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SYNTHESIS, STRUCTURAL CHARACTERISATION AND THERMAL DECOMPOSITION STUDIES OF SOME 2,4'-BIPYRIDYL COMPLEXES WITH COBALT(II), NICKEL(II) AND COPPER(II)

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Abstract

2,4'-Bipyridyl (2,4'-bipy or *L*) complexes with cobalt(II), nickel(II) and copper(II) of the formulae $M(2,4'\text{-bipy})_2(CH_3COO)_2 \cdot 2H_2O$ (M(II)=Co, Ni, Cu), $Co(2,4'\text{-bipy})_2SO_4 \cdot 3H_2O$ or $Ni(2,4'\text{-bipy})_2SO_4 \cdot 4H_2O$ have been prepared and their IR and electronic (VIS) spectra are discussed. The thermal behaviour of the obtained compounds has also been studied. The intermediate products of decomposition at different temperatures have been characterized by chemical analysis and X-ray diffraction.

Keywords: 2,4'-bipyridyl complexes, thermal behaviour, transition-metal complexes

Introduction

Reports on synthesis and thermal behaviour of 2,4'-bipyridyl (2,4'-bipy or *L*) complexes with metal ions are very rare in the literature [1–6]. In the present work, new 2,4'-bipy compounds with cobalt(II), nickel(II) or copper(II) acetates and cobalt(II) or nickel(II) sulphates were characterized by X-ray diffraction analysis, IR spectroscopy and electronic spectroscopy (VIS). The thermal decomposition of these compounds was studied under non-isothermal conditions in air.

Experimental

Apparatus

The X-ray diffractograms were recorded using D-5000 diffractometer and CuK_α radiation (graphite monochromator). The measurements were made within the range $2\theta = 2–80°$. Spectral studies were performed on the M-40 or M-80 Specord Instrument. The IR spectra the within 4000–400 cm^{-1} region were recorded using KBr pellets. The VIS spectra were obtained in a Nujol mull. DTA, TG and DTG measurements of the compounds under study were carried out in air, using type Q-1500 derivatograph over the temperature range from 20 to 1000°C at a heating rate of 5°C min^{-1}, with sample mass 100 mg galvanometer and $\alpha\text{-}Al_2O_3$ as reference ma-

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terial. The analyses of the solid decomposition products were performed using derivatographic curves, analytical data and X-ray diffractograms. The X-ray diffraction analysis of the decomposition products of the investigated complexes (obtained at particular temperatures) was carried out using Powder Diffraction File [7].

Synthesis and analysis

2,4'-Bipy (25.8 mmol) was dissolved in 20 ml water (with a few drops of 95%v/v ethanol) and mixed with aqueous solutions of cobalt(II), nickel(II) and copper(II) acetates and cobalt(II) or nickel(II) sulphates (8.6 mmol in 20 ml). The mixture was heated up to 80°C for 10 min. The crystalline complexes were filtered off, washed with a mixture of cold ethanol and ethyl ether (1:1) and dried in open air. The complexes isolated from the solutions were analysed: carbon, hydrogen and nitrogen – by elementary analysis; sulphate gravimetrically; Co(II), Ni(II) and Cu(II) in mineralized samples were determined complexometrically by using murexide as indicator. The analytical results for the complexes are shown in Table 1.

Table 1 Analytical data and solubility (S) of complexes in water at 21°C

Complex	Analysis: found (calculated)/%					$S \cdot 10^2$
	M	C	N	H	SO_4^{2-}	mol l^{-1}
$CoL_2(CH_3COO)_2 \cdot 2H_2O$	11.31	54.94	10.60	4.90		3.00
pink	(11.22)	(54.86)	(10.66)	(4.99)		
$NiL_2(CH_3COO)_2 \cdot 2H_2O$	11.33	54.99	10.68	4.93		2.53
light green	(11.18)	(54.89)	(10.67)	(5.00)		
$CuL_2(CH_3COO)_2 \cdot 2H_2O$	12.15	54.48	10.43	4.87		1.00
dark blue	(11.99)	(54.39)	(10.57)	(4.94)		
$CoL_2SO_4 \cdot 3H_2O$	11.48	46.09	10.05	4.18	18.69	2.50
pink	(11.30)	(46.07)	(10.75)	(4.25)	(18.42)	
$NiL_2SO_4 \cdot 4H_2O$	10.69	44.64	9.55	4.40	17.70	1.00
light blue	(10.89)	(44.55)	(10.39)	(4.49)	(17.82)	

Results and discussion

The analytical results show an empirical formulae $ML_2(CH_3COO)_2 \cdot 2H_2O$ (*M*=Co(II), Ni(II), Cu(II)), $CoL_2SO_2 \cdot 3H_2O$ and $NiL_2SO_4 \cdot 4H_2O$ for isolated compounds (Table 1). All complexes are stable in air. The solubility of these compounds in water was found to be in the range of 10^{-2}mol l^{-1} (Table 1). The analysis of the diffractograms shows that the prepared complexes are crystalline compounds. Complexes $CoL_2(CH_3COO)_2 \cdot 2H_2O$ and $NiL_2(CH_3COO)_2 \cdot 2H_2O$ are isostructural.

Electronic and IR spectra

The ligand-field spectra of the investigated complexes (Table 2) are characteristic of distorted octahedral environment around the Co(II), Ni(II) and Cu(II)

[8]. The cobalt(II) complexes exhibit bands at ca. 20000 cm^{-1} which correspond to this transition $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$. All these bands are apparently asymmetrical and have a shoulder in the higher-energy region (at ca. 21000 cm^{-1}) which indicates tetragonal distortion. The electronic spectra of Ni(II) complexes show only two spin allowed d–d transitions at ca. 15500 cm^{-1} ($^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$) and at ca. 26000 cm^{-1} ($^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$). The single band observed for Cu(II) complex at 16160 cm^{-1} can be associated with three transitions lying within one broad envelope ($^2B_{1g}\rightarrow{}^2E_g$, $^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2A_{1g}$). It is known that copper(II) *d–d* transitions are normally close in energy [9]. The position and shape of this band indicates pseudooctahedral configuration with a tetragonal distortion from the one electron orbital ground state $d_{x^2-y^2}$ [10, 11].

Table 2 Some IR bands for 2,4'-bipy and its complexes and ligand field spectral data in cm^{-1}

Compound	ν(C=N) (4-sub)	ν_{ring} (4-sub)	Pyridine "breathing" (4-sub)	Ligand [a] field spectra	
2,4'-bipy	1595vs	1405vs	990sh		
$CoL_2(CH_3COO)_2{\cdot}2H_2O$	1609vs	1408sh	1018s	20000	21000sh
$NiL_2(CH_3COO)_2{\cdot}2H_2O$	1612vs	1411s	1018s	15640	~26000sh
$CuL_2(CH_3COO)_2{\cdot}2H_2O$	1608vs	1410vs	1012vs	16160	
$CoL_2SO_4{\cdot}3H_2O$	1618s	1418s	1016m	19580	20800sh
$NiL_2SO_4{\cdot}4H_2O$	1610s	1416s	1020m	15500	26500

[a] from Nujol

The IR spectrum of 2,4'-bipy (unsymmetrical isomer of the bipyridyl) is the sum of the characteristic patterns of the 2-substituted and 4-substituted pyridine. Furthermore, vibrational absorptions due to the interaction between the rings might be expected. The IR spectrum of free 2,4'-bipyridyl [12] undergoes a change only in the region of ring vibration mode for 4-substituted pyridine, when coordinated with Co(II), Ni(II) and Cu(II). Bands for in-plane and out-of-plane CH vibration modes do not change. The characteristic pyridine breathing vibration of 4-substituted pyridine, ring stretching C=N (4-sub) mode and ring stretching (4-sub) vibration are shifted towards higher values (Table 2). These data indicate that 2,4'-bipy is bonded to the Co(II), Ni(II) and Cu(II) ions through the least hindering 4'N atom [1]. Such an effect has been observed previously for some compounds of 2,4'-bipy Co(II), Ni(II) and Cu(II) [1, 3–6].

The spectra of all the complexes obtained show strong and broad absorption bands in the water stretching region (3100–3480 cm^{-1}) and medium band (or shoulder) in the water bending region (1620–1650 cm^{-1}). Moreover, coordination water frequencies have been observed in all investigated compounds [13]. The bands of medium intensity at ca. 500 cm^{-1} (except $NiL_2SO_4{\cdot}4H_2O$ at 525 cm^{-1}) have been assigned to the H_2O wagging modes, whereas the band observed in the range 450–470 cm^{-1} has been associated with metal-oxygen (for coodinated water) stretching vibrations. In the IR spectra of $NiL_2SO_4{\cdot}4H_2O$ and $CoL_2SO_4{\cdot}3H_2O$ the following bands appear, attributed to sulphate group: ν_3 at 1160 cm^{-1}, 1125 cm^{-1}, 1101 cm^{-1} and 1164 cm^{-1}, 1088 cm^{-1}; ν_2 at 430 cm^{-1} and 434 cm^{-1}; ν_1 at 982 cm^{-1}

Table 3 Thermal decomposition data for the 2,4'-bipyridyl complexes with Co(II), Ni(II) and Cu(II)

Complex	DTA peaks/ °C	Ranges of decomp./ °C	Mass loss/%		The observed process
			found	calc.	
$CoL_2(CH_3COO)_2 \cdot 2H_2O$	120 endo	98–140	6.4	6.86	$-2H_2O$
	135, 165 endo 210, 240 endo	140–250	29.0	29.73	$-L$
	298 endo 310, 400 exo	250–430	48.5	48.14	$-L$; decomp. of acetates forms $Co_3O_4^a$
	910 endo	760–910	~1	1.02	CoO^b
$NiL_2(CH_3COO)_2 \cdot 2H_2O$	145 endo	112–165	7.0	6.86	$-2H_2O$
	335, 445 exo	165–480	80.0	78.92	$-2L$; decomp. of acetates forms NiO
$CuL_2(CH_3COO)_2 \cdot 2H_2O$	132 endo	105–140	6.0	6.80	$-2H_2O$
	blurred	153–400	52.0	51.57	$-1.75L$
	540 exo	400–850	27.0	26.62	$-0.25L$; decomp.of acetates, forms CuO^c
	920 endo	>850			Cu_2O^d

Table 3 Continued

Complex	DTA peaks/ °C	Ranges of decomp./ °C	Mass loss/%		The observed process
			found	calc.	
$CoL_2SO_4\cdot 3H_2O$	100 endo	80–110	10.0	10.37	$-3H_2O$
	160 endo	120–210	14.0	14.98	$-0.5L$
	265 endo	210–280	7.5	7.49	$-0.25L$
	325 endo	280–358	30.0	29.95	$-L$
	505 exo	358–760	7.5	7.49	decomp. products of L, forms $CoSO_4$
	860, 910 endo	760–910	16.0	15.36	decomp. of $CoSO_4$ to mixture Co-oxides, finally forms CoO
$NiL_2SO_4\cdot 4H_2O$	70 endo	50– 80	3.0	3.34	$-H_2O$
	160 endo	120–170	10.0	10.02	$-3H_2O$
	230 endo 260 endo	170–310	29.0	28.97	$-L$
	420 endo 495 exo	310–520	36.0	36.39	$-L$; forms Ni_2OSO_4
	615 exo 780 endo	600–800	8.0	7.42	forms NiO

[a] transitionally with a trace of CoO; [b] very slowly conversion of Co_3O_4 to CoO; [c] transitionally with a trace of Cu_2O; [d] very slowly conversion of CuO to Cu_2O; endo – endothermic; exo – exothermic

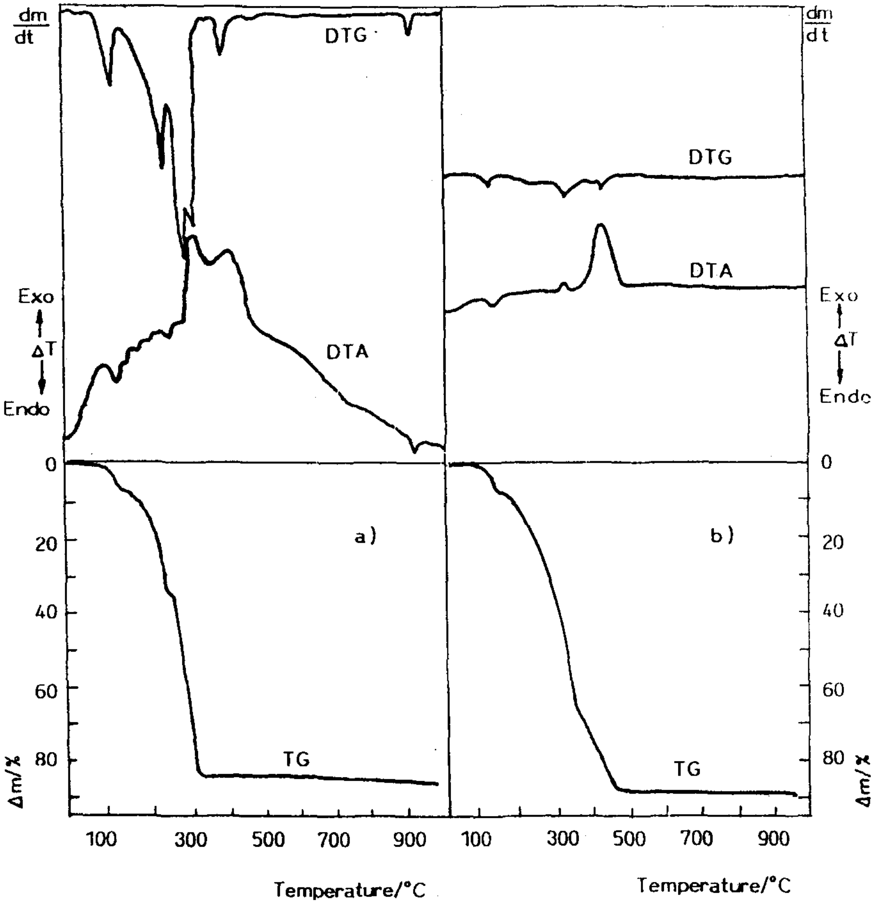

Fig. 1 Thermoanalytical curves of $CoL_2(CH_3COO)_2{\cdot}2H_2O$ (a), $NiL_2(CH_3COO)_2{\cdot}2H_2O$ (b)

and 992 cm^{-1}; ν_4 at 610 cm^{-1} and 662 cm^{-1} for Co(II) and Ni(II) complexes, respectively. Therefore, it may be concluded that T_d symmetry of the SO_4^{2-} ion is lowered [14]. The spectra of the investigated acetate compounds are very complicated. The frequencies $\nu_{asym(CO_2)}$, and $\nu_{sym(CO_2)}$, from acetates are superimposed on some 2,4'-bipy bands [15]. Thus, it is difficult to discuss the nature of the metal-acetate bonds.

Thermal properties of complexes

The thermal decomposition data obtained for the studied complexes are collected in Table 3.

The thermoanalytical curves of 2,4'-bipy compounds with Co(II), Ni(II) and Cu(II) acetates are presented in Figs 1 and 2. The hydrated complexes $ML_2(CH_3COO)_2{\cdot}2H_2O$ (M(II)=Co, Ni, Cu) lose two water molecules in one stage on heating within

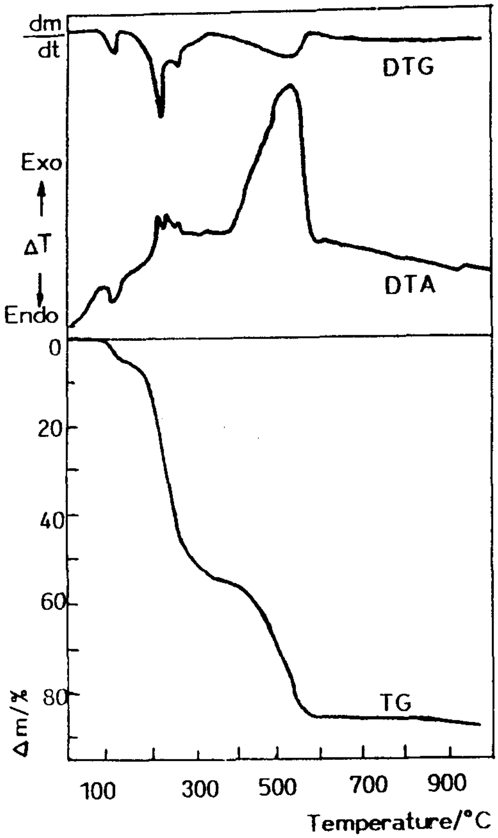

Fig. 2 Thermoanalytical curves of $CuL_2(CH_3COO)_2{\cdot}2H_2O$

the temperature range 98–140°C for Co(II), 112–165°C for Ni(II) and 105–140°C for Cu(II). The dehydration process is followed by weak endothermic peaks between 120 and 145°C for all compounds.

The first stage of thermal decomposition of $CoL_2(CH_3COO)_2$ occurs within the range 140–250°C. In this stage 1 mol of 2,4'-bipy is liberated. The endothermic effects on DTA curves are not sharp. Further weight loss is observed within the temperature range 250–430°C. It is attributed to the loss of the remaining 2,4'-bipy, decomposition of acetate and formation of Co_3O_4 (transitionally with a trace of CoO, Fig. 3a). The combustion of the organic ligand is accompanied by very strong exothermic effect with DTA maximum at 310°C. A horizontal weight level of Co_3O_4 begins at 430°C (strong exothermic effect in the DTA curve at 400°C). The X-ray diffraction patterns indicate that Co_3O_4 is present in the sinters of $CoL_2(CH_3COO)_2{\cdot}2H_2O$ heated up to 430 and 750°C (Fig. 3b). Cobalt(II) oxide is formed at 760–910°C. The temperature of formation of CoO from Co_3O_4 is similar to that reported in the literature [16].

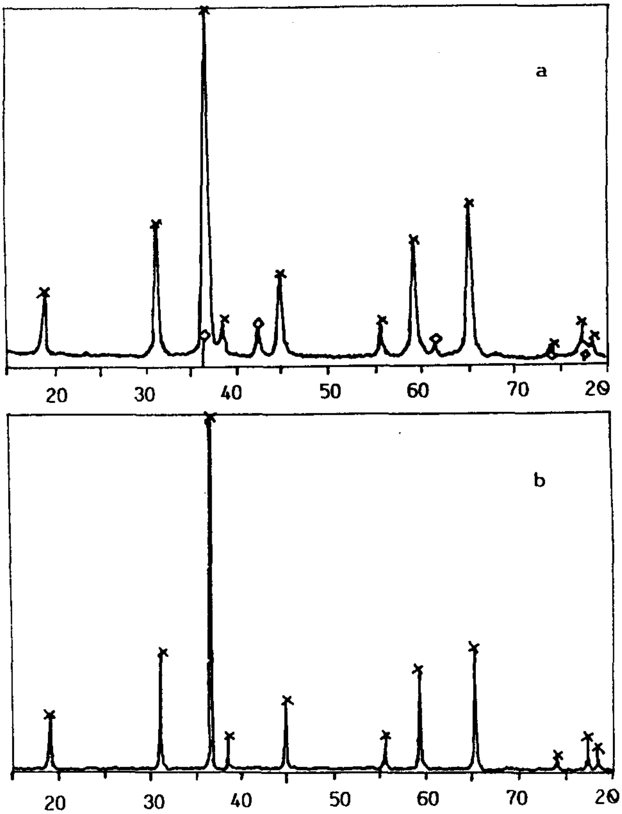

Fig. 3 X-ray diffraction patterns of decomposition products of $CoL_2(CH_3COO)_2 \cdot 2H_2O$ heated up to 330°C (a), $CoL_2(CH_3COO)_2 \cdot 2H_2O$ heated up to 430 and 750°C (b); (x) Co_3O_4; (◊) CoO

On heating, $NiL_2(CH_3COO)_2$ complex it decomposes directly to NiO (temperature range 165–480°C). The combustion of the organic ligand is accompanied by two exothermic effects with DTA maxima at 335 and 445°C (strong).

The thermal decomposition of $CuL_2(CH_3COO)_2$ takes place in two stages. At the first stage, 1.75 mol of 2,4'-bipy are eliminated in the temperature range 153–400°C. The effects on the DTA curve are small and blurred. With increasing temperature, the remaining 2,4'-bipy is lost, the process of acetate decomposition takes place and CuO with a trace of Cu_2O forms transitionally (Fig. 4a). The DTA curve exhibits strong and large exothermic peak which begins at 400°C and finishes at 600°C. Further heating causes decomposition of the trace Cu_2O and results in pure CuO (Fig. 4b). Above 850°C copper(II) oxide converts very slowly to Cu_2O.

$CoL_2SO_4 \cdot 3H_2O$ loses water within the temperature range 80–110°C with endothermic peak at 100°C. 2,4'-Bipyridyl is released in several stages. The intermediate products are formed. These processes are accompanied by three endothermic effects at 160, 265 and 325°C. Between 358 and 760°C a very slow weight loss is ob-

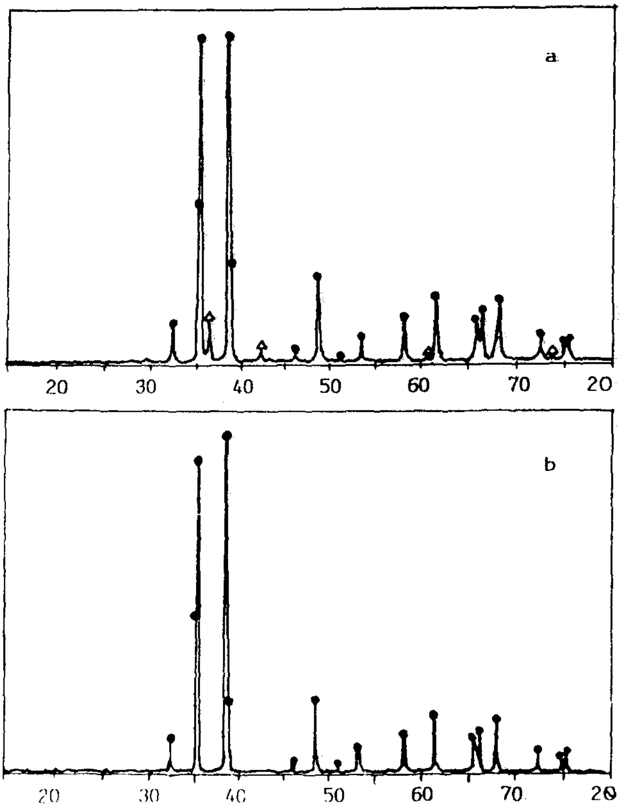

Fig. 4 X-ray diffraction patterns of decomposition products of $CuL_2(CH_3COO)_2{\cdot}2H_2O$ heated up to 560°C (a), $CuL_2(CH_3COO)_2{\cdot}2H_2O$ heated up to 850°C (b); (Δ)Cu_2O; (•) CuO

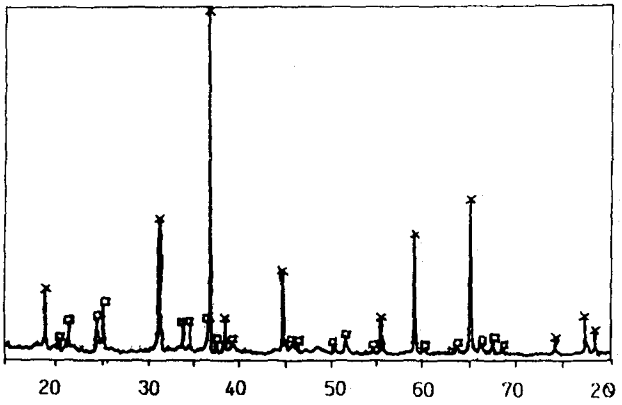

Fig. 5 X-ray diffraction patterns of decomposition products of $CuL_2SO_4{\cdot}3H_2O$ heated up to 800°C; (□) $CoSO_4$; (x) Co_3O_4

served. In this range of temperature, the elimination of the remaining 2,4'-bipy and of the residual carbon takes place. The DTA curve exhibits an exothermic effect at 505°C. The diffraction pattern of $CoL_2SO_4{\cdot}3H_2O$ heated up to 580°C shows the presence of $CoSO_4$ with a small amount of carbonized products (ca. 6% from analytical data). Above 760°C a more rapid loss in mass occurs which is connected with gradual decomposition of $CoSO_4$. On the basis of the literature data [16], the thermal decomposition of $CoSO_4$ begins at ca. 750°C (or 800°C). The diffraction pattern of the sample heated to 800°C indicates peaks corresponding to $CoSO_4$ and Co_3O_4 (Fig. 5). Gradual increase of temperature causes formation of a mixture of non-stoichiometric oxides Co_3O_4 and CoO. Finally pure CoO is formed (the horizontal weight level beginning at about 910°C). Thermal decomposition curves for $CoL_2SO_4{\cdot}3H_2O$ are shown in Fig. 6a.

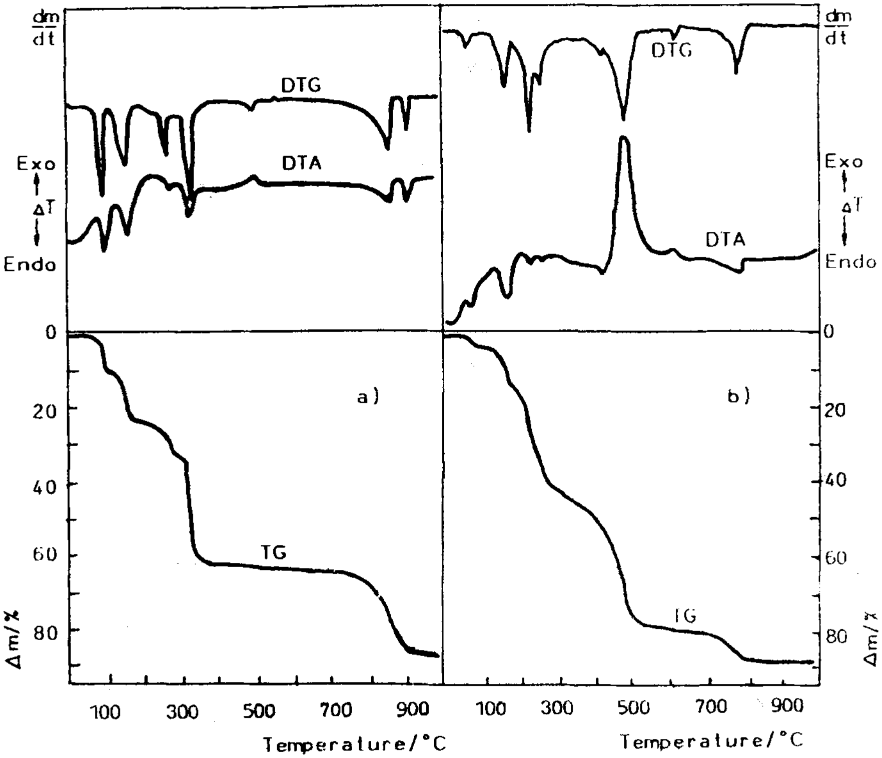

Fig. 6 Thermoanalytical curves of $CoL_2SO_4{\cdot}3H_2O$ (a), $NiL_2SO_4{\cdot}4H_2O$ (b)

$NiL_2SO_4{\cdot}4H_2O$ is dehydrated progressively. In the first step (50–80°C) one water molecule is split off and the residual water is lost at 120–170°C. DTA curve minima are observed at 70 and 160°C. During thermal decomposition of the anhydrous complex, gradual deamination takes place. In the temperature range 170–310°C one mol of 2,4'-bipy is eliminated. The corresponding small endothermic peaks on the DTA curve are observed at 230 and 260°C. With increasing temperature, the intermediate compound $NiLSO_4$ decomposes to Ni_2OSO_4 and finally to NiO. The curve two weak endothermic peaks at 420 and 780°C. The exothermic peaks are observed at 495°C (strong) and 615°C (weak). Thermal decomposition curves for $NiL_2SO_4 \cdot 4H_2O$ are shown in Fig. 6b.

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