

SYNTHESIS AND THERMAL DECOMPOSITION OF MIXED 2,4'-BIPYRIDINE-OXALATO COMPLEXES WITH Mn(II), Co(II), Ni(II) AND Cu(II)

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Abstract

The mixed 2,4'-bipyridine-oxalato complexes of the formulae $M(2,4'\text{-bipy})_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ($M(\text{II})=\text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$; 2,4'-bipyridine=2,4'-bipy or *L*; $\text{C}_2\text{O}_4^{2-}=\text{ox}$) have been prepared and characterized. IR data show that the 2,4'-bipy coordinated with these metals(II) via the least hindered (4')N atom; that oxalate group acts as bidentate chelating ligand. Room temperature magnetic moments are normal for the orbital singlet states. The thermal decomposition of these complexes was investigated by TG, DTA and DTG in air. The endothermic or exothermic character of the decomposition of $\text{ML}_2(\text{ox})\cdot 2\text{H}_2\text{O}$ was discussed.

Keywords: 2,4'-bipyridine-oxalato complexes, IR spectra, thermal decomposition, transition metals(II)

Introduction

Various workers [1–9] have reported the thermal decomposition of oxalates of transition metals and mixed metal oxalates of the types M' (or M'') $[\text{M}(\text{ox})_n]\cdot \text{H}_2\text{O}$ (where $\text{ox}=\text{C}_2\text{O}_4^{2-}$; $M'=\text{K}^+, \text{NH}_4^+, \text{Na}^+$; $M''=\text{Fe}^{++}, \text{Co}^{++}, \text{Ni}^{++}$; $M=\text{other metals(II)}$). In the literature, very little is known about thermal stability of mixed amine-oxalato complexes [10–13]. 2,4'-Bipyridine (2,4'-bipy or *L*) complexes with metal oxalates are unknown. The work presented here is a continuation of our studies on the thermal decomposition of metal complexes with bipyridine isomers [14–17]. The paper includes the results of the synthesis and properties of 2,4'-bipy compounds with Mn(II), Co(II), Ni(II) and Cu(II) oxalates. Thermal decomposition of these complexes in order to find their thermal stability, intermediate solids and final products was analysed and discussed.

Experimental

Preparation and analyses of the complexes

The mixed 2,4'-bipyridine-oxalato complexes of Mn(II), Co(II), Ni(II) and Cu(II) of the type $\text{M}(2,4'\text{-bipy})_2(\text{ox})\cdot 2\text{H}_2\text{O}$, were prepared as follows: 2.6 mmol of Mox was dissolved in 50 cm^3 of 0.3 molar water solution of $\text{Na}_2(\text{ox})$ (containing 0.1 cm^3 of 0.5 molar $\text{H}_2(\text{ox})$ solution) and gradual residue of $\text{M}(\text{ox})$ was filtered off. This solution was mixed with

Table 1 Selected bands (cm^{-1}) in IR spectra for the complexes $\text{ML}_2(\text{ox})\cdot 2\text{H}_2\text{O}$

Assignment		$\text{MnL}_2(\text{ox})\cdot 2\text{H}_2\text{O}$	$\text{CoL}_2(\text{ox})\cdot 2\text{H}_2\text{O}$	$\text{NiL}_2(\text{ox})\cdot 2\text{H}_2\text{O}$	$\text{CuL}_2(\text{ox})\cdot 2\text{H}_2\text{O}$
Coordinated 2,4'-bipy modes					
$\nu(\text{C}=\text{N})(4\text{-sub})$		1610.5vs	1616.2vs	1612.4vs	1606.3vs
$\nu_{\text{ring}}(4\text{-sub})$		1415.7m	1411.8m	1415.5s	1417.6s
breathing (4-sub)		1012.6s	1014.5m	1016.4m	1022.2m
Coordinated oxalate modes					
$\nu_{\text{as}}(\text{C}=\text{O})$	ν_7		1749.3, 1733.9, 1716.5vw	1749.3, 1733.9, 1716.5vw	1749.3, 1733.4, 1716.5vw
$\nu_{\text{as}}\text{C}=\text{O}$	ν_1	1670.0sh	1662.5w	1662.5, 1652.9sh	1668.3, 1647.1m
$\nu_{\text{s}}(\text{C}-\text{O}) + \nu(\text{C}-\text{C})$	ν_2		1390.0sh	1390.0sh	1390.2vw
$\nu_{\text{s}}(\text{C}-\text{O}) + \delta(\text{O}-\text{C}=\text{O})$	ν_8	1365.0vw	1353.9, 1338.5w, 1309.6s	1357.8m, 1340.4w	1352.0m, 1338.0vw
$\delta(\text{O}-\text{C}=\text{O}) + \nu(\text{M}-\text{O})$	ν_9		798.5w	802.3s	806.2m
$\nu(\text{M}-\text{O}) + \nu(\text{C}-\text{C})$	ν_4	505.0w	529.0vw	516.9w	528.5w
ring def. + $\delta(\text{O}-\text{C}=\text{O})$	ν_{10}		488.6s	486.8s	486.0s
$\nu(\text{M}-\text{O}) + \text{ring def.}$	ν_{11}	418.5w	418.5w	418.5s	418.6w

s, m, v, w, sh – strong, medium, very, weak, shoulder; ν_{as} – asymmetric, ν_{s} – symmetric stretch, δ – bending

10 cm³ of water solution (with a few drops of 95 v/v% EtOH) containing 7.7 mmol of 2,4'-bipy. The reaction mixture was heated on a water-bath for 10 min. The resulting solid product was filtered off, washed with a mixture of EtOH and Et₂O (1:1) and dried at room temperature. The isolated compounds and solid thermal decomposition products (sinters) were analysed by standard methods. The theoretical composition was confirmed by analysis inside 0.0±0.3%. The intermediate products of decomposition were also identified by X-ray diffraction. The sinters of the obtained complexes were prepared under conditions similar to those used in thermal analysis.

Physical measurements

The thermal investigations were carried out with a derivatograph Q-1500 in air atmosphere. Each sample (100 mg) was heated from room temperature to 1000°C at a rate of 5°C min⁻¹; Al₂O₃ was used as the reference, other apparatus and measuring conditions were the same as described in our papers [15, 16].

Results and discussion

All complexes are air stable. The solubility of these compounds in water at 21°C was found to be in the range of 10⁻²–10⁻³ mol l⁻¹.

The room temperature effective magnetic moments of Mn(II), Co(II), Ni(II) and Cu(II) complexes are 5.75, 4.94, 2.89 and 1.85 M.B., respectively, being normal for the orbital singlet states [18–20] for pseudo-octahedral coordination of the metal atom in these complexes.

Infrared spectra

Selection IR bands of 2,4'-bipy and oxalate group as well as assignments [3, 21, 22] of their frequencies are presented in Table 1. Upon coordination with M(ox), the IR spectrum of free 2,4'-bipy undergoes a change only in the ring vibration modes of 4-substituted pyridine (4-sub). Such an effect has been observed previously for compounds of 2,4'-bipy with other of *nd^m* metal salts [15–17]. IR spectra of these complexes suggest that 2,4'-bipy is coordinated to these metals(II) via the least hindered (4')N atom [15–17, 21]. In addition to the 2,4'-bipy frequencies IR spectra of ML₂(ox)2H₂O complexes exhibit new absorption bands (Table 1), which are identified as ν_7 , ν_{11} , ν_2 , ν_8 , ν_9 , ν_4 , ν_{10} and ν_{11} modes of the oxalate group, respectively. The frequency values of these bands suggest that the oxalate group is bonded as normal chelating ligand [3, 22–25]. The bands with the maximum at 3600–3400 cm⁻¹ confirm the presence of water molecules. Peak in the water bending region is superimposed on oxalato bands.

Thermal decomposition

Thermoanalytical curves of ML₂(ox)2H₂O (*M*(II)=Ni, Cu) in air are shown, as an example in Figs 1a and 1b. The results of the thermal decomposition studies of ML₂(ox)2H₂O are given in Table 2. All the complexes decompose progressively.

Table 2 Characteristic of thermal decomposition of the complexes in air

Complex	$T_{\text{range}}/$ $^{\circ}\text{C}$	DTA _{peak} / $^{\circ}\text{C}$	Mass loss/%		Intermediate and residue
			found	calcd.	
MnL ₂ (ox)2H ₂ O	60–95	90endo	8.0	7.33	MnL ₂ (ox)
	170–240	220exo	67.5	63.57	Mn(ox) with ca 4% mixture of metal oxides
	>700	300exo	8.0	13.57*	pure Mn ₃ O ₄
CoL ₂ (ox)2H ₂ O	160–320	280exo	46.0	46.68	CoL _{0.75} (ox)
	320–390	365exo, vs	36.5	37.13	pure Co ₃ O ₄
	>750		2.0	1.08	CoO
NiL ₂ (ox)2H ₂ O	138–365	305endo, br	71.0	70.36	Ni(ox)
	365–410	380exo, vs	15.0	14.54	NiO with traces of Ni
	>430				pure NiO
CuL ₂ (ox)2H ₂ O	60–158	70endo	3.6	3.64	CuL ₂ (ox)H ₂ O
	158–190	170exo	35.0	34.88	CuL(ox)
	190–260	230endo	42.0	41.91	mixture of Cu ₂ O+Cu(ox) (1:1) with traces of Cu
	260–330	260, 310exo	3.0	3.73	pure CuO

* Theoretical calculation for pure Mn(ox)

The thermal stability of complexes and their further thermal decomposition are different. CoL₂(ox)2H₂O and NiL₂(ox)2H₂O complexes are thermally the most stable. They start to decompose at 160 and 138°C, respectively. The intermediate products 2Co(ox)L_{1.5} (the fragmentary elimination of amine was observed in other complexes [26, 27]) and Ni(ox) are formed. These products are converted quantitatively in pure Co₃O₄ and into NiO with Ni (as an example Fig. 1c). Forming of such NiO with Ni during pyrolysis of NiOx has been reported in the literature [1, 28]. With increasing of the temperature pure NiO is formed. The DTA curve showed weak endothermic peak at 280 (Co) and 305°C (Ni); a strong exothermic peak was seen at 365 (Co) and 400°C (Ni). The remaining complexes are stable only till 60°C. MnL₂(ox)2H₂O loses all its water within the temperature range 60–95°C (clearly separated step with endothermic peak at 90°C). In the temperature range 170–240°C Mn(ox) (with ca 4% other products of decomposition) is formed; exothermic peak at 220°C. Next, the process of Mn(ox) decomposition takes place. At ca 450°C we identified Mn₃O₄, traces of Mn₂O₃ and other amorphous products. DTA curve showed strong exothermic peak at 300°C. A horizontal mass level of Mn₃O₄ began at ca 700°C. However, the decomposition of Mn(ox) yields a series of different oxide products depending on experimental conditions. The product in air is one of the manganese oxides: MnO₂, Mn₂O₃ or Mn₃O₄ [1]. In the first step of decomposition CuL₂(ox)2H₂O loses 1 mol H₂O at 60–158°C (endo peak at 70°C). Between 158–190°C CuL(ox) is formed. In the last deamination step at 190–260°C the remaining 2,4'-bipy is eliminated, accom-

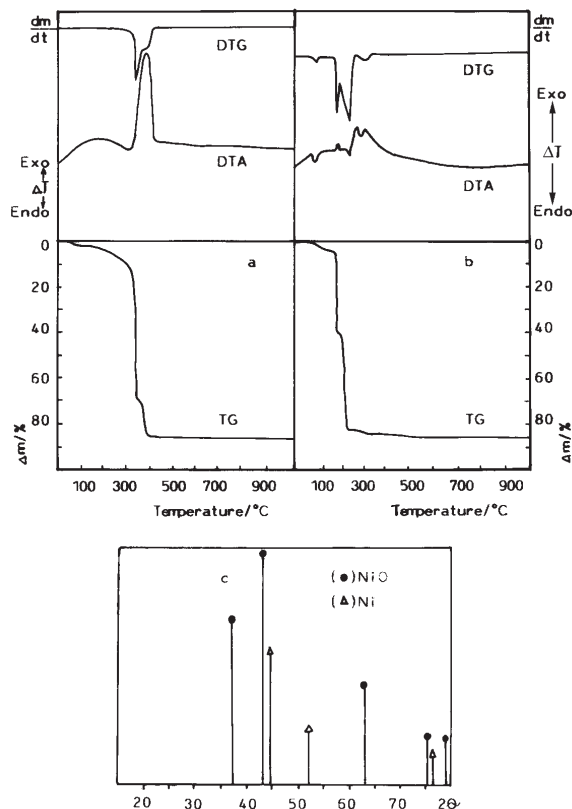
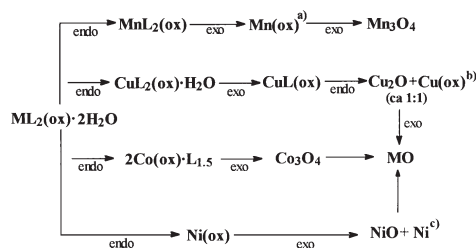


Fig. 1 Thermoanalytical curves of a – NiL₂(ox)·2H₂O; b – CuL₂(ox)·2H₂O and c – X-ray diffraction patterns of decomposition products of NiL₂(ox)·2H₂O heated up to 380°C

panied by oxalate partial decomposition, and mixture of Cu₂O and CuO (ca 1:1) with traces of Cu is formed. A horizontal level of CuO begins at 330°C. Exothermic peaks are observed at 170, 260 and 310°C; endothermic – at 230°C.

The general Scheme of the thermal decomposition for ML₂(ox)·2H₂O compounds can be thus showed as follows:



where: M(II)=Mn, Co, Ni, C; ^{a)} with ca 4% mixture of metal oxides; ^{b)} with a trace of Cu; ^{c)} transitionally with Ni

Some processes of elimination of water and 2,4'-bipy, as well as of elimination of 2,4'-bipy and decomposition of oxalate partially overlap for Co(II), Ni(II) and Cu(II) compounds, without no clearly separated steps.

Generally the intermediate compounds (Mn(ox), Ni(ox), Cu(ox) and $2\text{Co(ox)}L_{1.5}$) decompose in our experimental conditions with an exothermic effect. The decarboxylation peak in air is endothermic, however DTA signals are more complicated in result of the oxidization reactions.

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We thank Dr. J. Kałużna-Czaplińska for performing some investigations.

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