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THERMAL PROPERTIES OF COMPLEXES OF Mn(II), Fe(II), Co(II), Ni(II) WITH 2,2'-BIPYRIDINE OR 4,4'-BIPYRIDINE AND THIOCYANATES

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Abstract

The compounds $ML_2(NCS)_2$, (M(II)=Mn, Co), $FeL_2(NCS)_2 \cdot 2H_2O$, $NiL_3(NCS)_2 \cdot 3H_2O$ (L=2,2'-bipyridine, 2-bipy) $MX_2(NCS)_2 \cdot 2H_2O$ (M(II)=Mn, Fe; X=4,4'-bipyridine, 4-bipy) have been prepared and their IR spectra and molar conductivity studied. The thermal decomposition of the complexes was studied under non-isothermal conditions in air. During heating the hydrated complexes lose crystallization water molecules in one or two steps and then decompose via different intermediate compounds to the oxides Mn_3O_4, Fe_2O_3, CoO, NiO.

Keywords: 2,2'-bipyridine, 4,4'-bipyridine, complexes of Mn(II), Fe(II), Co(II), Ni(II), IR spectra, molar conductivity, thermal decomposition

Introduction

In the last few decades interest has grown in the thermal properties of transition metal complexes with thiocyanates and nitrogen donor ligands [1–13]. There are some data on the preparation and physico-chemical properties of the compounds of Mn(II), Fe(II), Ni(II) with 2-bipy and thiocyanates. König and Watson [14] synthesized $Fe(2\text{-bipy})_2(NCS)_2$ and determined its structure. The complex $Ni(2\text{-bipy})_3(NCS)_2 \cdot 3H_2O$ was obtained by Pfeiffer and Tapperman [15], but information about its properties are fragmentary. Ahuja *et al*. [16] also prepared complexes with empirical formulae: $Mn(2\text{-bipy})_2(NCS)_2$ and $Mn(4\text{-bipy})_2(NCS)_2$. These compounds have been characterized by electronic, infrared spectra and magnetic moments.

Previously, we described the preparation, IR spectra and thermal decomposition of mixed 4,4'-bipyridine-thiocyanato complexes of Co(II), Ni(II), Cu(II) [17]. The compounds: $M(2,4'\text{-bipy})_2(NCS)_2 \cdot nH_2O$ (where M(II)=Mn, Fe, n=2, 1, respectively) were characterized by thermal analysis and by IR spectroscopic, magnetic and molar conductivity studies [18, 19]. The complexes of Cu(I) and Ag(I) [20] of the general formula MLSCN (M(I)=Cu, Ag; L=2,2'-bipyridine, 4,4'-bipyridine or 2,4'-bi-

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pyridine) have been prepared, their IR spectra and thermal properties discussed. This paper is the continuation of our investigations.

The survey of literature shows that the thermal behaviour of the compounds presented in this paper was not known. Here we describe the synthesis, IR spectra, molar conductivity and thermal decomposition in air of mixed bipyridine-thiocyanato (bipyridine=2-bipy or 4-bipy) complexes of title metals(II).

Experimental

Materials and physical measurements

2,2’-Bipyridine (*m.p.*=72°C), 4,4’-bipyridine (*m.p.*=69.5°C) and $Co(NCS)_2$ were obtained from Aldrich; methanol (anhydroscan) from Lab-Scan., hydroxylamine (50% water solution) from Fluka; other chemicals were p.a. from POCh-Gliwice. The thiocyanates of Mn(II), Fe(II), Ni(II) as hydrated products were prepared according to the reaction:

$$M(ClO_4)_2+2KNCS\rightarrow M(NCS)_2+2KClO_4\downarrow, \text{ in 96\% } (v/v) \text{ EtOH.}$$

The apparatus and measuring conditions were the same as described in previous publications [20–22].

Preparation and chemical analysis

The $M(NCS)_2$ (4.3 mmol in 22 cm^3) and 2-bipy or 4-bipy (12.8 mmol in 28 cm^3) were dissolved in warm 75% (*v/v*) EtOH. The mixture was heated on the water-bath at 80°C for 10 min. Next, the mixture was left to cool. All complexes were filtered off, washed with a mixture of EtOH and Et_2O (1:1), and dried in air. During the synthesis of complexes of iron(II) was added 1 cm^3 of 10% (*v/v*) hydroxylamine, to stop the oxidation process of Fe(II) to Fe(III).

The chemical composition of the studied complexes was confirmed by standard chemical analyses. Metal(II) contents were determined complexometrically with EDTA as the complexing agent. Thiocyanates were analysed by the Volhard method, C, H and N by standard microanalytical technique (Carlo-Erba analyser) with V_2O_5 as oxidizing agent. The analyses of the solid decomposition products were performed by using TG, DTG and DTA 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 [23]. A sample of 100 mg was heated in a silite furnace at a heating rate of about 5°C min^{-1} up to an appropriate temperature determined from the TG curves.

Result and discussion

The analytical data of synthesized compounds are presented in Table 1.

Table 1 Analytical data, molar conductivity Λ_M in methanol at 25°C of complexes

Compound	Colour	Analysis/%										Λ_M/ Ω^{-1} cm^2 mol^{-1}
		M		NCS		N		C		H		
		found	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	
Mn(2-bipy)$_2$(NCS)$_2$	yellow	11.37	11.36	24.13	24.03	17.24	17.38	54.26	54.65	3.33	3.22	77.3
Fe(2-bipy)$_2$(NCS)$_2$·2H$_2$O	brown	10.72	10.73	23.20	22.32	15.80	16.15	50.92	50.78	3.74	3.87	108.5*
Co(2-bipy)$_2$(NCS)$_2$	brown	11.82	12.09	22.87	23.83	17.17	17.24	54.33	54.21	3.30	3.31	118.5*
Ni(2-bipy)$_3$(NCS)$_2$·3H$_2$O	pink	8.64	8.42	16.60	16.65	16.06	16.27	55.03	55.10	4.07	4.33	159.9
Mn(4-bipy)$_2$(NCS)$_2$·2H$_2$O	yellow	10.73	10.57	22.87	22.36	50.86	50.74	16.23	16.18	3.67	3.88	76.4
Fe(4-bipy)$_2$(NCS)$_2$·2H$_2$O	brown	11.13	10.73	23.95	22.32	15.77	16.15	50.60	50.78	3.67	3.87	85.7*

*Concentration of these compounds is lower than standard [24]. It results from their lower solubility in methanol

From mixture containing molar ratio M:bipy=1:3, the new complexes in the solid state with empirical formulae: $Co(2\text{-bipy})_2(NCS)_2$, $Fe(2\text{-bipy})_2(NCS)_2\cdot 2H_2O$ and $M(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$ (M(II)=Mn, Fe) were prepared. In these conditions two compounds were also obtained: $Ni(2\text{-bipy})_3(NCS)_2\cdot 3H_2O$, $Mn(2\text{-bipy})_2(NCS)_2$. The last isolated complexes have identical composition as those described in literature [15, 16]. In the case of $Mn(2\text{-bipy})_2(NCS)_2$ we studied only thermal behaviour and molar conductivity in methanol (Table 1). The $Fe(2\text{-bipy})_2(NCS)_2\cdot 2H_2O$, $Mn(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$ reported in the present paper are hydrated, in comparison with complex described earlier [15, 16]. All the complexes are coloured, stable in air and partly soluble in EtOH. They are insoluble in benzene, CCl_4, $CHCl_3$. The obtained compounds of manganese(II) are very easily soluble in water. Complexes of iron(II) are practically insoluble in water. The solubility of the compounds $Co(2\text{-bipy})_2(NCS)_2$ and $Ni(2\text{-bipy})_3(NCS)_2\cdot 3H_2O$ at 21°C is $0.7\cdot 10^{-3}$ and $2.7\cdot 10^{-3}$ mol dm^{-3}, respectively.

The molar conductance at 25°C in methanol of the complexes is in the range 76.4÷118.5 Ω^{-1} cm^2 mol^{-1} (except $Ni(2\text{-bipy})_3(NCS)_2\cdot 3H_2O$) (Table 1). The molar conductance in methanol of the $Ni(2\text{-bipy})_3(NCS)_2\cdot 3H_2O$ is 159.9 Ω^{-1} cm^2 mol^{-1}. This complex present behaviour as 1:2 electrolyte [24]. The conductivity of other compounds indicates as 1:1 electrolyte. In the case of all compounds, the higher than anticipated Λ_M value (vide infra IR) is usually due to displacement of isothiocyanato ligand by solvent molecules. A similar situation has been observed in metal complexes with other aromatic amines [25].

Infrared spectra

IR spectra for compounds: $Fe(2\text{-bipy})_2(NCS)_2\cdot 2H_2O$, $Co(2\text{-bipy})_2(NCS)_2$, $Ni(2\text{-bipy})_3(NCS)_2\cdot 3H_2O$ and $M(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$ (M(II)=Mn, Fe) were studied. IR spectra of free 2-bipy and 4-bipy undergo a modification when coordinated with a metal ion. In the spectra of all complexes, the new absorption bands occur in the region 1488–1508, 956–962 cm^{-1} (in the case 2-bipy compounds) and 1220–1330, 920–956 cm^{-1} (for 4-bipy complexes). The most characteristic ring vibrations ν(C=C) and ν(C=N) in free 2-bipy appear at 1553 and at 1579 cm^{-1}. In the compounds these vibrations are observed in the ranges: 1564–1568 and 1596–1604 cm^{-1}, respectively. The characteristic pyridine-breathing frequency at 991 cm^{-1}, is shifted by 15–29 cm^{-1} to higher frequencies in the complexes. The symmetric out-of plane mode of the C–H group observed at 753 cm^{-1} in the uncoordinated 2-bipy appearing at: 769 cm^{-1} ($Fe(2\text{-bipy})_2(NCS)_2\cdot 2H_2O$), 766 cm^{-1} ($Co(2\text{-bipy})_2(NCS)_2$) and 779 cm^{-1} ($Ni(2\text{-bipy})_3(NCS)_2\cdot 3H_2O$). The ring vibration ν(C=N) at 1590 cm^{-1} for uncoordinated 4-bipy, is shifted by 5–20 cm^{-1} towards higher frequencies in the compounds. The ring vibration ν(C=C) at 1530 cm^{-1} for the free ligand, is observed in the region 1537–1545 cm^{-1}. The characteristic ring-breathing mode at 982 cm^{-1} for substituted pyridine is shifted in the complexes to 999–1010 cm^{-1}.

IR spectra of these compounds suggest that 2-bipy and 4-bipy are coordinated to a metal ion. In the case of 2-bipy complexes, the IR data indicated the presence of *cis*-2,2’-bipyridine chelates [26–29].

The fundamental modes of thiocyanato NCS group in the compounds are observed at (cm^{-1}): ν(CN) (2042–2100 cm^{-1}), ν(CS) (804–815 cm^{-1}) and δ(NCS) (441–482 cm^{-1}) are characteristic of the N-coordinated thiocyanate group [30].

In the IR spectra for the hydrated complexes a strong and broad band was present in the water-stretching region (ca 3400–3600 cm^{-1}). A medium peak in the water bending region, is observed at: ca 1640 and 1660 cm^{-1} in the case of compounds with 2,2'-bipyridine and 4,4'-bipyridine, respectively.

Thermal analyses

The complexes prepared are stable at room temperature. During heating they decompose in different ways. The results of thermal decomposition of compounds are summarized in Table 2.

Figure 1 presents, as an example, the thermoanalytical curves of $Mn(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$ and $Fe(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$. All of the compounds decompose progressively. The most thermally stable are: the anhydrated complex $Co(2\text{-bipy})_2(NCS)_2$ and hydrated compound $Mn(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$. After the dehydrated process the progressive elimination of bipyridine takes place. In the case of anhydrated complexes: $Mn(2\text{-bipy})_2(NCS)_2$, and $Co(2\text{-bipy})_2(NCS)_2$, elimination of bipyridine begins at higher temperature than for intermediate compounds, which are formed after the dehydration: $Fe(2\text{-bipy})_2(NCS)_2$, $Ni(2\text{-bipy})_3(NCS)_2$ and $M(4\text{-bipy})_2(NCS)_2$ (M(II)=Mn, Fe).

$Mn(2\text{-bipy})_2(NCS)_2$ begins to decompose at 220°C. The loss of mass corresponds to the release of 0.5 mole 2-bipy. The endothermic peak is observed on the DTA at 305°C. Above 310°C the deamination of 1.5 mole 2-bipy takes place and

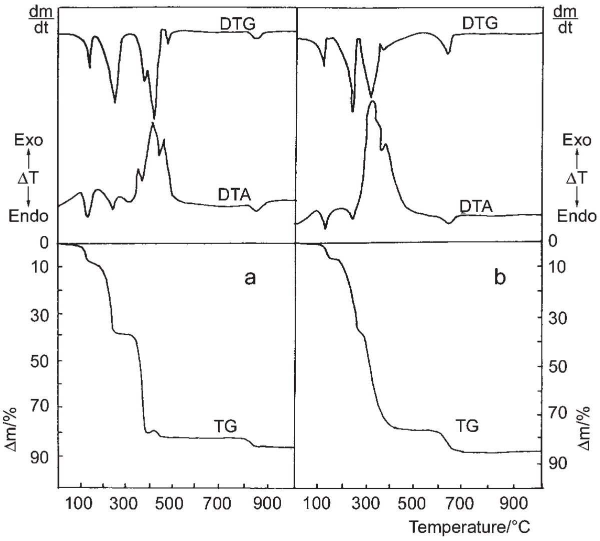

Fig. 1 Thermal analysis curves of a – $Mn(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$; b – $Fe(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$

Table 2 Decomposition process of complexes in air

Compound	T_{DTA}/	T_{range}/	Mass loss/%		Intermediate and residue
	°C		found	calcd.	
$Mn(2\text{-bipy})_2(NCS)_2$	305 endo	220–310	15.0	16.2	$Mn(2\text{-bipy})_{1.5}(NCS)_2$
	422 endo	310–440	50.0	48.5	$Mn(NCS)_2$[a]
	438 exo				
	530 exo	440–940	20.0	19.6	Mn_3O_4
	870 endo				
$Fe(2\text{-bipy})_2(NCS)_2\cdot 2H_2O$	65 endo	50–90	4.0	3.5	$Fe(2\text{-bipy})_2(NCS)_2\cdot H_2O$
	170 endo	110–195	4.0	3.5	$Fe(2\text{-bipy})_2(NCS)_2$
	275, 305 exo	210–315	23.0	22.5	$Fe(2\text{-bipy})_{1.25}(NCS)_2$
	340 endo 365 exo	315–385	23.0	22.5	$Fe(2\text{-bipy})_{0.5}(NCS)_2$[b]
	495 exo	430–580	31.5	32.7	Fe_2O_3
$Co(2\text{-bipy})_2(NCS)_2$	296 endo	230–298	16.0	16.0	$Co(2\text{-bipy})_{1.5}(NCS)_2$
		298–338	16.0	16.0	$Co(2\text{-bipy})(NCS)_2$[c]
	360, 380 endo	338–400	30.0	32.0	$Co(NCS)_2$[d]
	410, 518 exo	400–550	21.0	19.5	mixture of Co_3O_4 and ca 2% $CoSO_4$
		~780			pure Co_3O_4
	900 endo	780–910	1.0	1.1	CoO

Table 2 Continued

Compound	T_{DTA}/	T_{range}/	Mass loss/%		Intermediate and residue
	°C		found	calcd.	
$Ni(2\text{-bipy})_3(NCS)_2\cdot 3H_2O$	120 endo	60–130	8.0	7.8	$Ni(2\text{-bipy})_3(NCS)_2$
	200 endo	130–210	21.5	22.4	$Ni(2\text{-bipy})_2(NCS)_2$
	328 exo, 370 endo	310–410	41.0	39.2	$Ni(2\text{-bipy})_{0.25}(NCS)_2$
	468, 520 exo	410–600	17.0	17.7	NiS[e]
	740 endo	600–770	2.5	2.3	NiO
$Mn(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$	120 endo	95–135	7.0	6.9	$Mn(4\text{-bipy})_2(NCS)_2$
	238 endo	142–250	29.0	30.1	$Mn(4\text{-bipy})(NCS)_2$
	360 endo, 405 exo	310–415	42.0	42.2	$Mn(NCS)_2$+MnS (1:3)[f]
	440 exo	425–480	2.0		mixture of MnS and different oxides of manganese
	830 endo	770–860	5.0	6.1	Mn_3O_4
$Fe(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$	125 endo	70–135	7.0	6.9	$Fe(4\text{-bipy})_2(NCS)_2$
	245 endo	142–250	30.0	30.0	$Fe(4\text{-bipy})(NCS)_2$
	320, 345 exo	275–360	31.0	30.0	$Fe(NCS)_2$
	385 exo	360–475	9.5	10.0	$Fe_2O_3\cdot SO_3$
	640 endo	570–660	7.5	7.7	Fe_2O_3

[a] via mixture containing MnS, $MnSO_4$, Mn_2O_3; [b] via mixture containing $Fe(NCS)_2$ and $Fe_2O_3\cdot SO_3$; [c] by projecting minimum of the DTG curve on TG curve [11]; [d] with organic fragments; [e] with traces of $NiSO_4$ and NiO; [f] molar ratio

$Mn(NCS)_2$ forms. This process is represented on the DTA curve by two peaks, the endothermic at 422 and exothermic at 438°C. Next, the decomposition of $Mn(NCS)_2$ begins at 440°C. The final product, Mn_3O_4 is formed in the range 440–940°C. The X-ray diffraction pattern indicates Mn_3O_4 in the sinter of $Mn(2\text{-bipy})_2(NCS)_2$ heated up to 940°C.

The hydrated complex $Fe(2\text{-bipy})_2(NCS)_2{\cdot}2H_2O$ loses 1 mole of water above 50°C. Next, in the interval 110–195°C the last water molecule is eliminated. Dehydration is an endothermic process. On increase of the temperature the decomposition of $Fe(2\text{-bipy})_2(NCS)_2$ takes place via intermediate compounds: $Fe(2\text{-bipy})_{1.25}(NCS)_2$ (210–315°C) and $Fe(2\text{-bipy})_{0.5}(NCS)_2$ (315–385°C). In the range 430–580°C Fe_2O_3 is formed. On the DTA curve at 495°C an exothermic peak appears.

In the first stage of the decomposition of $Co(2\text{-bipy})_2(NCS)_2$ (above 230°C), the 0.5 mole of 2-bipy is liberated. The endothermic peak on the DTA curve at 296°C is associated with this transformation. The intermediate product $Co(2\text{-bipy})_{1.5}(NCS)_2$ deaminates in two stages. In the last deamination process (338–400°C) $Co(NCS)_2$ is formed. The decomposition of $Co(NCS)_2$ takes place at 400–550°C via a mixture of Co_3O_4 and $CoSO_4$. Two exothermic peaks on the DTA appear at 410 and 518°C. At higher temperature (~780°C) pure Co_3O_4 is observed. Above 780°C Co_3O_4 decomposes to CoO very slowly.

When $Ni(2\text{-bipy})_3(NCS)_2{\cdot}3H_2O$ is heated in the first stage 3 moles of H_2O (60–130°C) are eliminated. The endothermic peak at 120°C corresponds to the dehydration process. The anhydrous compound $Ni(2\text{-bipy})_3(NCS)_2$ deaminates in three stages, and in the temperature range 410–600°C the formation of NiS (with traces of $NiSO_4$ and NiO) takes place. The decomposition of NiS to NiO begins above 600°C. On the DTA curve an endothermic peak appears at 740°C.

The two water molecules for $Mn(4\text{-bipy})_2(NCS)_2{\cdot}2H_2O$ are lost in the temperature interval 95–135°C. Next, $Mn(4\text{-bipy})_2(NCS)_2$ eliminates 4-bipy in two steps and the mixture of $Mn(NCS)_2$ and MnS (310–415°C) is formed. On the DTA curve two peaks: at 360 an endothermic one and at 405°C an exothermic one are observed. Next, in the range 425–480°C the mixture MnS and different oxides of manganese forms. A constant mass level for pure Mn_3O_4 appears above 860°C.

In the case of $Fe(4\text{-bipy})_2(NCS)_2{\cdot}2H_2O$, two water molecules are eliminated in one stage (70–135°C). In the first step of deamination of $Fe(4\text{-bipy})_2(NCS)_2$, it loses 1 mole of 4-bipy at 142–250°C. Next, in the temperature interval 275–360°C the last mole of 4-bipy is liberated and forms $Fe(NCS)_2$. The DTA curve shows two exothermic peaks at 320 and 345°C. The decomposition of iron(II) thiocyanates to $Fe_2O_3{\cdot}SO_3$ takes place between 360–475°C. The intermediate products $Fe_2O_3{\cdot}n SO_3$ are known in the literature [31, 32]. Fe_2O_3 is formed at 570–660°C. The DTA curve exhibits an endothermic peak at 640°C. The X-ray diffraction pattern of $Fe(4\text{-bipy})_2(NCS)_2{\cdot}2H_2O$ heated up to 660°C is similar to that of the original Fe_2O_3.

Conclusions

The new complexes of the type: $M(2\text{-bipy})_2(NCS)_2$ (M(II)=Mn, Co), $Fe(2\text{-bipy})_2(NCS)_2\cdot 2H_2O$, $Ni(2\text{-bipy})_3(NCS)_2\cdot 3H_2O$ and $M(4\text{-bipy})_2(NCS)_2\cdot 2H_2O$ (M(II)=Mn, Fe) have been isolated as small-crystalline compounds. The decomposition of complexes occurs in several steps and in various ways. By heating of the obtained compounds partial deamination takes place and several new complexes with 2-bipy or 4-bipy are formed as intermediates. The transition products formed during pyrolysis process: $Fe(2\text{-bipy})_2(NCS)_2$, $Fe(4\text{-bipy})_2(NCS)_2$ and $Co(2\text{-bipy})_2(NCS)_2$ are isomeric with 2,4'-bipyrdine or 4,4'-bipyridine complexes, respectively [17, 19].

From previous thermal studies on the mixed bipyridine–thiocyanate complexes [17–19] and data presented in this paper, it is seen that the anhydrous 2,2'-bipyridine-thiocyanate complex of Ni(II) is more stable, than the Fe(II) complex (initial temperatures of decomposition 60 and 50°C, respectively).

For the anhydrous 4,4'-bipyridine-thiocyanate complexes the order of decreasing stability was:

$$\text{Mn(II)}>\text{Fe(II)}\approx\text{Co(II)}^{*}>\text{Cu(II)}^{*}>\text{Ni(II)}^{*}\quad \text{where}^{*}\ [17]$$

$$(95°\text{C})\ \ (70°\text{C})\ \ (70°\text{C})\ \ (60°\text{C})\ \ (50°\text{C})$$

The initial temperature of the decomposition of the compounds is presented in the brackets.

The temperatures of decomposition of hydrated 2,4'-bipyridine-thiocyanate compounds [18, 19] change in the following sequence:

$$\text{Mn(II)}\approx\text{Fe(II)}>\text{Co(II)}$$

$$(100°\text{C})\ (100°\text{C})\ (55°\text{C}).$$

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