}\cdot\text{min}^{-1}$ from ambient temperature to about 900°C . The reference substance was pure alumina.

Simultaneous DTA/TG was not used for thermal analyses. Two different instruments with different thermal conditions were applied for thermal measurements. The sample masses taken for DTA were about 8 times greater than those for TG. This could be a reason for the DTA peaks moving to higher temperature, as found earlier [10]. During the heating, sample transport was observed from the bottom of the DTA crucibles (where the thermocouple was situated) to its top, and thus the sample and the thermocouple were not always in contact.

Results and discussion

Under the conditions described in the Experimental part, different products were obtained. The X-ray powder diffraction patterns (Figs 1–3) and the IR spectra (Figs 4 and 5) revealed that the compounds were not all isostructural. Two different compounds were obtained from Zn(II) oxalate, depending on the conditions of their synthesis. All products had different stoichiometries with or without crystal water: $\text{MnOx}\cdot\text{R}\cdot\text{H}_2\text{O}$, $\text{CoOx}\cdot 2\text{R}$, $\text{Ni}_2(\text{Ox})_2\cdot 5\text{R}\cdot 3\text{H}_2\text{O}$, $\text{Cu}_2(\text{Ox})_2\cdot 5\text{R}$, $\text{Zn}_2(\text{Ox})_2\cdot 5\text{R}\cdot 3\text{H}_2\text{O}$, $\text{ZnOx}\cdot\text{R}\cdot 2\text{H}_2\text{O}^1$ and $\text{Cd}_2(\text{Ox})_2\cdot\text{R}\cdot 2\text{H}_2\text{O}$ (where $\text{R} = \text{HOCH}_2\text{CH}_2\text{NH}_2$ and $\text{Ox} = \text{C}_2\text{O}_4$). As may be seen in Figs 6 and 7, great differences were obtained in the thermal decompositions of these compounds.

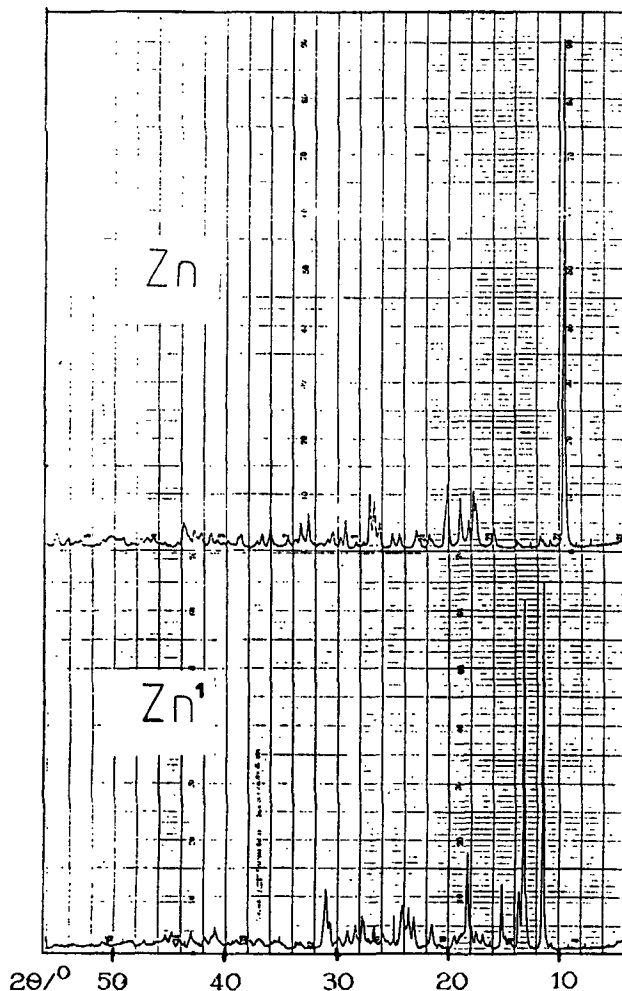
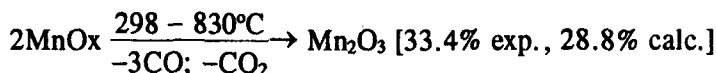
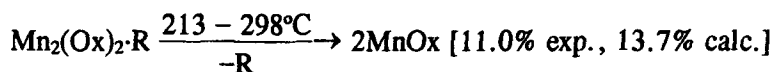
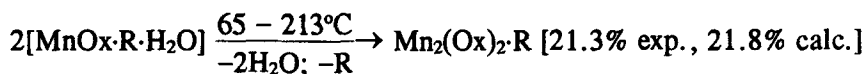


Fig. 3 X-ray powder diffraction patterns of oxalate-2-ethanolamine complexes of Zn

For this reason, it is easier to present the thermal decomposition of each compound separately.

$MnOx \cdot R \cdot H_2O$ ($M_r = 222.06$)

The thermal decomposition of $MnOx \cdot R \cdot H_2O$ occurs in several steps (Fig. 6). In step 1, the compound loses water and half of the 2-ethanolamine; in step 2, it loses the other half of the 2-ethanolamine; and in step 3, $MnOx$ decomposes. This may be described by the following equations:

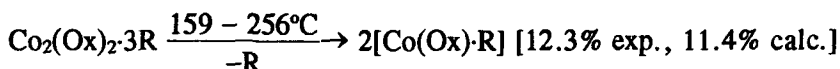
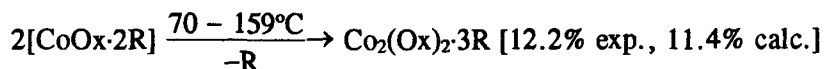


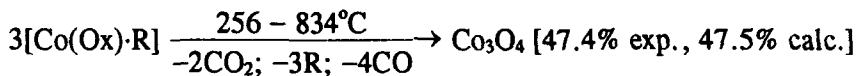
Carbon monoxide and carbon dioxide are liberated suddenly, with no formation of the carbonate.

As may be seen from the DTA curve, the decomposition involves several thermal effects. A marked exotherm at about $407^\circ C$ can be attributed to the last step in the TG curve, but shifted towards higher temperatures (see the Experimental part and Ref. [10]). As final products, Mn_2O_3 is obtained (Power Diffraction File No. 10-69) [8]. The calculated value for Mn_2O_3 is 35.6%, while the value observed for the residue was 34.4%.

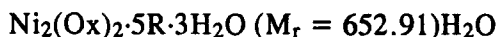
$CoOx \cdot 2R$ ($M_r = 269.11$)

The thermal decomposition of $CoOx \cdot 2R$ involves three steps. The first occurs after the moisture has been dried off (1.33% at $70^\circ C$), extending up to $159^\circ C$, as for the Mn compound. It could be described in three steps by the following equations:

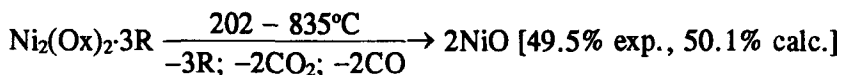
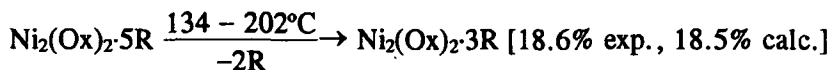
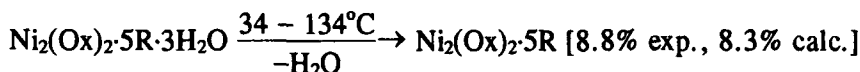




$\text{CoOx}\cdot\text{R}$ decomposes with the simultaneous loss of ethanolamine, carbon monoxide and carbon dioxide, with temporary formation of the metal and its oxidation to oxide. The endotherm at about 370°C indicates the temporary formation of metallic cobalt, whereas the exotherm at about 480°C can be attributed to the oxidation of metallic cobalt to its oxide. As final product, Co_3O_4 is obtained, as confirmed by its powder diffraction pattern (Powder Diffraction File No. 4-418) [8]. This is in agreement with earlier results on the thermal decomposition of CoOx [4, 10].



The thermal decomposition of the above compound (Fig. 6) occurs in three well-resolved steps:

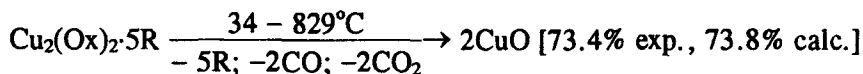


Several effects can be seen in the DTA curve. A characteristic exotherm at 430°C relates to step 3 in the TG curve, but shifted towards higher values (see Experimental part). As a final product, NiO is obtained, as confirmed by its X-ray powder diffraction pattern (Powder Diffraction File No. 4-835) [8].



From Fig. 4, it may be observed that the above compound decomposed almost in one step, but with many thermal effects. This indicates that the decomposition is in fact a multistep process in a small temperature interval.

As a final product CuO is obtained at 829°C , as confirmed by its X-ray powder diffraction pattern (Powder Diffraction Pattern File Card No. 5-661) [8]. The thermal decomposition can be described by the following equation:



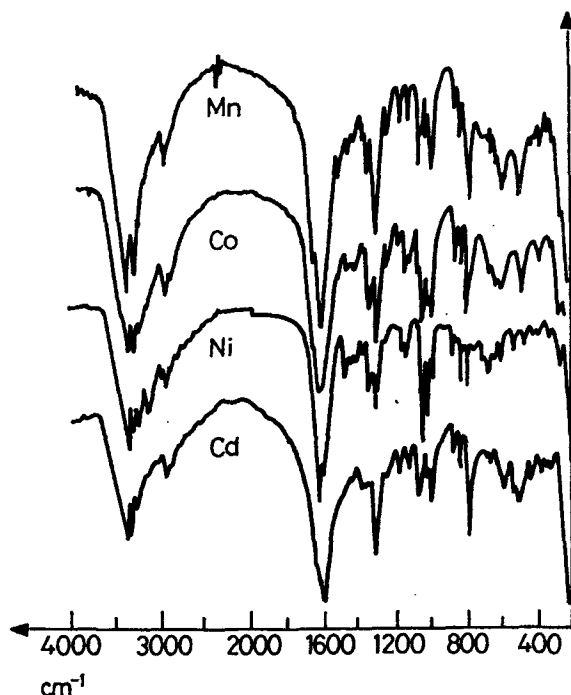
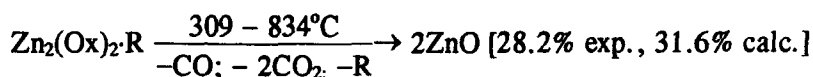
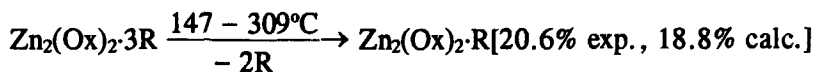
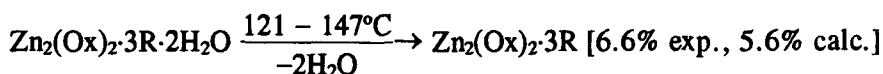
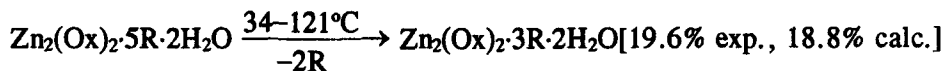


Fig. 4 IR spectra of oxalate 2-ethanolamine complexes of Mn, Co, Ni and Cd



The above compound has a similar empirical formula to that of the Ni compound, but decomposes in a different way (Fig. 7). The TG curve suggests four steps:



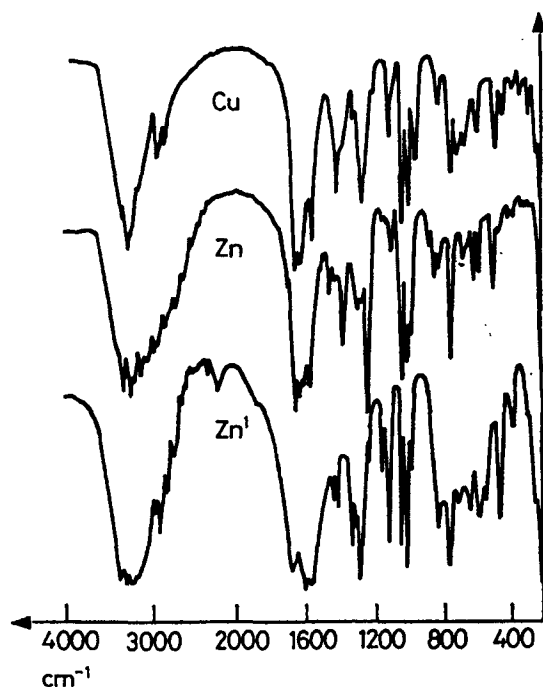
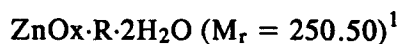
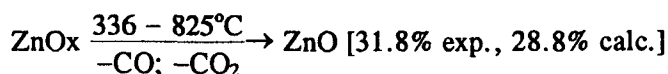
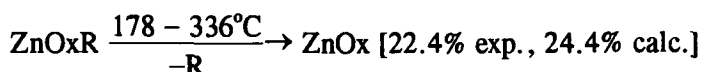
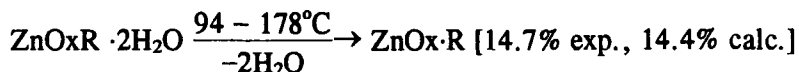


Fig. 5 Ir-spectra of oxalate-2-ethanolamine complexes of Cu and Zn

The decomposition involves many thermal effects, but the exotherm at about 420–430°C is particularly marked and can be attributed to the decomposition of $\text{ZnC}_2\text{O}_4\cdot\text{R}$. As a final product, ZnO is obtained (Powder Diffraction File No. 36-1451) [8].



This compound decomposes in a different way (Fig. 7) from the Zn compound described above. The decomposition occurs in three well-resolved steps, as follows:



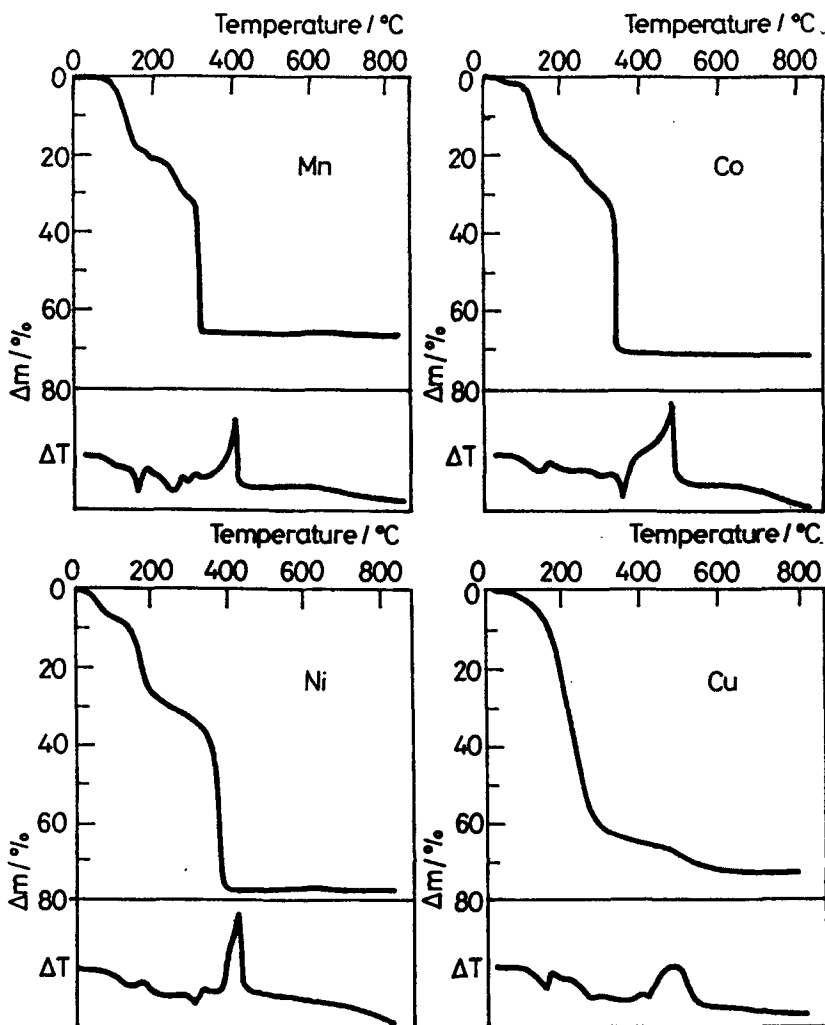


Fig. 6 TG and DTA curves of oxalate-2-ethanolamine complexes of Mn, Co, Ni and Cu

The decomposition is accompanied by many thermal effects (DTA curve). An exotherm peak at about 390–430°C, can be attributed to the decomposition of Zn oxalate. White ZnO is obtained at about 400°C.



The thermal decomposition of this Cd compound (Fig. 7) takes place in three steps, as follows:

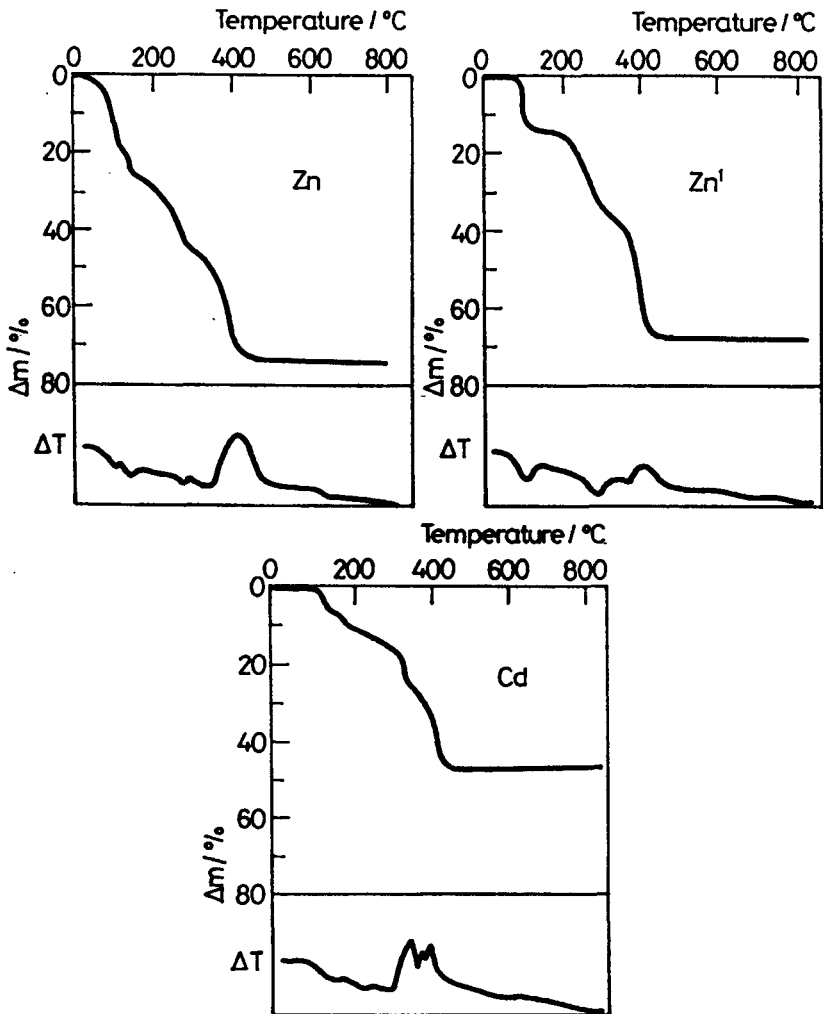
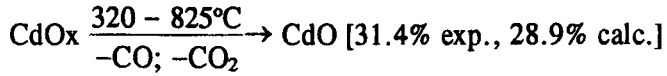
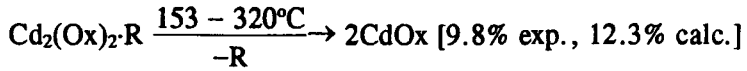
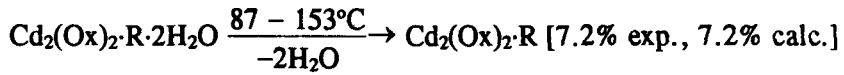


Fig. 7 TG and DTA curves of oxalate-2-ethanolamine complexes of Zn and Cd

The thermal decomposition in the last step occurs in two stages (DTA curve): in the first stage, CdOx losses CO and CO₂ at about 320°C, producing a mixture of the oxide and basic carbonate [4], which decomposes in the second stage, at about 400°C, to CdO (Powder Diffraction File No. 6-540) [8].

Conclusions

The thermal decompositions of the complexes generally occurred in a step-wise manner with the formation of different amine complexes. As the thermal decompositions begin at about 100°C, it can be concluded that they are not stable complexes. The instability is particularly marked for the Ni and Zn compounds, which decompose at lower temperatures than the others.

The IR spectra (Figs 4 and 5) confirmed the different structures of the complexes. The characteristic bands at 400–380 cm⁻¹, due to $\nu(\text{M-N})$, and at 520–500 cm⁻¹, due to $\nu(\text{M-O})$, permit the conclusion that in the amine of M(II)Ox the M-O bond is stronger than the M-N bond. This has also been observed for other amine complexes [6]. The characteristic bands due to $\nu(\text{COO}^-)$, $\nu(\text{CH}_2)$, $\nu(\text{NH}_2)$ and $\gamma(\text{CH}_2)$ are in agreement with the results of earlier investigations [6, 9]. It is difficult to distinguish characteristic bands due to $\nu(\text{OH})$ of the water or of the ethanolamine ligands $\nu(\text{NH}_2)$ bands occur in the same range [9].

Under the conditions described in the Experimental part for the preparation of $\text{ZnOxR} \cdot 2\text{H}_2\text{O}^1$, it was not possible to isolate new compounds of the other bivalent metals investigated in this article. Only the starting compounds were isolated.

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Zusammenfassung — Beim Kochen von $M(II)$ -oxalat ($M = \text{Mn, Co, Ni, Cu, Zn}$ oder Cd) und 2-Ethanolamin in Chloroform am Rückfluß wurden nachstehende Komplexe erhalten: $\text{MnC}_2\text{O}_4 \cdot \text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, $\text{CoC}_2\text{O}_4 \cdot 2\text{HOCH}_2\text{CH}_2\text{NH}_2$, $\text{Ni}_2(\text{C}_2\text{O}_4)_2 \cdot 5\text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}_2(\text{C}_2\text{O}_4)_2 \cdot 5\text{HOCH}_2\text{CH}_2\text{NH}_2$, $\text{Zn}_2(\text{C}_2\text{O}_4)_2 \cdot 5\text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{H}_2\text{O}$ und $\text{Cd}_2(\text{C}_2\text{O}_4)_2 \cdot \text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{H}_2\text{O}$.

Verfolgt man die Reaktion von $M(II)$ -oxalat mit 2-Ethanolamin in der Gegenwart von Ethanolammoniumoxalat, kann eine Verbindung mit der empirischen Formel $\text{ZnC}_2\text{O}_4 \cdot \text{HOCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{H}_2\text{O}$ [1] isoliert werden. Die Komplexe wurden mittels Elementaranalyse, Röntgenpulveraufnahmen, IR-Spektren sowie TG- und DTA charakterisiert. IR-Spektren und Röntgenpulveraufnahmen zeigten, daß die erhaltenen Komplexe nicht die gleiche Struktur haben. Ihre thermische Zersetzung im Temperaturbereich von 20 bis 900°C verläuft ebenfalls auf zwei verschiedenen Wegen, hauptsächlich über die Bildung verschiedener Aminkomplexe. Die DTA-Kurven weisen eine Anzahl thermischer Effekte auf.