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THERMAL PROPERTIES OF SOLID COMPLEXES WITH BIOLOGICALLY IMPORTANT HETEROCYCLIC LIGANDS

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The stoichiometry of thermal decomposition of the complexes $Ni(NCS)_2(fpy)_4$ (**I**), $Ni(NCS)_2(bfpy)_4$ (**II**) and $Ni(NCS)_2(CF_3Phfpy)_4$ (**III**) (where fpy=furopyridine, bfpy=benzo-[2,3]furo[3,2-c]pyridine, CF_3Phfpy=2-(3-fluoromethylphenyl) furo[3,2-c]pyridine) have been investigated in nitrogen atmosphere from room temperature to 500°C by means of TG and DTG. The results revealed that release of the heterocyclic ligands occurs in two steps. IR data suggested that fpy, bfpy and CF_3Phfpy ligands were coordinated to Ni(II) through the N atom of the respective heterocyclic rings and same is the case with the anionic NCS group.

Keywords: *furopyridine derivatives, infrared spectra, Ni(II) complexes, thermal analysis*

Introduction

It is well known that many metal cations and different heterocyclic compounds play a significant role in several biological systems [1]. Especially six-membered ring systems are a component of several vitamins and drugs [2, 3]. Also investigations of quinoline isoesters (furopyridines) in which the benzene ring is replaced by furan rings have resulted in discovering many biologically active compounds. New pharmacophores with potential antipsychotic activity possess the furo[3,2-c]pyridines ring system [4]. It is, therefore, not surprising that many authors have investigated heterocyclic compounds as ligands in coordination compounds of several central atoms and also examined their antimicrobial activities [5–10]. From our point of view, it is challenging to study the thermophysical properties of solid complexes with heterocyclic nitrogen compounds. This work is a continuation of our previous research on organometallic compounds including their thermal, spectral, structural and biological activities [11–24] and was aimed at the study of thermal and spectral properties of isothiocyanato Ni(II) complexes with biologically important furopyridine (fpy) and its derivates viz., benzo-[2,3]furo[3,2-c] pyridine (bfpy) and 2-(3-fluoromethylphenyl)furo[3,2-c]pyridine (CF_3Phfpy) (Fig. 1):

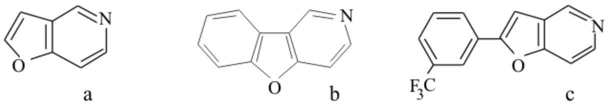

Fig. 1 Structures of a – furopyridine (fpy), b – benzo-[2,3]furo[3,2-c] pyridine (bfpy) and c – 2-(3-fluoromethylphenyl)furo[3,2-c]pyridine (CF_3Phfpy)

Experimental

Synthesis of Ni(II) complexes

Complexes $Ni(NCS)_2(fpy)_4$ (**I**), $Ni(NCS)_2(bfpy)_4$ (**II**) and $Ni(NCS)_2(CF_3Phfpy)_4$ (**III**) were prepared by treating (0.002 mol) fpy, bfpy and CF_3Phfpy, respectively, with $Ni(NCS)_2{\cdot}6H_2O$ (0.001 mol) in methanol (50 mL). The solutions were kept at room temperature. The fine precipitated monocrystals were filtered out, washed with cold methanol and dried at room temperature.

Measurements

Elemental analyses (C, H, N) were carried out on a Carlo Erba 1106 Analyser and the content of Ni(II) was determined by complexometric titration.

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Thermal decomposition was studied on a TA Instruments (model SDT 2960) in nitrogen atmosphere using a platinum crucible with a sample mass 20–22 mg from room temperature to 500°C. A heating rate of 10°C $\mathrm{min^{-1}}$ was chosen for all measurements.

The infrared (IR) spectra were obtained on a Philips analytical PU 9800 FTIR spectrometer using KBr tablets in the range 400–4000 $\mathrm{cm^{-1}}$.

Results and discussion

The Ni(II) complexes reported in this paper are soluble in water, ethanol, acetone and DMSO. The content of carbon, hydrogen and nitrogen was determined by elemental analysis and the content of nickel was established by complexometric titration. The analysis confirms (Table 1) the theoretical composition of complex **I**–**III**.

The data for the thermal decomposition of complexes **I**–**III** are summarized in Table 2. The thermal decomposition of the studied complexes is a multi-stage process. The subsequent detachment of the ligands was observed. The final solid products were NiS. The TG and DTG curves for $\mathrm{Ni(NCS)_2(CF_3Phfpy)_4}$ **(III)** are shown in Fig. 2 as an example.

The TG and DTG curve for the complex $\mathrm{Ni(NCS)_2(fpy)_4}$ (**I**) indicate that it is stable up to ~130°C. The release of furopyridine molecules takes place in two separate steps. The mass losses corresponding to the decomposition stages are 36.1, 36.2 and 12.5%, respectively and are in good agreement with the theoretical values. They correspond to the presence of two intermediate decomposition products: $\mathrm{Ni(NCS)_2(fpy)_2}$ and $\mathrm{Ni(NCS)_2}$. The decomposition rate maxima (from DTG curve) for the studied processes are at ~180, 230 and 380°C. The stoichiometry of thermal decomposition of complex **I** can be expressed by equations:

$$\mathrm{Ni(NCS)_2(fpy)_4}(s)\xrightarrow{130\text{–}190^{\circ}\mathrm{C}}\mathrm{Ni(NCS)_2(fpy)_2}(s)+\mathrm{2fpy}(g) \tag{1}$$

$$\mathrm{Ni(NCS)_2(fpy)_2}(s)\xrightarrow{190\text{–}340^{\circ}\mathrm{C}}\mathrm{Ni(NCS)_2}(s)+\mathrm{2fpy}(g) \tag{2}$$

$$\mathrm{Ni(NCS)_2}(s)\xrightarrow{340\text{–}450^{\circ}\mathrm{C}}\mathrm{NiS}+\text{decomposition product} \tag{3}$$

Table 2 Thermal decomposition data

Complex	DTG		TG	
	T_{max}/°C	Temp. interval/°C	Δm (found/calc.)/%	Lost component
	180	130–190	36.1/36.6	2fpy
I	230	190–340	36.2/36.6	2fpy
	380	340–450	12.5/12.9	SCN, CN
	243	127–284	50.5/49.7	2.5bfpy
II	307	284–350	29.7/29.8	1.5bfpy
	383	350–450	9.8/9.9	SCN, CN
	220	124–254	42.6/42.6	$\mathrm{2CF_3Phfpy}$
III	282	254–326	41.4/42.6	$\mathrm{2CF_3Phfpy}$
	353	326–450	7.8/7.1	SCN, CN

NiS was identified by X-ray diffraction measurements as final solid residue of these thermal decompositions (in the temperature range 20–450°C).

As summarized in Table 2, the TG and DTG curve for the complex $\mathrm{Ni(NCS)_2(bfpy)_4}$ (**II**) indicate that mass loss becomes observable at 127°C and (in the temperature range 20–450°C) three mass loss steps were observed. The first step between 127–284°C is accompanied by 50.5% mass loss and corresponds to the release of 2.5bfpy. The second step took place between 284–350°C and is accompanied by 29.7% mass loss. It is attributed to the release of the remaining 1.5bfpy. The third step took place between 350–467°C and is accompanied by 9.8% mass loss. It is attributed to the decomposition of the $\mathrm{Ni(NCS)_2}$ to NiS.

The stoichiometry of thermal decomposition of complex **II** can be expressed by equations:

$$\mathrm{Ni(NCS)_2(bfpy)_4}(s)\xrightarrow{127\text{–}284^{\circ}\mathrm{C}}\mathrm{Ni(NCS)_2(bfpy)_{1.5}}(s)+\mathrm{2.5bfpy}(g) \tag{4}$$

$$\mathrm{Ni(NCS)_2(bfpy)_{1.5}}(s)\xrightarrow{284\text{–}350^{\circ}\mathrm{C}}\mathrm{Ni(NCS)_2}(s)+\mathrm{1.5bfpy}(g) \tag{5}$$

$$\mathrm{Ni(NCS)_2}(s)\xrightarrow{350\text{–}467^{\circ}\mathrm{C}}\mathrm{NiS}+\text{decomposition product} \tag{6}$$

The decomposition rate maxima (from DTG curve) for the studied samples are at ~243, 307 and 383°C, respectively.

Table 1 Elemental analysis and complexometric titration data of the complexes **I**–**III**

Complex	Mass/%							
	Theoretical				Experimental			
	C	H	N	Ni	C	H	N	Ni
$\mathrm{Ni(NCS)_2(fpy)_4}$ (**I**)	55.32	3.10	12.90	9.01	54.91	3.02	12.85	8.91
$\mathrm{Ni(NCS)_2(bfpy)_4}$ (**II**)	64.88	3.31	9.87	6.89	63.55	3.30	9.79	6.81
$\mathrm{Ni(NCS)_2(CF_3Phfpy)_4}$ (**III**)	54.98	2.73	7.12	4.98	56.30	2.74	6.81	4.95

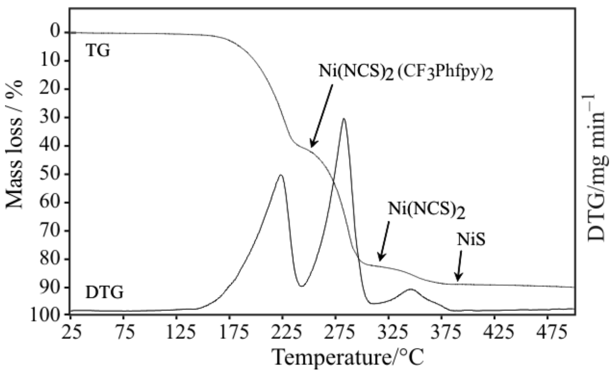

Fig. 2 TG and DTG curves of $Ni(NCS)_2(CF_3Phfpy)_4$ (**III**)

The data from TG and DTG curve (Table 2) for the complex $Ni(NCS)_2(CF_3Phfpy)_4$ (**III**) indicate that it is stable up to 124°C and then three mass loss steps were observed. The first step between 124–254°C is accompanied by 40.8% mass loss and the second step between 254–326°C is accompanied by 41.4% mass loss. Both steps are attributed to the release of $2(CF_3Phfpy)$ and $2(CF_3Phfpy)$, respectively. The third step between 326–450°C is accompanied by 7.8% mass loss. It is attributed to the decomposition of $Ni(NCS)_2$ to NiS. The stoichiometry of thermal decomposition of complex **III** can be expressed by equations:

$$Ni(NCS)_2(CF_3Phfpy)_4(s) \xrightarrow{124\text{–}254°C} Ni(SCN)_2(CF_3Phfpy)_2(s)+2CF_3Phfpy(g) \quad (7)$$

$$Ni(NCS)_2(CF_3Phfpy)_2(s) \xrightarrow{254\text{–}326°C} Ni(SCN)_2(s)+2CF_3Phfpy(g) \quad (8)$$

$$Ni(NCS)_2(s) \xrightarrow{326\text{–}450°C} NiS+\text{decomposition product} \quad (9)$$

The modes of the coordinated ligands in the complexes have been investigated by means of IR spectra. The most important IR frequencies attributed to the vibration of the complexes **I**–**III** are reported in Table 3.

For the NCS group those bands are characteristic that correspond to the valence vibrations of $\nu_{C–N}$ and of $\nu_{C–S}$. In accordance with literature data [25], Table 2 shows that for studied complexes, the NCS group appears and bonded through the N atom since the absorption band in the interval 690–730 cm^{-1}, known for the coordination M-SCN is missing.

The stretching vibration of the C–H in the pyridine ring appeared at 1590 cm^{-1} [26]. Upon complex formation the band shifts to higher frequency. The bands at 1597–1599 cm^{-1} in complexes suggests the bond formation by Ni(II) with the nitrogen atom of the respective pyridine ring. The band shifts to higher frequencies for the dipolar contribution of $C{\equiv}N^+$ in the heterocyclic ring [27].

Table 3 Some IR spectral data (450–2600 cm^{-1}) of complexes **I**–**III**

Assignment	Complex		
	I	**II**	**III**
ν_{CN} NCS	2072	2074	2073
ν_{CS} NCS	801	774	802
ν_{CN} py ring	1597	1597	1599
ν_{CC}	957	926	928
ν_{CH} ring	868	876	829
γ_{CCC}	638	633	654

Conclusions

All of the complexes are stable in air and soluble in water, ethanol and dimethylsulfoxide. The loss of the neutral heterocyclic ligands occurs (on the TG and DTG curves) in two steps in complexes **I**–**III**. The thermal stability of the complexes (on the base of T_{max} of first peak on the DTG curves) can be ordered in the sequence **I**<**II**<**III**. Furopyridine (fpy) and furopyridine derivates (bfpy, CF_3Phfpy) were coordinated to Ni(II) through the nitrogen atom of the respective heterocyclic ring and the anionic ligand was coordinated through the nitrogen atom of NCS groups. Without X-ray analysis, no define structure can be described for the different components. However, spectroscopic and analytical data together with the thermal analyses techniques available enabled us to predict composition of these complexes.

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