

Synthesis, Thermal and Spectral Properties of Cu(II) and Ni(II) Complexes with Furopyridines or Quinoline

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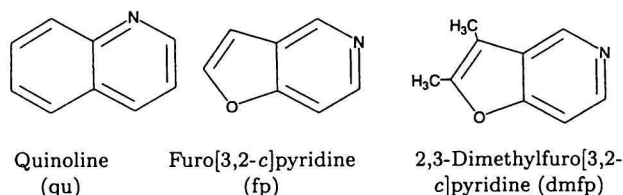
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The thermal decomposition of the complexes $\text{Cu}(\text{NO}_3)_2(\text{fp})_2 \cdot \text{MeOH}$ (*I*), $\text{Cu}(\text{NO}_3)_2(\text{dmfp})_2$ (*II*), and $\text{Ni}(\text{NO}_3)_2(\text{qu})_4 \cdot 2\text{MeOH}$ (*III*) (where fp = furo[3,2-*c*]pyridine, dmfp = 2,3-dimethylfuro[3,2-*c*]pyridine, qu = quinoline, and Me = methyl) had been investigated in dynamic air from room temperature to 1000 °C by means of thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermal analysis (DTA). The possible scheme of thermal decomposition of the complexes is suggested. The chemical composition of the solid intermediates and the resultant products of thermolysis has been identified by means of elemental analysis and complexometric titration. The thermal stability (according to TG temperature) of these complexes can be ordered in the increasing sequence: *I*, *III*, *II*. The results revealed that CuO or NiO were left as residues at the end of the thermal degradation experiments. Fp, dmfp, and qu were coordinated to Cu(II) through the N atom of the respective heterocyclic ring. IR data suggested the bidentate coordination of nitrates to Cu(II) in complexes *I* and *II* and unidentate coordination of nitrates to Ni(II) in complex *III*.

Investigations of quinoline isoesters (furopyridines, thienopyridines) in which the benzene ring is replaced by furan or thiophene ring have resulted in discovering many biologically active compounds. New pharmacophores with potential antipsychotic activity possess the thieno[3,2-*c*]- and 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 papers [2–7]. 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 properties [8–21]. Up to our best knowledge furo[3,2-*c*]pyridine, 2,3-dimethylfuro[3,2-*c*]pyridine, and quinoline were never used as ligands for coordination compounds. This fact has prompted us to undertake a systematic study in complexation reactions of these heterocyclic ligands. This paper describes the preparation of Cu(II) and Ni(II) complexes with fp, dmfp, and qu along with thermal analyses and spectral investigation of the complexes.



EXPERIMENTAL

Complexes *I–III* were prepared by treating fp, dmfp or qu (0.002 mol), respectively with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.001 mol) in methanol (50 cm³). The solutions were left to stand at room temperature. The fine precipitated microcrystals were filtered off, washed with cold methanol and air-dried at room temperature.

Elemental analyses (C, H, N) were carried out by means of Erba 1106 Analyser and the content of Cu(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, 10–28 kK were measured with a Perkin–Elmer 450 spectrophotometer, while thermal decomposition studies were carried out on T.A.I. SDT 2960

Table 1. Analytical Data of the Complexes *I–III*

Complex	$w_i(\text{calc.})/\%$			
	C	H	N	M(II)
<i>I</i>	39.32	3.05	12.23	13.88
	40.70	2.98	12.90	13.82
<i>II</i>	44.86	3.76	11.62	13.19
	44.90	3.88	11.63	13.22
<i>III</i>	59.91	4.73	11.04	7.71
	59.51	4.65	11.10	7.78

M(II) = Cu(II) or Ni(II).

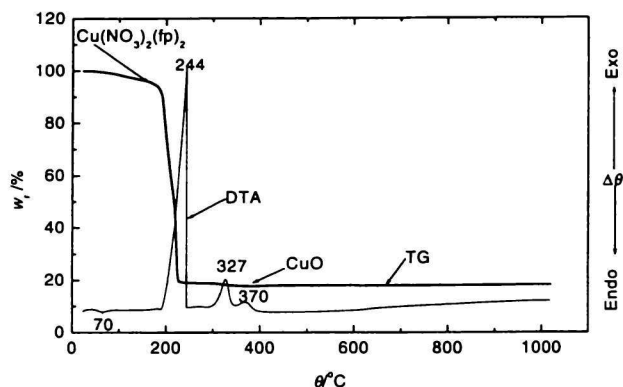
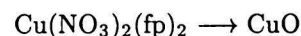
instrument in air atmosphere by using a platinum crucible with a sample mass of 20 mg from room temperature to 1000°C. The rate of temperature increase of 10°C min⁻¹ was chosen for all measurements.

RESULTS AND DISCUSSION

The data of chemical analyses of complexes *I–III*, given in Table 1, are in good agreement with theoretical expectations. The composition of the solid intermediates and the resultant products of thermolysis has been identified by elemental analysis and complexometric titration (variation < 1 %).

Thermal decomposition data of complexes *I–III* are summarized in Table 2. Thermal decomposition of the compounds is a multi-stage process. The subsequent detachment of the ligands was observed. The final solid products were CuO or NiO.

The TG and DTA curves for Cu(NO₃)₂(fp)₂·MeOH (*I*) are shown in Fig. 1. The TG curve for that complex indicates that it is stable at temperature up to 60°C, when there begins the slow decomposition to Cu(NO₃)₂(fp)₂ and then the rapid decomposition to CuO as the final solid product formed at 275°C. The most probable thermal decomposition scheme is

**Fig. 1.** TG and DTA curves of *I*.

The DTA curve for the complex *I* presents a weak endothermic peak at 70°C corresponding to the loss of methanol and a strong exothermic peak at 244°C corresponding to decomposition reactions of two furo[3,2-*c*]pyridine and two nitrate molecules with simultaneous formation of CuO. The DTA curve also exhibits two more exothermic peaks at 327°C and 370°C corresponding to recrystallization reaction and/or phase transition of CuO [22].

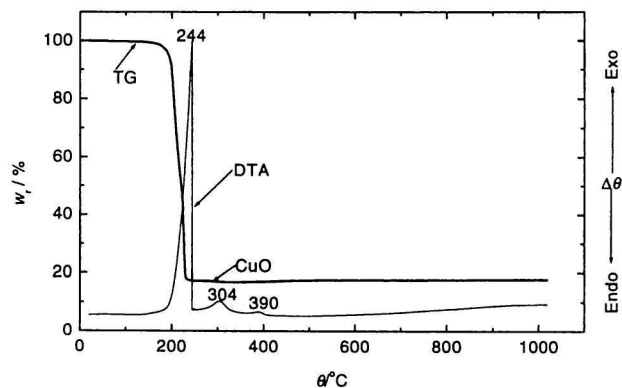
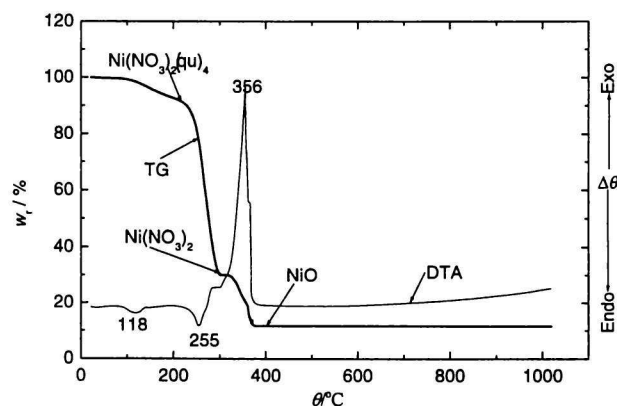
The TG and DTA curves for Cu(NO₃)₂(dmfp)₂ (*II*) are shown in Fig. 2. The TG curve for that complex indicates that it is stable at temperature up to 180°C, when there begins the decomposition to CuO, as to the final product formed at 270°C. The most probable thermal decomposition scheme is



The DTA curve for the complex presents an exothermic peak at 244°C corresponding to the decomposition reactions of 2dmfp and 2NO₃⁻ with simultaneous formation of CuO. The DTA curve also exhibits two more exothermic peaks at 304°C and 390°C

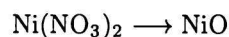
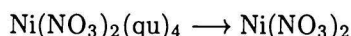
Table 2. Thermal Decomposition Data of the Complexes *I–III*

Complex	DTA		TG			
	θ_{max} °C	Process	Temp. interval °C	$\Delta w(\text{found}/\text{calc.})$ %	Released component	Residue
<i>I</i>	70	endo	60–170	7.06/6.99	MeOH	
	244	exo	170–275	75.50/75.63	2fp, NO ₃ , NO ₂	CuO
<i>II</i>	244	exo	180–270	82.96/83.40	2dmfp, NO ₃ , NO ₂	CuO
	118	endo	110–220	8.50/8.41	2MeOH	
<i>III</i>	255	endo	220–300	67.00/67.88	4qu	
	356	exo	300–380	14.00/14.19	NO ₃ , NO ₂	NiO

Fig. 2. TG and DTA curves of *II*.Fig. 3. TG and DTA curves of *III*.

corresponding to recrystallization reaction and/or phase transition of CuO [22].

The TG and DTA curves for $\text{Ni}(\text{NO}_3)_2(\text{qu})_4 \cdot 2\text{MeOH}$ (*III*) are shown in Fig. 3. The TG curve for that complex indicates that it is stable at temperature up to 110°C, when there begins the slow decomposition to $\text{Ni}(\text{NO}_3)_2(\text{qu})_4$. The TG curve shows two bendings at 220°C and 300°C. They correspond to the presence of two intermediate decomposition products: $\text{Ni}(\text{NO}_3)_2(\text{qu})_4$ and $\text{Ni}(\text{NO}_3)_2$. The most probable thermal decomposition reaction of complex *III* can be represented as



The DTA curve for the complex presents two endothermic peaks at 118°C and 255°C corresponding to the loss of 2MeOH and 4qu, respectively, and an exothermic maximum at 356°C corresponding to de-

Table 3. Infrared Spectral Data ($\bar{\nu} = 400\text{--}4000\text{ cm}^{-1}$) of Complexes *I—III*

Assignment	$\bar{\nu}_i/\text{cm}^{-1}$		
	<i>I</i>	<i>II</i>	<i>III</i>
$\nu(\text{CN})$	1614	1601	1604
$\gamma(\text{CCC})$	650	630	660
	613	601	605
$\nu_{\text{as}}(\text{NO}_3^-)$	1495	1483	1420
$\nu_{\text{s}}(\text{NO}_3^-)$	1274	1279	1306
$\Delta(\text{NO}_3^-)$	221	204	114
$\nu(\text{C—C})$	929	958	928
$\nu(\text{C—H})_{\text{ring}}$	862	865	864
$\nu(\text{OH})$	3475		3472
$\delta(\text{HOH})$	1624		1615

as – asymmetric, s – symmetric.

composition reaction of 2NO_3^- with simultaneous formation of NiO.

The solid state electronic spectra of complexes *I—III* exhibit ligand field bands with maxima at 15 800 cm^{-1} , 19 200 cm^{-1} , and 18 500 cm^{-1} , respectively. These bands were identified as *d—d* transitions of the copper and nickel atoms and are typical for tetragonal distorted octahedral Cu(II) and Ni(II) complexes [23, 24].

The modes of the coordinated ligands in the complexes have been investigated by means of infrared absorption spectra. The most important infrared frequencies attributed to the vibrations of the complexes *I—III* are reported in Table 3. The IR spectra of complexes *I* and *III* show broad absorption bands $\nu(\text{OH})$ at 3475 cm^{-1} , respectively. These bands clearly confirm the presence of methanol in the complexes [25]. Nitrate anions can be coordinated to metal ions in a number of ways such as unidentate or bidentate (chelating or bridging). The analysis of NO_3^- group band frequencies allowed for the determination of the parameter $\Delta(\text{NO}_3^-) = \bar{\nu}(\nu_{\text{as}}(\nu_5) - \nu_{\text{s}}(\nu_1))$. The magnitude of $\Delta(\text{NO}_3^-)$ serves as a criterion of the way by which nitrates bind to metal ions. The calculated values of $\Delta(\text{NO}_3^-)$ of the complexes *I*, *II*, and *III* are 221 cm^{-1} , 204 cm^{-1} , and 114 cm^{-1} , respectively, which is in good agreement with the literature data for the bidentate nitrate structures in complexes *I* and *II* and unidentate nitrate structures in complex *III*. The values of ΔNO_3^- in complexes $\text{Cu}(\text{NO}_3)_2(\text{py})_2$ (bidentate) and $\text{Cu}(\text{NO}_3)_2(\text{py})_4$ (unidentate) are 198 cm^{-1} and 100 cm^{-1} , respectively [26, 27]. The stretching vibration of the C=N in the pyridine ring appeared at 1590 cm^{-1} [28, 29]. Upon complex formation the band shifts to higher frequencies. The bands in the $\bar{\nu}$ range (1601–1614 cm^{-1}) in complexes *I—III* may suggest the bond formation by the Cu(II) or 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 [30].

Without X-ray analysis, no definite structure can be described for the different components. Unfortunately, we are not able to get suitable single crystal for the X-ray analysis. However, predictions have been made by using spectroscopic and analytical data as well as thermal decomposition studies.

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