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FUROPYRIDINES AND FUROPYRIDINE-Ni(II) COMPLEXES
Synthesis, thermal and spectral characterization

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The thermal decomposition of the complexes $Ni(SCN)_2(fp)_4{\cdot}2H_2O$ (I), $Ni(SCN)_2(mfp)_4$ (II) and $Ni(SCN)_2(dmfp)_3$ (III) (where *fp*=furo[3,2-c]pyridine, *mfp*=2-methylfuro[3,2-*c*]pyridine and *dmfp*=2,3-dimethylfuro[3,2-*c*]pyridine) have been investigated in dynamic air from room temperature to 1000°C by means of TG, DTG and DTA. The chemical composition of the complexes, solid intermediates and the resultant products of thermolysis have been identified by means of elemental analysis and complexometric titration. The results revealed that NiO was left as residue at the end of the thermal degradation experiments. IR data suggested that *fp*, *mfp* and *dmfp* were coordinated to Ni(II) through the N atom of the respective heterocyclic ring.

Keywords: *DTA, FTIR, furopyridine-Ni(II) complexes, furopyridines, TG, UV-VIS*

Introduction

Investigations of quinoline isosters (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*]pyridine ring system [1]. Therefore, efficient synthetic methods for these types of heterocycles are of a great interest. Recently, the syntheses of the furo[3,2-*c*]pyridines and pyrrolo[2´,3´:4,5]furo[3,2-*c*]pyridines have been reported in [2–5]. The study of the influence of metal and ligand nature on the process of thermal decomposition is of a certain interest. Therefore, many authors have investigated many heterocyclic compounds as ligands in coordination complexes of several central atoms and also examined their thermal and spectral properties [6–31]. In our previous papers, we described the thermoanalytical properties of Mg(II), Cu(II), Co(II) and Fe(III) complexes with pyridine and its derivatives [32–44]. Up to our best knowledge furo[3,2-*c*]pyridine (*fp*), 2-methylfuro[3,2-*c*]pyridine (*mfp*) and 2,3-dimethylfuro[3,2-*c*] pyridine (*dmfp*) were never used as ligands for coordination compounds with Ni(II). This fact has prompted us to undertake a systematic study in complexation reactions of these heterocyclic ligands. This paper describes the preparation of Ni(II) complexes with *fp*, *mfp* and *dmfp* along with thermal analyses and spectral investigation of the complexes.

Experimental

Synthesis of furo[3,2-c]pyridines

Starting from furan-2-carbaldehydes 1a–c via Doebner condensation we synthesized the corresponding acids 2a–c (Fig. 1). The acylazides were prepared by treatment of 2a–c with ethyl chloroformate and sodium azide in a one-pot reaction and then were transformed by thermal cyclisation in Dowtherm with tributylamine to 4,5-dihydropyridines 3a–c. Refluxing of 3a–c with phosphorus oxychloride and the reduction of the obtained chloroderivatives led to furo[3, 2-c]pyridines 4a–c.

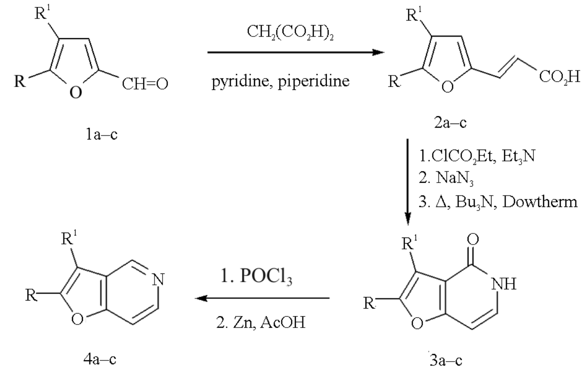

Fig. 1 The scheme for the synthesis of furo[3,2-c]pyridines. For compounds a – R=R^1=H; b – R=CH_3, R^1=H and c – R=R^1=CH_3

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*Synthesis of Ni(**II**) complexes*

Complexes **I–III** were prepared by treating (0.002 mol) *fp*, *mfp* or *dmfp*, respectively with $Ni(SCN)_2·6H_2O$ (0.001 mol) in methanol (50 mL). The solutions were kept at room temperature. The fine precipitated microcrystals were filtered out, washed with cold methanol and air-dried at room temperature.

Measurements

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

The IR spectra were obtained on Philips analytical PU9800 FTIR spectrometer by using Nujol mulls in the range 400–4000 cm^{-1}.

Electronic spectra in the T-region, 10–2 $·10^3$ K was measured with a PerkinElmer 450 spectrophotometer.

Thermal decomposition studies were carried out using a TA Instruments (model SDT 2960) in dynamic air atmosphere (flow rate 90 cm^3 min^{-1}) by using a platinum crucible with a sample mass of 20 mg from room temperature to 1000°C. A heating rate of 10°C min^{-1} was chosen for all measurements.

X-ray powder diffraction was carried out using a MIROMETA II instrument, using CuK_α radiation. The records were compared with ASTM tables.

Results and discussion

The composition of the complexes **I–III**, the solid intermediates and the resultant final products of thermolysis have been identified by elemental analysis and complexometric titration. The data of elemental analysis and complexometric titration of complexes **I–III** are given in Table 1.

The data for the thermal decomposition of complexes **I–III** are summarized in Table 2. The thermal decomposition of the compounds is a multi-stage process. The subsequent detachment of the ligands was observed. The final solid products were NiO. The TG and DTA curves for $Ni(SCN)_2(dmfp)_3$ (**III**) are shown in Fig. 2 as an example.

The TG curve for the complex $Ni(SCN)_2(fp)_4·2H_2O$ (**I**) indicates that it is stable at temperature up to 60°C, where the slow decomposition to $Ni(SCN)_2(fp)_4$ begins. The TG curve shows four mass losses at 140, 190, 340 and 420°C. They correspond to the presence of four intermediate decomposition products: $Ni(SCN)_2(fp)_4$, $Ni(SCN)_2(fp)_2$,

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

Complex	Theoretical/%				Experimental/%			
	C	H	N	Ni	C	H	N	Ni
$Ni(SCN)_2(fp)_4·2H_2O$ (**I**)	52.43	3.50	12.23	8.55	52.51	3.48	12.20	8.53
$Ni(SCN)_2(mfp)_4$ (**II**)	57.73	3.96	11.89	8.30	57.68	3.97	11.91	8.32
$Ni(SCN)_2(dmfp)_3$ (**III**)	56.52	4.38	11.37	9.53	56.45	4.39	11.40	9.55

Table 2 Thermal decomposition data of the complexes **I–III**

Complex	DTA		TG			
	Peak/°C	Process	Temp. interval/°C	Δ*m*(found/calc.)/%	Lost component	Residue
I	135	endo	60–140	5.50/5.24	$2H_2O$	
	180	endo	140–190	35.00/34.67	2fp	
	232	endo	190–340	34.50/34.67	2fp	
	379	exo	340–450	12.00/12.22	SCN, CN	
	513	exo	450–800	2.25/2.33	S	NiO
II	186	endo	110–207	41.00/41.03	2mfp	
	254	endo	207–350	40.50/41.03	2mfp	
	369	exo	350–400	9.00/8.67	SCN, CN	
	519	exo	400–770	2.00/1.64	S	NiO
III	222	endo	150–240	48.00/47.77	2dmfp	
	273	endo	240–335	24.00/23.88	dmfp	
	391	exo	335–420	13.50/13.63	SCN, CN	
	520	exo	420–840	2.50/2.60	S	NiO

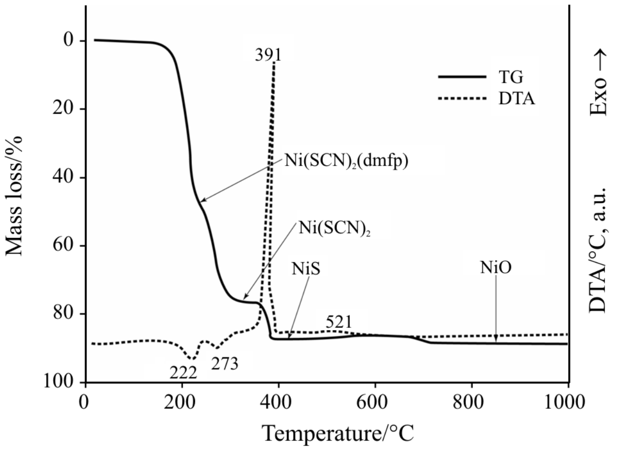

Fig. 2 TG and DTA curves of $Ni(SCN)_2(dmfp)_3$ (**III**)

$Ni(SCN)_2$ and NiS. The chemical composition of the solid intermediates and the resultant final products of thermolysis have been identified by means of elemental analysis and complexometric titration. NiS and NiO were also identified by X-ray diffraction. The most probable thermal decomposition reaction of complex **I** can be represented as:

$$Ni(SCN)_2(fp)_4{\cdot}2H_2O \rightarrow Ni(SCN)_2(fp)_4+2H_2O$$

$$Ni(SCN)_2(fp)_4 \rightarrow Ni(SCN)_2(fp)_2+2fp$$

$$Ni(SCN)_2(fp)_2 \rightarrow Ni(SCN)_2+2fp$$

$$Ni(SCN)_2 \rightarrow NiS+\text{decomposition product}$$

$$NiS+O_2 \rightarrow NiO+\text{decomposition product}$$

The DTA curve for the complex **I** shows three endotherms and two exotherms (Table 2). The three endothermic peaks observed at 135, 180 and 232°C corresponding to the loss of $2H_2O$, 2fp and 2fp, respectively. The two exothermic peaks observed at 379 and 513°C corresponding to decomposition reactions of $Ni(SCN)_2$ and NiS, respectively. NiO, which was identified by X-ray diffraction measurements, was found to be final solid residue of these thermal decompositions.

As summarized in Table 2, the TG curve for the complex $Ni(SCN)_2(mfp)_4$ (**II**) indicates that mass loss becomes observable at 110°C , and four mass loss steps were observed. The first step between 110–207°C is accompanied by 41.0% mass loss. It is attributed to the decomposition of 2mfp. The second step took place between 207–350°C and is accompanied by 40.5% mass loss. It is attributed to the decomposition of the remaining 2mfp. The third step took place between 350–400°C and is accompanied by 9.0% mass loss. It is attributed to the decomposition of the $Ni(SCN)_2$ to NiS. The fourth step took place between 400 –770°C and is accompained by 2.0% mass loss. It is attributed to the oxidation reaction of NiS to NiO as the final solid product (oxygen is from the air atmosphere). The thermal reaction of complex **II** can be represented as:

$$Ni(SCN)_2(mfp)_4 \rightarrow Ni(SCN)_2(mfp)+3mfp$$

$$Ni(SCN)_2(mfp) \rightarrow Ni(SCN)_2+mfp$$

$$Ni(SCN)_2 \rightarrow NiS+\text{decomposition product}$$

$$NiS+O_2 \rightarrow NiO+\text{decomposition product}$$

The DTA curve for the complex **II** shows two endotherms and two exotherms (Table 2). The two endothermic peaks observed at 186 and 254°C corresponding to the loss of 3mfp and mfp, respectively. The two exothermic peaks observed at 369 and 519°C corresponding to decomposition reactions of $Ni(SCN)_2$ and NiS, respectively. NiO, which was identified by X-ray diffraction measurements, was to be final solid residue of these thermal decompositions.

As summarized in Table 2, the TG curve of complex $Ni(SCN)_2(dmfp)_3$ (**III**) indicates that it is stable at temperature up to 150°C and four mass loss steps (Fig. 2) were observed. The first step between 150–240°C is accompanied by 48.0% mass loss and the second step between 240–335°C is accompanied by 24.0% mass loss. Both steps are attributed to the decomposition of 2,3-dimethylfuro[3,2-c]pyridine (2dmfp and dmfp, respectively). The third step between 335–420°C is accompanied by 13.5% mass loss. It is attributed to the decomposition of the $Ni(SCN)_2$ to NiS. The fourth step took place between 420–840°C is accompanied by 2.5% mass loss. It is attributed to the oxidation reaction of NiS with atmospheric oxygen to NiO. The thermal decomposition reaction of complex **III** can be represented as:

$$Ni(SCN)_2(dmfp)_3 \rightarrow Ni(SCN)_2(dmfp)+2dmfp$$

$$Ni(SCN)_2(dmfp) \rightarrow Ni(SCN)_2+dmfp$$

$$Ni(SCN)_2 \rightarrow NiS+\text{decomposition product}$$

$$NiS+O_2 \rightarrow NiO+\text{decomposition product}$$

The DTA curve for the complex **III** shows two endotherms and two exotherms (Table 2). The two endothermic peaks observed at 222 and 273°C ascribed to the loss of 2dmfp and dmfp, respectively. The two exothermic peaks observed at 391 and 520°C ascribed to decomposition reactions of $Ni(SCN)_2$ and NiS, respectively. NiO, which was identified by X-ray diffraction measurements, was to be final solid residue of these thermal decompositions.

The solid state electronic spectra of complexes I–III exhibit ligand field bands with maxima at 17800–18500 cm^{-1}. These bands were identified as d-d transitions of nickel atoms and are typical for tetragonal distorted octahedral Ni(II) complexes [45, 46].

Table 3 IR spectral data (400–4000 cm^{-1}) of complexes **I–III**

Assignment	**I**	**II**	**III**
$\nu(CN)$	1610	1605	1608
$\gamma(CCC)$	650	630	660
	613	601	605
$\nu(C–C)$	929	958	928
$\nu(C–C)$	1605	1608	1610
$\nu(C–H)_{ring}$	862	865	864
$\nu(OH)$	3472		
$\delta(HOH)$	1615		

a=asymmetric, *s*=symmetric

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 vibrations of the complexes **I–III** are reported in Table 3. IR spectrum of complex **I** showed a broad absorption band at 3472 cm^{-1} (antisymmetric and symmetric OH stretching) and 1615 cm^{-1} (HOH bending). These bands clearly confirm the presence of water of crystallization in the compound **I**. The presence of water as water of crystallization in these compounds was further shown by the thermal decomposition data [47, 48]. The stretching vibration of the C=N in the pyridine ring appeared at 1590 cm^{-1} [29]. Upon complex formation the band shifts to higher frequencies. The bands in the range (1605–1610 cm^{-1}) in complexes **I–III** may suggest the bond formation by the Ni(II) with the nitrogen atom of the respective pyridine ring. The band shifts to higher frequencies for the dipolar contribution of $C=N^+$ in the heterocyclic ring [50].

Information obtained from ASTM tables of NiS and NiO shows a good correlation with X-ray powder diffraction data of the last intermediate product (NiS) and final product (NiO), respectively of thermal decomposition of complexes **I–III**.

Conclusions

Complex **I** is hydrated and complexes **II** and **III** are unhydrated. All of the complexes are stable in air and soluble in water, ethanol, methanol and dimethylsulfoxide. The loss of the neutral ligands occurs (on the TG curves) in two steps in complexes **I–III**. The thermal stability of the complexes can be ordered in the sequence: **I**<**II**<**III**. NiO is left as residue at the end of the thermal degradation experiments of the compounds **I–III**. Fp, mfp and dmfp were coordinated to Ni(II) through the nitrogen atom of the respective heterocyclic ring in complexes **I–III**. Without X–ray analysis, no definite structure can be described for the different components. However, spectroscopic and analytical data available enable us to predict the structures and we can also use thermal decomposition studies to help us.

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