

SYNTHESIS, CHARACTERIZATION AND THERMAL DECOMPOSITION OF $M^1[M^2(C_2O_4)_2] \cdot xH_2O$ ($x=5$ FOR $M^1=Co$ AND $x=4$ FOR $M^1=Cd$; $M^2=Ni$)

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Abstract

Cobalt bis(oxalato)nickelate pentahydrate, $Co[Ni(C_2O_4)_2] \cdot 5H_2O$ and cadmium bis(oxalato)nickelate tetrahydrate, $Cd[Ni(C_2O_4)_2] \cdot 4H_2O$ have been synthesized and characterized by elemental analysis, reflectance and IR spectral studies. Thermal decomposition studies (TG, DTG and DTA) in air showed that both the compound of cobalt and cadmium produced the oxide, $MNiO_x$ ($x=3$ for $M=Co$; $x=2$ for $M=Cd$) at 325 and 360°C respectively. DSC studies in nitrogen attributed only the mixture of both the metal at the end.

Keywords: IR, oxalato complexes, thermal decomposition

Introduction

Cation deficient one-dimensional (I-D) metallic complexes for platinum with oxalate as ligand i.e. $Rb_{1.67}[Pt(C_2O_4)_2] \cdot 1.5H_2O$ and a series of divalent CD bis(oxalato) platinum salts, $M_{0.8}[Pt(C_2O_4)_2] \cdot 6H_2O$ (where $M=Mg^{2+}$, Mn^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+}) which are found to be isostructural at room temperature had been reviewed [1] some time back. Verdaguer *et al.* [2] synthesized, $NiCu(C_2O_4)_2 \cdot 4H_2O$, which was the simplest one-dimensional ordered bimetallic system with different electronic spins. The structure and magnetic properties of the system were also investigated. The thermal decomposition of $LnCo(C_2O_4)_3 \cdot xH_2O$ (where $Ln=La, Pr, Nd$) led to [3] the rare earth cobaltites, $LnCoO_3$; while a mixture of CeO_2 and Co_3O_4 was formed from $CeCo(C_2O_4)_3 \cdot 8H_2O$. While studying [4] the same compounds later on, the cobaltites were found to be influenced by surrounding gas atmosphere. Thermal decomposition of coprecipitated zinc-copper oxalates in nitrogen was reported [5] a long time ago. The study indicated the formation of an interpenetrating structure or mixed crystals during coprecipitation and the end product was mixed oxide and copper metal. We have studied [6–8] the compounds of the type $M[M(C_2O_4)_2] \cdot xH_2O$ (where M =same metal) with Co, Ni and Cd, and found the different

intermediates and end products in different atmospheres. Although there have been quite a few reports on the mixed two metal oxalates, so far oxalates of cobalt and nickel, and cadmium and nickel have not been reported. Keeping in view of the possibility of formation of mixed metal oxides as end product, we report here the synthesis, characterization and thermal decomposition of $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O}$ and $\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 4\text{H}_2\text{O}$. We have followed similar method of preparation adopted earlier for $\text{M}[\text{M}(\text{C}_2\text{O}_4)_2]\cdot x\text{H}_2\text{O}$ [6–8].

Experimental

All the reagents used were AR grade. The chloride free nickel hydroxide prepared from nickel chloride was dissolved in glacial acetic acid and heated on a steam bath. A light pink precipitate was separated by adding cobaltous chloride followed by dropwise addition of saturated solution of oxalic acid. The precipitate was washed several times with distilled water and dried over calcium chloride. Similarly, after adding cadmium chloride the respective powder compound of light blue colour was isolated. The water content of the compounds were determined gravimetrically. The metal content were estimated using standard methods. A Carlo Erba 1108 elemental analyser was used to determine the carbon and hydrogen contents. Analysis as calculated for $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O}$: Co, 15.35%; Ni, 15.29%; C, 12.51%; H, 2.63%; H_2O , 23.46%; found: Co, 14.97%; Ni, 14.93%; C, 12.62%; H, 2.61%; H_2O , 23.52%; calc. for $\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 4\text{H}_2\text{O}$: Cd, 26.80%; Ni, 13.99%; C, 11.46%; H, 1.92%; H_2O , 17.18%; found: Cd, 26.63%; Ni, 14.12%; C, 11.24%; H, 1.89%; H_2O , 17.08%.

IR spectra ($4000\text{--}200\text{ cm}^{-1}$) were recorded as nujol mulls using a Perkin Elmer IR 883 spectrophotometer. Diffuse reflectance spectra were recorded with a Shimadzu UV-240 spectrophotometer. TG, DTG and DTA upto 1000°C were carried out in air at $10^\circ\text{C min}^{-1}$ using a Shimadzu DT 30B instrument. DSC was carried out in dynamic nitrogen using a Perkin Elmer PC series DSC 7 at a heating rate of 5 and $10^\circ\text{C min}^{-1}$. X-ray powder diffraction were obtained using a Rigaku X-ray diffractometer system D/Max. IIC.

Results and discussion

The light pink compound, $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O}$ and blue compound, $\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 4\text{H}_2\text{O}$ were insoluble in water and common organic solvents. However, they decomposed in the presence of strong acid or alkali. The analytical and microanalytical results supports the proposed formula of the compounds. The XRD pattern (Table 1) of the compounds differed from each other which suggests they are not isomorphous. The IR peaks were assigned (Table 2) on the basis of earlier studies [6–8, 10, 11] and reported data [9]. These suggests the presence of coordinated oxalato group. However, the possibility of the association of some of the water molecules with coordinated oxalato groups through hydrogen bonding cannot be ruled out as shown by the presence of a broad band between $2800\text{--}3800\text{ cm}^{-1}$.

Table 1 Prominent lines in the X-ray powder diffraction pattern of $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O}$ and pyrolysed product at 400°C , $\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 4\text{H}_2\text{O}$ and product from TG at 500°C

$\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O}$		Pyrolysed product of $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O}$ at 400°C		$\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 4\text{H}_2\text{O}$		Product of $\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 4\text{H}_2\text{O}$ from TG at 500°C	
D(Å)	I(REL)	D(Å)	I(REL)	D(Å)	I(REL)	D(Å)	I(REL)
14.98	16.26	8.53	100.00	19.21	18.07	1.78	85.6
5.58	100.00	8.03	87.65	14.03	17.81	1.73	95.4
5.11	75.38	7.31	83.50	10.28	30.26	1.66	91.4
4.41	80.63	6.24	64.86	7.84	38.11	1.59	90.5
4.37	75.44	5.28	31.13	6.42	46.85	1.57	87.3
4.11	71.85	4.79	26.70	5.55	100.00	1.53	100.0
3.62	62.25	4.42	24.29	4.86	53.23	1.48	76.9
3.59	62.67	4.04	14.37	4.46	68.56	1.44	77.4
3.33	62.64	3.83	17.15	4.07	53.91	1.43	70.6
2.74	49.38	3.39	14.08	3.52	37.39	1.42	63.1
2.48	4.68	3.26	15.61	3.20	52.93	1.36	76.3
2.30	37.73	3.06	13.61	2.84	33.45	1.34	75.4
2.19	37.01	2.93	12.73	2.85	35.71	1.32	64.2
2.00	35.44	2.76	12.74	2.62	23.60	1.29	71.3
2.01	33.94	2.75	12.98	2.25	22.21	1.26	60.4
1.97	30.93	2.19	9.70	2.15	19.96	1.24	61.6
		2.33	11.82	2.11	19.41	1.22	74.2
		2.21	1.21	1.99	23.31	1.19	64.7
		2.11	8.16	1.90	19.08	1.18	87.3
		2.04	11.84			1.15	72.2
		1.95	8.77			1.13	56.1
		1.92	8.03			1.14	56.6
		1.86	9.35			1.09	53.3
		1.83	7.43			1.07	63.8
		1.78	10.54			1.06	53.6
		1.71	9.18			1.05	52.4
		1.69	8.61			1.02	57.6
		1.66	8.45			1.01	58.8

The removal of water molecule at high temperature further indicates this type of association. The electronic spectrum of the solid sample of $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2]\cdot 5\text{H}_2\text{O}$ displayed a complex multicomponent band centered around 20,000 ($16,890$, $22,200$, $32,670\text{ cm}^{-1}$). The complexity could be due to severe distortion from ideal

geometry for octahedral/tetrahedral or square planar geometries around cobalt and nickel atoms. The multicomponent bands, 16,890, 20,000, 27,170 and 30,770 cm^{-1} showed in reflectance spectrum of $\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$ also suggests the distorted geometries of nickel environment. The distorted structure of oxalates of the type $\text{M}[\text{M}(\text{C}_2\text{O}_4)_2] \cdot x\text{H}_2\text{O}$ with cobalt and nickel had been concluded [6, 7] earlier. The band around 45,450 cm^{-1} in the UV region of both compounds were due [7, 10] to intraligand $\pi \rightarrow \pi^*$ transition.

Table 2 Selected bands in the IR spectra of $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$ and $\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$

IR bands/ cm^{-1}		Assignments
$\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$	$\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$	
2840–3800 b	2800–3800 b	$\nu_{\text{sy}}(\text{O-H}) + \nu_{\text{asy}}(\text{O-H})$ or hydrogen bonding
1640 S	1660 S	$\delta_{\text{sy}}(\text{H-O-H})$
1500–1800 b	1500–1800 b	$\nu_{\text{asy}}(\text{C=O})$
1360 S	1370 S	$\nu_{\text{sy}}(\text{C-O})$ and/or $\nu(\text{C-C})$
1320 S	1320 S	$\nu_{\text{sy}}(\text{C-O})$ and/or $\delta(\text{O-C=O})$
825 m	830 m, 780 m	$\delta(\text{O-C=O})$ and/or $\nu(\text{M-O})$ or coordinated water
605 s	620 s	crystal water
530 w	–	$\nu(\text{M-O})$ and/or $\nu(\text{C-C})$
455 mS	460 mS	$\nu(\text{M-O})$ and/or ring deformation
310 s	320 m	π (out-of-plane bending)

s – small; m – medium; S – strong; b – broad; w – weak

The TG profile (Fig. 1) of $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$, shows the removal of the first water molecule at 160°C, followed by an inclined slope upto 235°C (mass loss, found 20% ; calc., 18.79%) indicating the removal of four molecules of water. Complete deaquated compound is produced at 307°C with 23% mass loss (calc., 23.47%). An endotherm between 165–250°C ($\Delta T_{\text{min}} = 215^\circ\text{C}$) in DTA and a change in DTG between 148–257°C corresponds to the dehydration step. The breakdown of the deaquated compound takes place within a very short temperature range (307–325°C) as shown by a step slope in TG upto 325°C with a mass loss of 57.4%. The mass loss apparently suggests that the product is CoNiO_3 (calc., 56.83%). XRD pattern (Table 1) of the black product obtained after independent pyrolysis upto 400°C indicates [12] the contamination with traces of oxides and carbides of cobalt and nickel as well as carbon along with the main product. The XRD pattern does not attribute the formation of CoNiO_2 at 400°C. The carbon formed due to disproportionation of $\text{CO}_{(\text{g})}$ which inturn converted to carbides. Though the simple oxalates of cobalt and nickel, $\text{MC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ produce [13] their respective oxides in air at 305 and 352°C, in this study the formation of mixed metal oxides is noticed

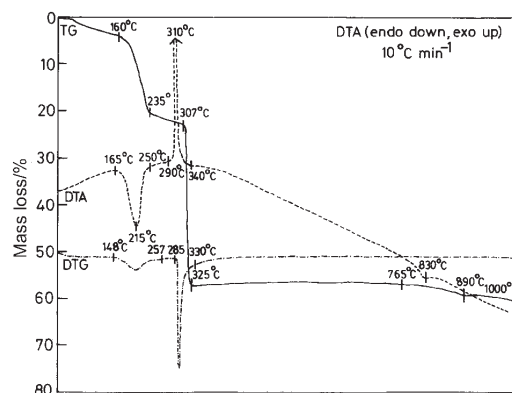


Fig. 1 TG, DTG and DTA curves of $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$ in air

at intermediate temperature of 325°C . In DTA an exothermic peak between $290\text{--}340^\circ\text{C}$ ($\Delta T_{\text{max}} = 310^\circ\text{C}$) and a sharp change in the range of $285\text{--}330^\circ\text{C}$ in DTG are for the decomposition step. The product formed at 325°C is stable upto 765°C in TG followed by a slight mass loss upto 1000°C (through a break at 890°C) with 60.5% mass loss might be due to change to CoNiO_2 (calc. 61%). A small downward hump in DTA around 830°C and a break in TG at 890°C are apparently due to change of phase at high temperature. The DSC profile in N_2 (Fig. 2) at 5°C min^{-1} shows two changes. By changing the heat flow axis the endotherm between $180.7\text{--}227.6^\circ\text{C}$ for dehydration clearly separates from the change $345\text{--}394^\circ\text{C}$ for decomposition. While the scanning is done at $10^\circ\text{C min}^{-1}$ (Fig. 3) the endotherm records between $173.6\text{--}251.7^\circ\text{C}$; the range of decomposition split into two. The first peak is between $353.9\text{--}366.5^\circ\text{C}$ and the second between $369.6\text{--}382.2^\circ\text{C}$. This suggests that the proper heat flow distinctly separate the phases during decomposition. The product formed in DSC study at 430°C with mass loss of 67.09% is stable in N_2 , indicated by no further change of DSC profile. The intimate mixture of metal cobalt and nickel could be assumed as an end product (calc. mass loss, 69.35%). Nagase et al. [14] reported the respective metal of Co and Ni formed in N_2 from the sim-

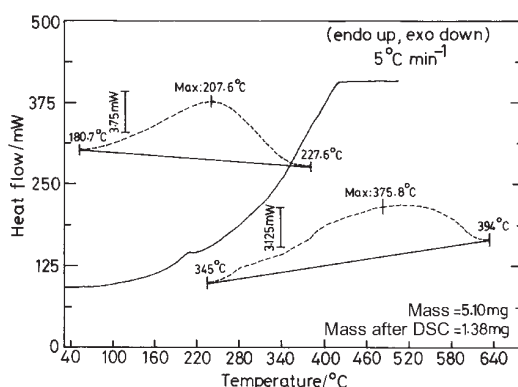


Fig. 2 DSC curve of $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$ at 5°C min^{-1} in nitrogen

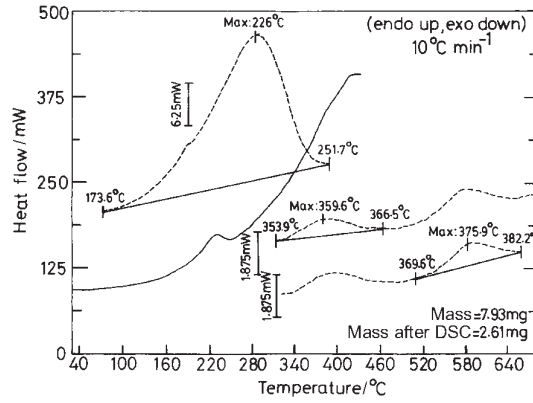


Fig. 3 DSC curve of $\text{Co}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 5\text{H}_2\text{O}$ at $10^\circ\text{C min}^{-1}$ in nitrogen

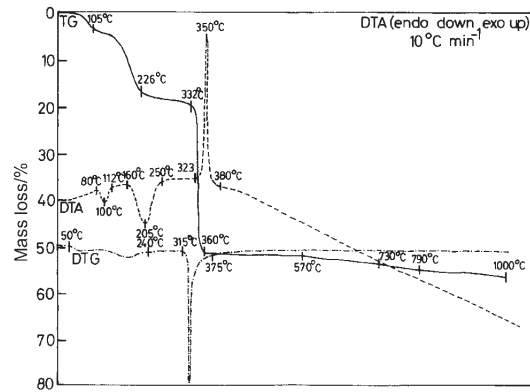


Fig. 4 TG, DTG and DTA curves of $\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$ in air

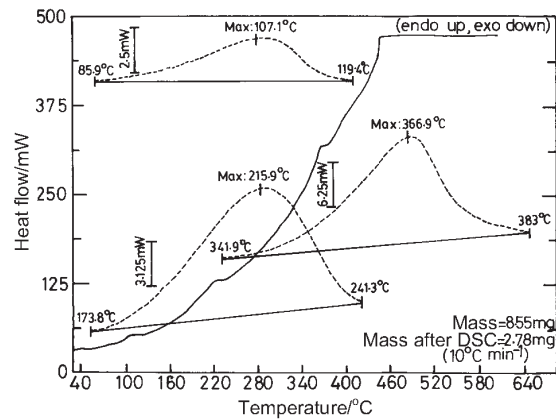


Fig. 5 DSC curve of $\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$ at $10^\circ\text{C min}^{-1}$ in nitrogen

ple oxalate, $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; however, initial mass loss temperature of decomposition of cobalt and nickel oxalates were 338 and 310°C respectively.

In the TG curve (Fig. 4) the compound, $\text{Cd}[\text{Ni}(\text{C}_2\text{O}_4)_2] \cdot 4\text{H}_2\text{O}$, loses first molecule of water at 105°C. The inclined nature of the curve upto 226°C (mass loss found, 17.4%; calc., 17.19%) indicates the formation of anhydrous compound. Two distinct changes in the range 50–240°C in DTG as well as two clear endotherm in DTA between 80–112°C ($\Delta T_{\text{min}} = 100^\circ\text{C}$) and 160–250°C ($\Delta T_{\text{min}} = 205^\circ\text{C}$) are for the stepwise removal of water molecules. The anhydrous compound loses mass of 2.6% in the range 226–332°C due to partial breaking of $\text{C}_2\text{O}_4^{2-}$ group; subsequently a steep slope upto 360°C apparently indicates the formation of grey coloured CdNiO_2 (mass loss found, 51.50%; calc., 51.55%). However, XRD pattern of the residue (Table 1) isolated at 500°C in TG confirms the presence of trace of CdCO_3 , CdO and NiO along with main product. An exothermic peak between 323–380°C ($\Delta T_{\text{min}} = 350^\circ\text{C}$) in DTA and the change in DTG (315–375°C) are accounted for this decomposition. The product loses mass very slowly in a wide range of temperature in TG and finally at 1000°C with a mass loss of 56.2% indicates the product might be CdNiO_x ($x < 1$). The DSC profile (Fig. 5) in N_2 shows three distinct steps for the decomposition. The first step ranges between 85.9–119.4°C is for dehydration, followed by two decomposition steps in the ranges 173.8–241.3 and 341.9–383°C. After 445°C the profile does not show any change, indicated by a straight DSC profile, which suggests no further change of the product formed at 445°C. The mass loss of 67.49% after scanning upto 600°C indicates that the product might be a mixture of both the metal only. The formation of respective metals were reported [13] in N_2 from their oxalates.

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