J Therm Anal Calorim (2010) 100:857–860
DOI 10.1007/s10973-010-0684-1

Thermal properties of solid complexes with biologically important heterocyclic ligands

Part II. Stoichiometry of thermal decomposition and infrared spectra of thiocyanatocobalt(II) complexes with furopyridine and furopyridine derivatives

**L'. Lajdová · E. Jóna · J. Miklovič ·
P. Segl'a · L'. Kvasnicová · S. Šnircová ·
R. Janík · S. C. Mojumdar**

CTAS2009 Special Chapter

Abstract The stoichiometry of thermal decomposition of the complexes Co(NCS)$_2$(fpy)$_4$ (I), Co(NCS)$_2$(Mefpy)$_4$ (II) and Co(NCS)$_2$(bfpy)$_4$ (III) (where fpy = furo[3,2-c]pyridine, Mefpy = methylfuro[3,2-c]pyridine, bfpy = benzo-[2, 3]furo[3,2-c]pyridine) have been investigated in nitrogen atmosphere from room temperature (RT) to 800 °C by means of TG and DTA. The results revealed that release of heterocyclic ligands occurs in one step. Infrared data suggested that fpy, Mefpy and bfpy were coordinated to Co(II) through the nitrogen atom of the respective heterocyclic ring and anionic ligands through nitrogen atom of the NCS groups.

Keywords Co(II) complexes · Furopyridine derivatives as ligands · Thermal analysis · IR spectra

Introduction

Many authors have studied heterocyclic compounds as ligands in coordination compounds of several central atoms and also investigated their antimicrobial activities [1–5]. Especially six-membered ring systems are a component of several vitamins and drugs [6, 7]. Also investigation of quinoline isoesters (furopyridines), in which the benzene ring is replaced by furan ring has resulted in discovering many biologically active compounds. New pharmacophores with potential antipsychotic activity possess the furo[3,2-c]pyridines ring system [8]. Therefore, efficient synthetic methods for these types of heterocycles have been reported [9, 10].

In our previous articles, we described the thermoanalytical properties of Ni(II) and Cu(II) complexes with furopyridine and furopyridine derivatives [11–13]. This work is aimed on the study of stoichiometry of thermal decomposition and spectral properties (IR spectra) of isothiocyanatocobalt (II) complexes with furo[3,2-c]pyridine (fpy), 2-methylfuro[3,2-c]pyridine (Mefpy) and benzo[2, 3]furo[3,2-c]pyridine (bfpy) (Fig. 1).

Experimental

Synthesis of Co(II) complexes

Complexes Co(NCS)$_2$(fpy)$_4$ (I), Co(NCS)$_2$(Mefpy)$_4$ (II) and Co(NCS)$_2$(bfpy)$_4$ (III) were prepared by treating (0.002 mol) fpy, Mefpy and bfpy, respectively, with Co(NCS)$_2$·6H$_2$O (0.001 mol) in methanol (50 mL). The solutions were kept at room temperature. The fine precipitated monocrystals were filtered off, washed with cold methanol and dried at room temperature.

L'. Lajdová · E. Jóna · L'. Kvasnicová · S. Šnircová · R. Janík
Department of Chemical Technologies and Environment,
Faculty of Industrial Technologies, Trenčín University,
020 32 Púchov, Slovakia

J. Miklovič
Department of Chemistry, Faculty of Natural Sciences,
University of St. Cyril and Methodius, 917 01 Trnava, Slovakia

P. Segl'a
Institute of Inorganic Chemistry, Technology and Materials
Faculty Chemical and Food Technology, Slovak Technical
University, 812 37 Bratislava, Slovakia

S. C. Mojumdar (✉)
Department of Engineering, University of New Brunswick,
Saint John, NB E2L 4L5, Canada
e-mail: mojumdar@unbsj.ca; scmojumdar@yahoo.com

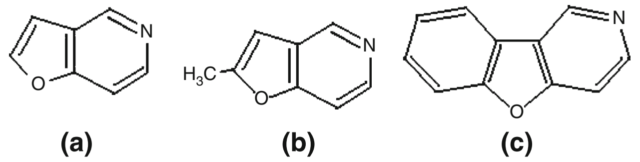

Fig. 1 Structures of furo[3,2-c]pyridine (**a**), 2-methylfuro[3,2-c]pyridine (**b**) and benzo[2, 3]furo[3,2-c]pyridine (**c**)

Measurements

The content of Co(II) was determined by complexometric titration. Elemental analysis (C, H and N) was carried by means of Carlo Erba 1106 Analyser.

Thermal decomposition studies were carried out on a TA Instruments (model SDT 2960) in dynamic air atmosphere (flow rate 90 cm^3 min^{-1}) on a platinum crucible with a sample mass of 20 mg from room temperature to 750 °C. A heating rate of 10 °C min^{-1} was chosen for all measurements.

The IR spectra were obtained on a Philips analytical PU 9800 FTIR spectrometer using Nujol mulls in the range of 400–4,000 cm^{-1}.

Results and discussion

Analytical results of the complexes

The content of N, C, H was determined by elemental analysis and the content of Co(II) was determined by complexometric titration. The analytical data of the complexes I–III, reported in Table 1, show a good agreement between the experimental and calculated data.

Thermal behaviour of the complexes

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 final solid product is CoS. The TG and DTA curves for $Co(NCS)_2(fpy)_4$ (I) are shown in Fig. 2 as an example. The TG and DTA curves for the complex $Co(NCS)_2(fpy)_4$ (I) indicate that it is stable up to ~120 °C. The release of furopyridine molecules takes place in one separate step. The mass loss corresponding to the decomposition stages is 73.5% and is in good agreement with the theoretical value (73.12%). It corresponds to the presence of one intermediate decomposition product $Co(NCS)_2$. The stoichiometry of thermal decomposition of complex I can be expressed in Eqs. 1, 2:

$$Co(NCS)_2(fpy)_4(s) \overset{120-445\ ^\circ C}{\rightarrow} Co(NCS)_2(s) + 4\ fpy\ (g) \quad (1)$$

$$Co(NCS)_2(s) \overset{445-675\ ^\circ C}{\rightarrow} CoS + \text{decomposition product} \quad (2)$$

CoS was identified by X-ray diffraction measurements as final solid residue of these thermal decompositions.

The DTA curve for the complex I (Fig. 1) presents one endothermic peak at ~178 °C corresponding to the loss of 4 fpy and one exothermic peak ~588 °C corresponding to decomposition reaction of $Co(NCS)_2$ with simultaneous formation of CoS.

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

Complex	Theoretical/%					Experimental/%				
	C	H	N	S	Co	C	H	N	S	Co
$Co(NCS)_2(FP)_4$ (I)	55.30	3.09	12.90	9.84	9.04	55.15	2.69	13.00	9.28	8.99
$Co(NCS)_2(MeFP)_4$ (II)	57.70	3.99	11.88	9.06	8.33	56.63	3.66	11.75	8.95	8.21
$Co(NCS)_2(BFP)_4$ (III)	64.86	3.31	9.87	7.53	6.92	63.79	3.27	9.60	7.08	6.89

Table 2 Thermal decomposition data

Complex	DTA		TG		
	T_{peaks}/ °C	T_{range}/ °C	Mass loss/% found/calc.	Lost component	Residue
I	178	120–445	73,50/73,12	4 fpy	
	588	445–675	13,00/12,90	SCN, CN	CoS
II	166	125–440	74,00/75,25	4 Mefpy	
	630	440–700	13,00/11,88	SCN, CN	CoS
III	188	130–447	80,00/79,44	4 bfpy	
	538	477–610	10,00/9,87	SCN, CN	CoS

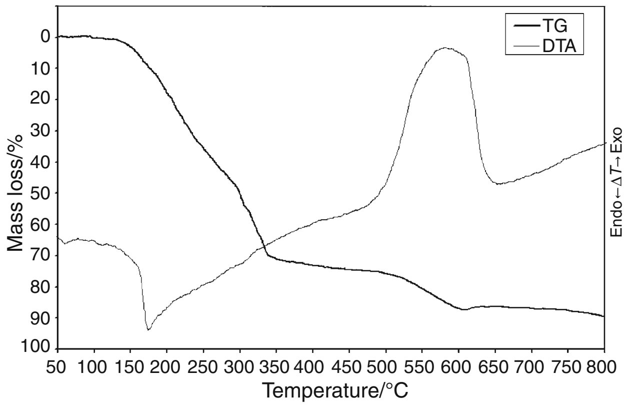

Fig. 2 TG and DTA curves of $\mathrm{Co(NCS)_2(fpy)_4}$ (I)

As summarized in Table 2, the TG curve for the complex $\mathrm{Co(NCS)_2(Mefpy)_4}$ (II) indicate that mass loss becomes observable at ~125 °C and (in the temperature range of 20–800 °C) two mass loss step were observed. The first step between 125 and 440 °C is accompanied by 74% mass loss and corresponds to the release of 4 Mefpy. The second step took place between 440 and 700 °C and is accompanied by 13% mass loss. It is attributed to the decomposition of the $\mathrm{Co(NCS)_2}$ to CoS. The stoichiometry of thermal decomposition of complex II can be expressed in Eqs. 3, 4.

$$\mathrm{Co(NCS)_2(Mefpy)_4(s)} \xrightarrow{125-440\,^{\circ}\mathrm{C}} \mathrm{Co(NCS)_2(s)} + 4\ \mathrm{Mefpy\ (g)} \tag{3}$$

$$\mathrm{Co(NCS)_2(s)} \xrightarrow{440-700\,^{\circ}\mathrm{C}} \mathrm{CoS} + \text{decomposition product} \tag{4}$$

The DTA curve for the complex II presents one endothermic peak at ~166 °C corresponding to the loss of 4 Mefpy and an exothermic maximum with centre about 630 °C corresponding to decomposition reaction of $\mathrm{Co(NCS)_2}$ with the formation of CoS.

The data from TG curve (Table 2) for the complex $\mathrm{Co(NCS)_2(bfpy)_4}$ (III) indicate that it is stable up to ~130 °C and then two mass loss steps were observed. The first step between 130 and 447 °C is accompanied by 80.0% mass loss and the second step between 447 and 610 °C is accompanied by 10% mass loss. The first step attributed to the release of 4 bfpy and the second step is connected with the decomposition of $\mathrm{Co(NCS)_2}$ to CoS. The stoichiometry of thermal decomposition of complex III can be expressed in Eqs. 5, 6.

$$\mathrm{Co(NCS)_2(bfpy)_4(s)} \xrightarrow{130-447\,^{\circ}\mathrm{C}} \mathrm{Co(NCS)_2(s)} + 4\ \mathrm{bfpy\ (g)} \tag{5}$$

$$\mathrm{Co(NCS)_2(s)} \xrightarrow{447-610\,^{\circ}\mathrm{C}} \mathrm{CoS} + \text{decomposition product} \tag{6}$$

Table 3 Some IR spectral data (450–2,600 $\mathrm{cm^{-1}}$) of complexes I–III

Assignment	Complex		
	I	II	III
$\nu_{\mathrm{(CN)\ NCS}}$	2,065	2,064	2,059
$\nu_{\mathrm{(CS)\ NCS}}$	783	791	775
$\nu_{\mathrm{(CN)\ py\ ring}}$	1,613	1,600	1,596
$\nu_{\mathrm{(CC)}}$	924	932	926
$\nu_{\mathrm{(CH)\ ring}}$	881	899	875
$\gamma_{\mathrm{(CCC)}}$	638	638	636

The DTA curve for the complex III shows one endotherm and one exotherm (Table 2). The endothermic peak observed at ~188 °C corresponds to the loss of 4 bfpy. The exothermic peak observed at ~538 °C corresponds to decomposition reaction of $\mathrm{Co(NCS)_2}$ to CoS.

IR spectra

The modes of coordination of the ligands have been investigated by means of infrared absorption spectra. The most important infrared frequencies attributed to the vibration of the bonds of the complexes I–III are reported in Table 3.

The infrared spectra (in particular stretching vibrations of ν(C–N) and ν(C–S) were used to investigate the type of bonding of NCS group in the studied complexes. Then the intensive band at 2,065 $\mathrm{cm^{-1}}$ (complex I), 2,064 $\mathrm{cm^{-1}}$ (complex II) and 2,059 $\mathrm{cm^{-1}}$ (complex III) can be assigned to NCS groups. The ν(C–S) bands at 783, 791 and 775 $\mathrm{cm^{-1}}$, respectively, are in agreement with Ni–N (NCS) bond [14].

The stretching vibration of the C–H in the pyridine ring appeared at ~1,590 $\mathrm{cm^{-1}}$ [15]. Upon complex formation the band shifts to higher frequency. The bands at ~1,596–1613 $\mathrm{cm^{-1}}$ in complexes suggest the bond formation by Co(II) with the nitrogen atom of the respective pyridine ring. The band shifts to higher frequencies for the dipolar contribution of $\mathrm{C{\equiv}N^{+}}$ in the heterocyclic ring [15].

Conclusions

All of the complexes are stable in air and soluble in water, ethanol, methanol and dimethylsulfoxide. The loss of the neutral heterocyclic ligands occurs (on the TG curves) in one steps in all studied complexes I–III. The thermal stability of the complexes (on the basis of the first T_{peaks} on the DTA curves) can be ordered in the sequence II < I < III. Furopyridine (fpy) and furopyridine derivates were coordinated to Co(II) through the nitrogen atom of the respective heterocyclic ring and the anionic ligand was coordinated through nitrogen atom of NCS groups.

Acknowledgements We wish to thank the Slovak Grant Agency (project VEGA 1/1005/09 and 1/330/09) for the financial support.

References

1. Mojumdar SC, Melník M, Jóna E. Thermoanalytical investigation of Mg(II) compounds containing SCN and heterocyclic N-donor ligands. J Anal Appl Pyrolysis. 1999;48:111–20.
2. Mojumdar SC, Melník M, Jóna E. Thermal and IR properties of Mg(II) complexes with heterocyclic ligands. Thermochim Acta. 2000;352:127–32.
3. Mojumdar SC, Melník M, Jóna E. Thermal and spectral properties of Mg(II) and Cu(II) complexes with heterocyclic N-donor ligands. J Anal Appl Pyrolysis. 2000;53:149–60.
4. Mojumdar SC, Ondrejkovičová I, Nevid̆anská L, Melník M. Thermoanalytical and IR-spectral investigation of Fe(III) complexes with nicotinamide. J Anal Appl Pyrolysis. 2002;64:59–69.
5. Mojumdar SC, Lebruškov K, Valigura D. Thermal stability and spectral properties of pyrazine-2,3-dicarboxylatocopper(II) complexes with ronicol. Chem Papers. 2003;57:245–9.
6. Jóna E, Sirota A, Šimon P, Kubranová M. Thermochemical investigation of nickel(II)–nicotinamide–solvent interactions in solid halogeno. Thermochem Acta. 1995;258:161–73.
7. Jóna E, Sirota A, Šimon P, Mrozovski J. Ni(II)-3-pyridylcarbinol (ronicol) interactions in solid halogeno and thiocyanato complexes. J Thermal Anal. 1996;46:1325–37.
8. New JS, Christopher WL, Yevich JP, Butler R, Francis Schlemmer Jr. R, VanderMaelen CP, et al. The thieno[3,2-c]pyridine and furo[3,2-c]pyridine rings: new pharmacophores with potential antipsychotic activity. J Med Chem. 1989;32:1147–56.
9. Bencková M, Krutošíková A. Synthesis of pyrrolo[2′,3′:4,5]furo[3,2-c]pyridines. Monatsh Chem. 1995;126:753–8.
10. Krutošíková A, Sleziak R. Synthesis of 2-arylfuro[3,2-c]pyridines and their derivatives. Collect Czech Chem Commun. 1996;C1:1627–36.
11. Krutošíková A, Mitarová B, Jóna E, Bobošíková M. Synthesis, thermal and spectral properties of Cu(II) and Ni(II) complexes with furopyridines or quinoline. Chem Papers. 2001;55:290–3.
12. Mojumdar SC, Miklovič J, Krutošíková A, Valigura D, Stewart JM. Furopyridines and furopyridine-Ni(II) complexes synthesis, thermal and spectral characterization. J Therm Anal Calorim. 2005;81:211–5.
13. Lajdová L', Jóna E, Šnircová S, Miklovič J, Segl'a P, Pajtášová M, et al. Thermal properties of solid complexes with biologically important heterocyclic ligands. J Therm Anal Calorim. 2009;96(2009):59–62.
14. Melník M, Potočňák I, Macášková L, Mikloš D. Spectral study of copper(II) flufenamates: crystal and molecular structure of biis(Flufenamato)DI(N,N-diethylnicotinamide)Di(Aqua)copper(II). Polyhedron. 1996;15:2159–64.
15. Melník M, Mojumdar SC, Koman M. Crystal structure, spectral and thermal properties of tetrakis(acatato) bis(methyl-3-pyridyl carbamate)dicopper(II) di(methanol). Polish J Chem. 1999;73:1293–9.