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SYNTHESIS AND THERMAL BEHAVIOUR OF 4,4'-BIPYRIDYL AND 2,4'-BIPYRIDYL COMPLEXES OF Co(II), Ni(II) AND Cu(II) THIOCYANATES

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Abstract

The synthesis and characterization of $CoL_2(NCS)_2{\cdot}2H_2O$, $NiL_2(NCS)_2{\cdot}2H_2O$, $CuL(NCS)_2{\cdot}3H_2O$ (L=4,4'-bipyridyl, 4-bipy) $CoX_3(NCS)_2{\cdot}H_2O$, $NiX_3(NCS)_2$ and $CuX_2(NCS)_2$ (X=2,4'-bipyridyl, 2,4'-bipy) are reported. The IR spectra and other physical properties of these compounds are discussed. The thermal properties of the complexes in the solid state were studied under non-isothermal conditions in air atmosphere. The intermediates of dehydration and decomposition at different temperatures were characterized by X-ray diffraction.

Keywords: 2,4'-bipyridyl complexes, 4,4'-bipyridyl complexes, IR spectra, thermal decomposition, transition-metal complexes

Introduction

The conditions of thermal decomposition of thiocyanato complexes of Co(II), Ni(II) and Cu(II) with various organic N-donors have been studied by many authors [1–10]. The synthesis and physico-chemical properties (except the thermal behaviour) of thiocyanato complexes of these metals have been studied intensively, but only with 2,2'-bipyridyl (2-bipy) and other amines [11–15]. Only fragmentary information is available in the literature on the 4,4'-bipyridyl (4-bipy) complexes of transition-metal thiocyanates [16, 17]. The complex Co(4-bipy)$(NCS)_2$ was described by Yadava *et al.* [16]. The compounds of Co(II), Ni(II) and Cu(II) thiocyanates with 2,4'-bipyridyl (2,4'-bipy) are unknown.

The aim of the present work was to obtain the 4-bipy and 2,4'-bipy complexes of Co(II), Ni(II) and Cu(II) thiocyanates in the solid state, to examine some of their physico-chemical properties and to study their thermal decomposition in air.

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Table 1 Analytical data and solubility (*S*) of complexes in water at 21°C (*L*=4,4′-bipyridyl; *X*=2,4′-bipyridyl)

Complex	Analysis: found (calculated)/%					$S\cdot 10^3$/
(colour)	M	C	N	H	SCN	mol dm^{-3}
I. $CoL_2(NCS)_2\cdot 2H_2O$	11.06	50.70	15.96	3.82	22.40	2.00
(light-rose)	(11.26)	(50.48)	(16.05)	(3.85)	(22.19)	
II. $NiL_2(NCS)_2\cdot 2H_2O$	11.24	50.60	16.25	3.82	22.50	2.50
(light-blue)	(11.22)	(50.50)	(16.10)	(3.85)	(22.20)	
III. $CuL(NCS)_2\cdot 3H_2O$	16.50	36.70	14.65	3.25	29.50	1.67
(green)	(16.29)	(36.96)	(14.37)	(3.62)	(29.79)	
IV. $CoX_3(NCS)_2\cdot H_2O$	9.50	58.20	17.00	3.90	17.32	2.00
(rose)	(8.91)	(58.11)	(16.93)	(3.96)	(17.55)	
V. $NiX_3(NCS)_2$	9.54	59.80	17.37	3.70	18.54	3.33
(blue-green)	(9.12)	(59.73)	(17.41)	(3.76)	(18.05)	
VI. $CuX_2(NCS)_2$	12.72	53.79	17.13	3.23	23.50	2.00
(light-green)	(12.91)	(53.70)	17.08)	(3.28)	(23.61)	

Experimental

Physical measurements

The apparatus and measuring conditions were the same as described previously [18].

Preparation and analysis of the complexes

4,4′-bipy (*m.p.* 69.5°C), 2,4′-bipy (*m.p.* 61°C) and $Co(NCS)_2$ were obtained from Aldrich; other chemicals were of p.a. grade from POCh-Gliwice. Solvated nickel thiocyanate was prepared according to the reaction:

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

Cobalt and nickel complexes

$Co(NCS)_2$ or $Ni(NCS)_2$ (4.3 mmol in 10 cm^3) and 4-bipy (12.9 mmol in 10 cm^3) were dissolved in warm 75% (*v*/*v*) EtOH and the mixture was heated on a water-bath. Crystallization occurred during the heating. The mixture was allowed to cool, and the products were filtered off, washed with a cold mixture of EtOH and Et_2O (1:1), and dried in air. The preparation of 2,4′-bipy complexes was similar, except that the reactants were dissolved in warm H_2O containing a few drops of 96% (*v*/*v*) EtOH.

Copper complex

$Cu(4\text{-bipy})(NCS)_2 \cdot 3H_2O$ was prepared by mixing 4.3 mmol $CuSO_4 \cdot 5H_2O$ in 50 cm^3 of 75% (*v*/*v*) EtOH and 12.9 mmol 4-bipy in 50 cm^3 of 75% (*v*/*v*) EtOH. This suspension was mixed with 4.3 cm^3 of an aqueous solution of 2*M* NH_4NCS (molar ratio $Cu^{II}:SCN^- = 1:2$). The reaction mixture was stirred at 50°C for about 20 min. The resulting solid green product was filtered off, washed with a mixture of EtOH and Et_2O (1:1) and dried at room temperature. $Cu(2,4'\text{-bipy})_2(NCS)_2$ was synthesized as for the 4-bipy complex, except that the reactants were dissolved in warm H_2O containing a few drops of 96% (*v*/*v*) EtOH. Many complexes of $Cu(NCS)_2$ with other N-donors have been prepared by a similar procedure [1, 11].

Metal analyses were carried out complexometrically with edta as the complexing agent, after decomposition of the compounds by HNO_3. The contents of C, H and N were determined by elemental analysis with V_2O_5 as oxidizing agent, and thiocyanate by the Volhard method. Solubilities were determined in H_2O at 21°C from the total M-ion concentration in saturated solution. Analytical data on the complexes obtained are presented in Table 1, together with the colours and solubilities in water. The solubilities of the complexes in water were similar $[(2-3)\times10^{-3}$ mol dm$^{-3}]$. They were practically insoluble in benzene, CCl_4 and $CHCl_3$, but fairly soluble in EtOH. All the isolated complexes were air stable at room temperature. The crystalline compound Cu(2,4'-bipy)$_2$(NCS)$_2$ is a new example of a complex exhibiting ligand isomerism. The complex Cu(2-bipy)$_2$(NCS)$_2$ has been described in the literature [11, 19].

Results and discussion

Infrared spectra

The IR spectra of free 4-bipy and 2,4'-bipy differ from those of their complexes with M(NCS)$_2$. The ring vibration $\nu_{(C=N)}$ at 1590 cm^{-1} for free 4-bipy is shifted by 15–20 cm^{-1} towards higher frequencies in the complexes. The ring vibration $\nu_{(C=C)}$ at 1530 cm^{-1} for the free ligand is observed in the region ca 1538 cm^{-1}. The characteristic ring breathing mode at 982 cm^{-1} for substituted pyridines is shifted for the complexes (1006–1012 cm^{-1}). These changes are ascribed to the fact that 4-bipy is coordinated to M [20]. The IR spectrum of 2,4'-bipy is the sum of the spectra of 2-substituted and 4-substituted pyridine [21]. Upon coordination with M(NCS)$_2$, the IR spectrum of free 2,4'-bipy undergoes a change only in the ring vibration modes of 4-substituted pyridine. The ring vibration $\nu_{(C=N)}$ of 4-substituted pyridine, at 1595 cm^{-1} for free 2,4'-bipy, is observed in the range 1610–1618 cm^{-1} for the complexes. The band attributed to the stretching ring vibration (4-sub), observed at 1405 cm^{-1} for the free ligand, is shifted by ca 10 cm^{-1} to higher frequencies. The breathing frequency for (4-sub), observed at 990 cm^{-1} for the free ligand, is displaced by ca 20 cm^{-1} towards higher frequencies. The positive shift of these bands of 4-substituted pyridine indicates coordination of 2,4'-bipy via the less hindering 4 N'-atom [22].

The thiocyanate fundamentals ν_{C-N}, ν_{C-S} and δ_{NCS} are listed in Table 2. The bands are typical of covalently bound isothiocyanate [8, 11]. A broad band in

Table 2 IR bands of thiocyanate groups, cm^{-1}

Complex	IR spectra		
	ν_{C-N}	ν_{C-S}	δ_{NCS}
$CoL_2(NCS)_2\cdot2H_2O$	2100 vs, 2065 sh	822 s	472 m
$NiL_2(NCS)_2\cdot2H_2O$	2070 vs	Δ	478 s
$CuL(NCS)_2\cdot3H_2O$	2090 vs, 2060 pd	820 s	472 s
$CoX_3(NCS)_2\cdot H_2O$	2103 vs, 2068 pd	Δ	474 s
$NiX_3(NCS)_2$	2106 vs, 2094 pd	Δ	476 s
$CuX_2(NCS)_2$	2070 vs, 2102 pd	821 s	474 m

Δ - overlaid by bipy absorption, v, m, s, sh, pd - very, medium, strong, shoulder, poorly resolved doublet the water stretching region (ca 3050 –3500 cm^{-1}) and a shoulder in the water bending region (ca 1660 cm^{-1}) are observed for complexes (I), (II), (III) and (IV); the water wagging modes appear at ca 530 –500 cm^{-1} for coordinated water. The M–O stretching vibrations are observed as weak bands in the interval ca 442–488 cm^{-1}.

Thermal properties of the complexes

The data obtained from the TG, DTG and DTA curves, supported by chemical analysis and the X-ray diffraction pattern investigations, permit the following conclusions (Table 3): all the complexes decompose progressively. They lose water and the volatile ligands differently. In compounds (I), (II) and (IV), the loss of the last molecule of 4-bipy (or 2,4′-bipy) is accompanied by

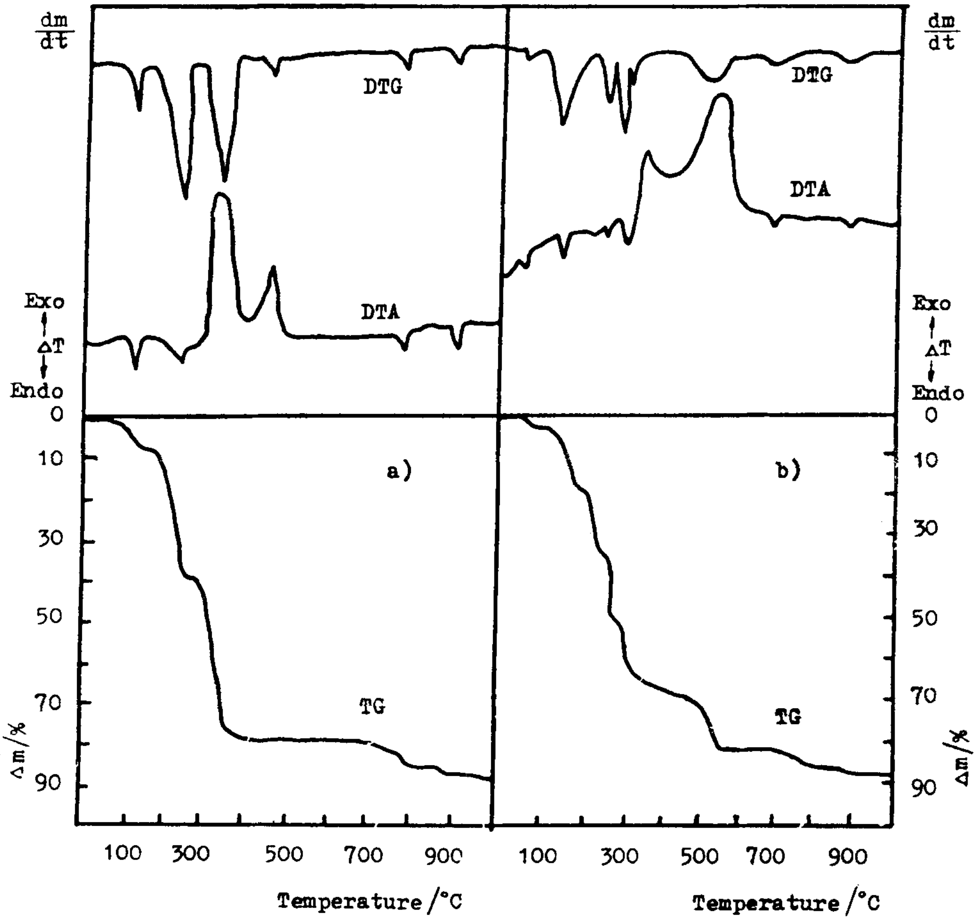

Fig. 1 Thermoanalytical curves of $Co(4\text{-bipy})_2(NCS)_2{\cdot}2H_2O$ (a), $Co(2,4'\text{-bipy})_3(NCS)_2{\cdot}H_2O$ (b)

Table 3 Decomposition process of complexes in air

Complex	DTA peaks/°C	Ranges of decomposition/°C	Mass loss/%		The observed process
			found	calcd.	
$CoL_2(NCS)_2 \cdot 2H_2O$	110 endo	70–120	7.0	6.88	$-2H_2O$
	238 endo	160–242	30.0	29.84	–L
	340, 462 exo	280–470	42.0		forms Co_3O_4 with 6% $CoSO_4$
	780 endo	~800	6.0	47.95	pure Co_3O_4
	900 endo	800–910	1.2	1.02	decompose to CoO
$NiL_2(NCS)_2 \cdot 2H_2O$	75 endo	50–100	3.5	3.44	$-H_2O$
	250 endo	140–270	34.0	33.29	$-H_2O$, –L
	318 endo, 390 exo	300–420	39.0		forms mixture $NiSO_4$ and NiO*
	490, 760 exo	> 780	9.5	48.99	forms pure NiO

Table 3 Continued

Complex	DTA peaks/°C	Ranges of decomposition/°C	Mass loss/%		The observed process
			found	calcd.	
$CuL(NCS)_2 \cdot 3H_2O$	100 endo	60–105	4.5	4.62	$-H_2O$
	180 endo	140–190	4.5	4.62	$-H_2O$
	240 endo	190–245	25.0	24.65	$-H_2O$, –0.5L
	305 endo	245–340	20.0	20.03	–0.5L
	370 endo	340–390	19.0	19.00	forms $Cu_2S(CN)_2$
	418 exo,	390–760	7.0	6.68	forms CuO via mixture
	750 endo				$CuSO_4 + Cu_2OSO_4$
		>850			Cu_2O**
$CoX_3(NCS)_2 \cdot H_2O$	70 endo	55–110	2.7	2.72	$-H_2O$
	145 endo	110–222	18.0	17.70	–0.75X
	250 endo	222–275	17.5	17.70	–0.75X
	288 endo	275–290	17.5	17.70	–0.75X
		290–300	11.0	11.80	–0.5X
	430–562	300–565	18.0		mixture $CoSO_4$
	exo				and Co_3O_4
	680 endo	~800	3.0	20.25	pure Co_3O_4
	895 endo	800–905	1.0	0.81	decomposition to CoO

Table 3 Continued

Complex	DTA peaks/°C	Ranges of decomposition/°C	Mass loss/%		The observed process
			found	calcd.	
$NiX_3(NCS)_2$	218 endo	140–240	12.0	12.14	–0.5X
	280 endo 315 exo	240–320	60.5	60.68	–2.5X, decomposes to $Ni(NCS)_2$
	390 exo	340–400	6.0	5.61	forms NiO_3S
	470, 500 exo	400–540	6.0		forms mixture of $NiSO_4$ and NiO***
	720 endo	> 775	4.0	9.96	forms pure NiO
$CuX_2(NCS)_2$	195 endo	120–220	31.5	31.74	–X
	260 endo	220–280	31.0	31.74	–X
	370 endo	280–388	15.0	15.06	forms $Cu_2S(CN)_2$
	420 exo, 740 endo	388–760	6.0	5.30	forms CuO via mixture $CuSO_4+Cu_2OSO_4$
		> 850			Cu_2O**

* - with trace of other products of decomposition; ** - very slowly; *** - with trace of NiO_3S

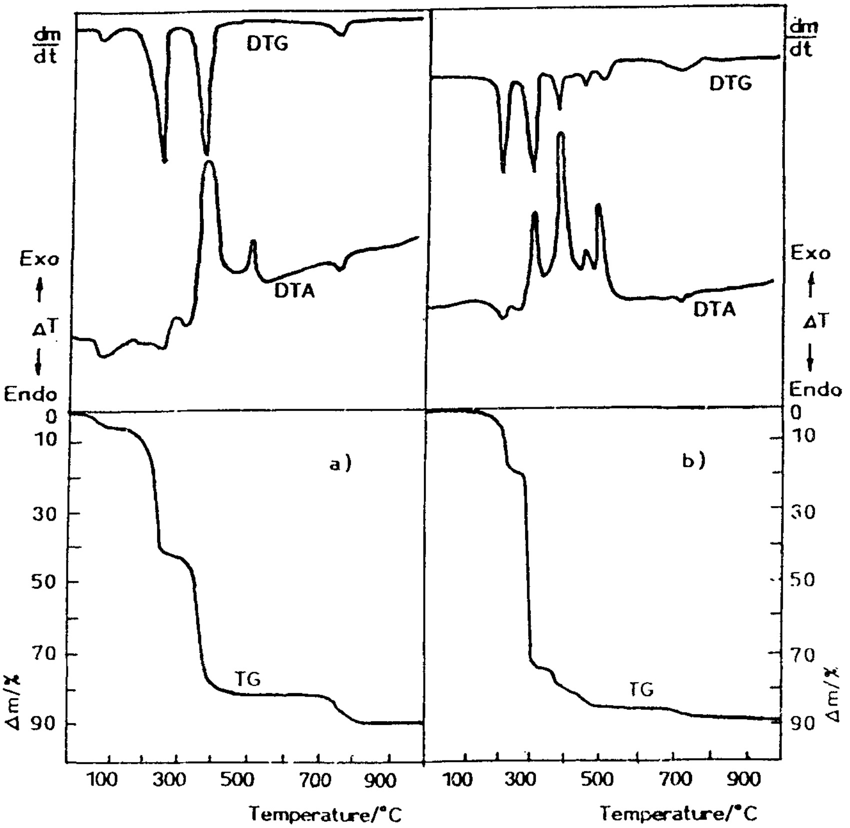

Fig. 2 Thermoanalytical curves of Ni(4-bipy)$_2$(NCS)$_2$·2H$_2$O (a), Ni(2,4'-bipy)$_3$(NCS)$_2$ (b)

decomposition of the NCS groups, as shown by a marked exothermic peak in the DTA curves (Table 3 and Figs 1–3).

$CoL_2(NCS)_2·2H_2O$ loses all its water within the temperature range 70–120°C, with an endothermic peak at 110°C. The anhydrous complex eliminates 1 mol of 4-bipy, and $CoL(NCS)_2$ is formed. This has been described in the literature [16]. On heating in air, the intermediate Co_3O_4 with ca. 6% $CoSO_4$ is formed at 470°C. The X-ray diffraction pattern indicates the formation of Co_3O_4 and $CoSO_4$ in the sinter of $CoL_2(NCS)_2·2H_2O$ heated up to 470°C (Fig. 4a). On temperature elevation, pure Co_3O_4 is formed. A horizontal mass level begins at 910°C (conversion of Co_3O_4 to CoO). The DTA curve exhibits several endothermic peaks and two very strong exothermic peaks, at 340 and 462°C.

In the first step of decomposition, the complex $NiL_2(NCS)_2·2H_2O$ loses 1 mol of H_2O at 50–100°C. The corresponding endothermic peak in the DTA curve is at 75°C. Next, the compound loses the remaining water and 1 mol of 4-bipy, and $NiL(NCS)_2$ is formed. In the last deamination step at 300–420°C,

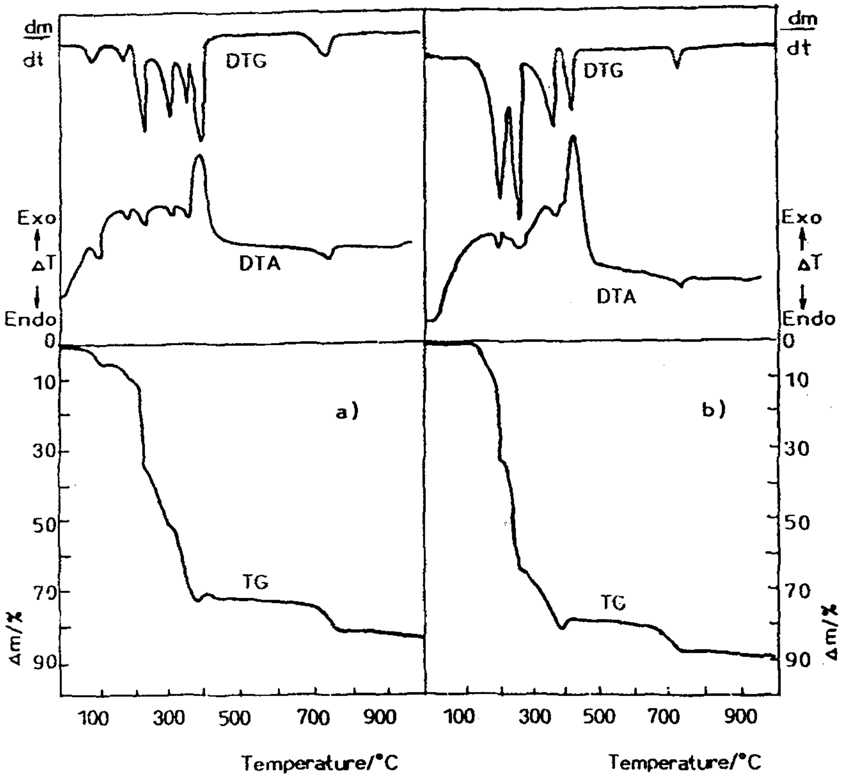

Fig. 3 Thermoanalytical curves of $Cu(4\text{-}bipy)(NCS)_2{\cdot}3H_2O$ (a), $Cu(2,4'\text{-}bipy)_2(NCS)_2$ (b)

the remaining 4-bipy is eliminated, accompanied by anion decomposition, and a non-stoichiometric mixture of $NiSO_4$ and NiO with traces of other decomposition products is formed. The corresponding exothermic peak in the DTA curve is high (390°C). Next, the process of $NiSO_4$ decomposition takes place. A plateau in the TG curve begins at 780°C. Calculations on the mass loss at this point indicate stoichiometry for NiO (found 14.0%; calcd. 14.28%). The diffraction pattern of $NiL_2(NCS)_2{\cdot}2H_2O$ heated up to 780°C is similar to that of original NiO.

When $CuL(NCS)_2{\cdot}3H_2O$ is heated, in the first stage 1 mol of H_2O is split off (60–105°C), at 140–190°C the next 1 mol of water is split off, and at 190–245°C all the water and 0.5 mol of 4-bipy are eliminated, to form the intermediate $2Cu(NCS)_2{\cdot}L$. In the temperature interval 245–340°C, further decomposition steps are observed and $Cu(NCS)_2$ is formed. This begins to decompose as the temperature increases.

At 340–390°C, $Cu_2S(CN)_2$ is probably formed temporarily. This intermediate was also observed by Kabešová *et al.* [3] during the thermal decomposition of thiocyanato Cu(II) complexes with pyridine. The product formed during the

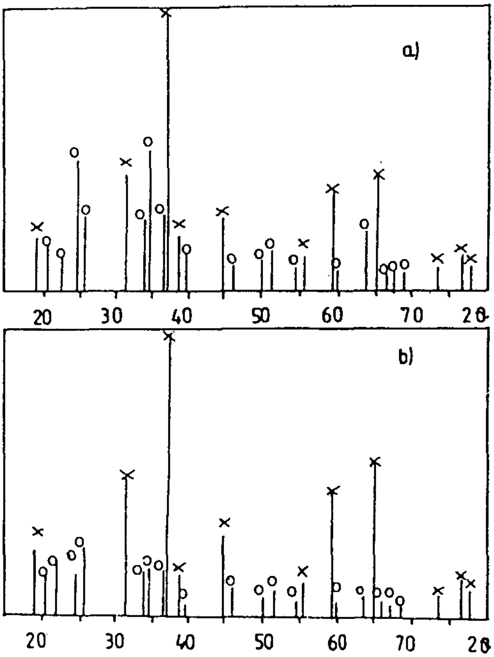

Fig. 4 X-ray diffraction patterns of decomposition products of $Co(4\text{-bipy})_2(NCS)_2{\cdot}2H_2O$ heated up to 470°C (a), $Co(2,4'\text{-bipy})_3(NCS)_2{\cdot}H_2O$ heated up to 570°C (b); (x) Co_3O_4; (o) $CoSO_4$

decomposition of $Cu_2S(CN)_2$ is oxidized to a non-stoichiometric mixture containing $CuSO_4$, $CuOSO_4$ and CuO (Fig. 5a). A reaction accompanied by a slight increase in mass proceeds in the range 390–440°C. An exothermic peak is observed at 418°C. The horizontal mass level occurs at about 760°C (endothermic peak at 750°C). Calculation from the mass loss at this point indicates stoichiometry for CuO (found 20.0%, calcd. 20.40%) (see also Fig. 5b). Above 850°C, CuO is converted very slowly to Cu_2O.

$CoX_3(NCS)_2{\cdot}H_2O$ displays very similar behaviour to that of $CoL_2(NCS)_2{\cdot}2H_2O$ during its thermal decomposition. However, compound (IV) loses the 2,4'-bipy in several steps, and formation of a non-stoichiometric mixture of $CoSO_4$ and Co_3O_4 occurs in different temperature ranges. The corresponding exothermic peak in the DTA curve for compound (IV) is high and broad (430–562°C). The diffraction pattern of $CoX_3(NCS)_2{\cdot}H_2O$ heated up to 570°C is similar to that of the sinter of compound(I) heated up to 470°C (Fig. 4b).

The thermal curves of $NiX_3(NCS)_2$ are shown in Fig. 2b. It can be seen that the complex has constant mass up to 140°C. The 2,4'-bipy is removed in two steps, after which the decomposition of $Ni(NCS)_2$ begins at 340°C. During this process, an intermediate NiO_3S (found 21.5%; calcd. 21.57%) is formed. The

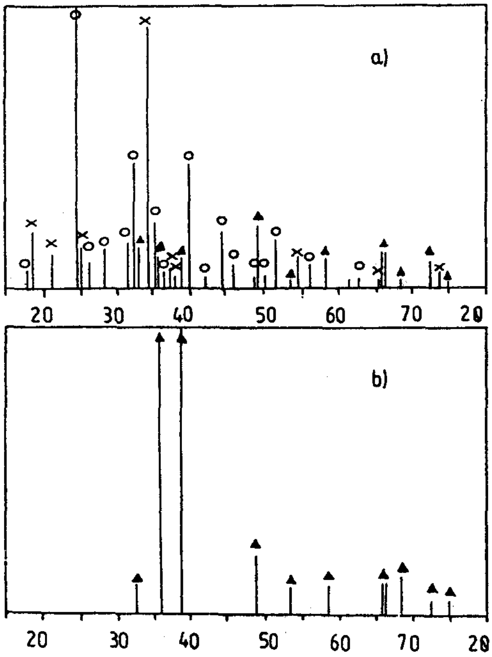

Fig. 5 X-ray diffraction patterns of decomposition products of $Cu(4\text{-bipy})(NCS)_2{\cdot}3H_2O$ heated up to 600°C (a), $Cu(4\text{-bipy})(NCS)_2{\cdot}3H_2O$ heated up to 760°C and 850°C (b); (x) $CuSO_4$; (o) Cu_2OSO_4; (▲) CuO

diffraction pattern of the decomposition products of compound (V) heated up to 400°C is also almost identical to that of NiO_3S (Fig. 6a). On increase of the temperature, NiO_3S is gradually oxidized to a mixture of $NiSO_4$ and NiO. In the sinter of $NiX_3(NCS)_2$ heated up to 600°C, these compounds also appear (Fig. 6b). The decompositions of $Ni(NS)_2$ and NiO_3S relate to the exothermic effects (three clear peaks in the DTA curve) at 390, 470 and 500°C. Above 775°C, pure NiO is formed.

$CuX_2(NCS)_2$ has constant mass up to 120°C. The 2,4′-bipy is lost in two stages, and $Cu(NCS)_2$ is formed at about 280°C. The products formed during the decomposition of $Cu(NCS)_2$ are similar to those appearing for $CuL(NCS)_2{\cdot}3H_2O$.

To summarize, the anhydrous complexes are more stable, and begin to decompose at higher temperatures than those containing water molecules. Many decomposition processes of the investigated complexes proceed simultaneously. Products of varying composition are formed, depending on the compound under investigation. However, it can be stated that in each case the molecules of 4-bipy or 2,4′-bipy are gradually eliminated, and the thiocyanates are partly oxidized (via products which are often difficult to identify) to sulphates, forming MSO_4 or M_2OSO_4. At higher temperatures, the sulphates decompose and the corre-

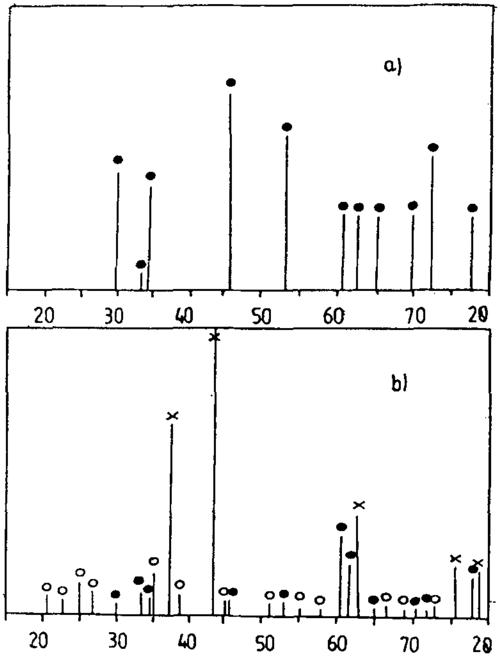

Fig. 6 X-ray diffraction patterns of decomposition products of Ni(2,4′-bipy)$_3$(NCS)$_2$ heated up to 400°C (a), Ni(2,4′-bipy)$_3$(NCS)$_2$ heated up to 600°C (b); (•) NiO$_3$S; (o) NiSO$_4$; (x) NiO

sponding oxides remain. These conclusions are in agreement with data given in the literature on other metal thiocyanato complexes with organic N-donors [2–7, 9, 10]. During the thermal decompositions, several new complexes with 4-bipy and 2,4′-bipy are formed as intermediates.

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