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THERMAL STUDY OF NICKEL(II) PYRAZOLYL COMPLEXES

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The thermal behavior of the pyrazolyl complexes $[NiCl_2(HPz)_4]$ (**1**), $[Ni(NCS)_2(HPz)_4]$ (**2**), $[NiCl_2(HdmPz)_4]\cdot 2H_2O$ (**3**) and $[Ni(NCS)_2(HdmPz)_4]\cdot 2H_2O$ (**4**) (*HPz*=pyrazole, *HdmPz*=3,5-dimethylpyrazole) has been studied by thermogravimetry (TG) and differential thermal analysis (DTA). The TG data indicated that the thermal stability of $[NiX_2(HL)_4]$ (*X*=Cl, NCS) compounds varies depending on the pyrazolyl ligand in the following order *HL=HPz>HdmPz*. From the thermal decomposition of **3** and **4** it was possible to isolate the intermediate compounds $[Ni(\mu\text{-}Cl)_2(HdmPz)_2]$ (**3a**) and $[Ni(\mu\text{-}1,3\text{-}NCS)_2(HdmPz)_2]$ (**4a**), respectively. The final products of the thermal decompositions of **1**–**4** were identified as NiO by X-ray powder diffraction.

Keywords: *DTA, nickel(II), pseudohalides, pyrazoles, TG*

Introduction

Transition metal compounds containing pyrazole ligands have received increasing attention due to their potential application as catalysts, liquid crystals and antitumoral drugs [1–3]. In supramolecular point of view, the coordination versatility as well the hydrogen bonding possibilities of the pyrazolyl ligands make these systems good candidates to generate sophisticated inorganic structures [4–8]. Extending our interests in the coordination chemistry of transition metal complexes containing N-based ligands and pseudohalides [4–8], herein we report the results obtained on a systematic thermal study on the complexes $[NiCl_2(HPz)_4]$ (**1**), $[Ni(NCS)_2(HPz)_4]$ (**2**), $[NiCl_2(HdmPz)_4]\cdot 2H_2O$ (**3**) and $[Ni(NCS)_2(HdmPz)_4]\cdot 2H_2O$ (**4**) (*HPz*=pyrazole, *HdmPz*=3,5-dimethylpyrazole). It is worth mentioning that analogous works dealing with the thermal behavior of nickel(II) complexes containing heterocyclic ligands have been recently published in the literature [9, 10].

Experimental

Preparation of the complexes

Compound $[NiCl_2(HPz)_4]$ (**1**) was prepared from the addition of 235 mg (3.45 mmol) of pyrazole to a deep green solution containing 200 mg (0.84 mmols) of $NiCl_2\cdot 6H_2O$, in water. After stirring for 1 h, the blue turquoise suspension was filtered off and the solid was washed and dried under vacuum. The yield was 70%. Complex $[Ni(NCS)_2(HPz)_4]$ (**2**) was synthesized by the following procedure: to an aqueous solution of $[NiCl_2(HPz)_4]$ (**1**) (338 mg; 0.84 mmol), dropwise NaSCN was added (144 mg; 1.78 mmols) in 2 mL of water, giving rise to a purple suspension. The stirring was maintained for 1 h, and the compound was isolated by filtration and dried under vacuum with a yield of 50%. Compound $[NiCl_2(HdmPz)_4]\cdot 2H_2O$ (**3**) was obtained from the addition of 332 mg (3.45 mmols) of 3,5-dimethylpyrazole to an aqueous solution of $NiCl_2\cdot 6H_2O$ (200 mg; 0.84 mmol). After stirring and warming at 60°C for 1 h, the solution was slowly evaporated yielding blue crystals. The obtained yield was 55%. Complex $[Ni(NCS)_2(HdmPz)_4]\cdot 2H_2O$ (**4**) was prepared following the procedure: to a deep green aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ (200 mg; 0.84 mmol), warmed at 50°C, NaSCN was added (144 mg; 1.78 mmols) in 2 mL of water. After 10 min, 3,5-dimethylpyrazole (271 mg; 2.82 mmols) was dissolved in 2 mL of CH_3OH and was added dropwise affording a blue suspension. The stirring was maintained for 5 h and the compound was isolated by filtration and dried under vacuum having a yield of 60%. On the basis of the TG curves, the blue precursors **3** and **4** were heated in a furnace from room temperature to 140 and 150°C, respectively, yielding the yellow $[Ni(\mu\text{-}Cl)_2(HdmPz)_2]$ (**3a**) and the green $[Ni(\mu\text{-}1,3\text{-}NCS)_2(HdmPz)_2]$ (**4a**) intermediate complexes.

Instrumentation

Elemental analyses of carbon, nitrogen, hydrogen, and sulphur were performed on a microanalyser CE Instruments, model EA 1110 – CHNS-O. Infrared spectra were recorded on a Nicolet FTIR-Impact 400 spectrometer in the spectral range of 4000–400 cm^{-1}

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Table 1 Results of chemical analysis of nickel(II) compounds

Complex	Carbon/%		Nitrogen/%		Hydrogen/%		Sulfur/%	
	found	calc.	found	calc.	found	calc.	found	calc.
1	35.51	35.85	27.41	27.88	4.21	4.01	–	–
2	37.92	37.60	31.08	31.33	3.34	3.61	13.33	14.34
3	43.71	43.66	20.37	20.37	6.52	6.61	–	–
3a	37.42	37.31	17.02	17.41	5.06	5.02	–	–
4	44.30	44.37	23.33	23.57	5.63	5.95	10.98	10.77
4a	38.76	39.25	22.33	22.89	4.64	4.40	16.44	17.46

(KBr pellets) and on a Perkin Elmer Spectrum 2000 in the spectral range of 700–50 cm^{-1} (CsI pellets). Thermal analyses (TG) and differential thermal analysis (DTA) were carried out using a TA system model SDT 2960, under flowing of dry synthetic air (100 mL min^{-1}), up to 900°C at a heating rate of 20°C min^{-1}, in α-alumina sample holders. The reference substance was pure α-alumina for DTA measurements. X-ray powder patterns of the residues were obtained with a SIEMENS D-5000 diffractometer equipped with a proportional counter and pulse height discriminator. The Bragg–Bretano arrangement was adopted using CuK$_\alpha$ radiation (λ=1.541 Å) and setting of 34 kV and 20 mA. The peaks were identified using PDF bases [11].

Results and discussion

The elemental analyses and thermogravimetric data, together with IR spectroscopy results, confirmed the proposed formulae for the synthesized compounds. The results of the analyses are presented in Table 1.

Infrared spectra

The neutral monodentate coordination of pyrazolyl ligands in **1**–**4** was evidenced by the presence of intense νNH bands from 3420 to 3217 cm^{-1} as well by the shift of the ring breathing bands to lower frequencies (1574–1515 cm^{-1}) when compared to those ones of the free ligands (1595–1558 cm^{-1}) [7, 8]. The presence of hydrogen bonds can also be evidenced by the unfolding of the νNH band. The existence of terminal N-bonded thiocyanate groups in **2** and **4** was detected by the ν_{as}SCN bands at ca. 2077 cm^{-1} [12]. Besides the typical bands of pyrazole molecules, the IR spectra of **3a** and **4a** showed some differences when compared to those ones recorded for **3** and **4**. According some authors, nickel(II) compounds containing chloro ligand coordinated in a terminal fashion exhibit νNi–Cl bands in a higher frequency than those ones observed for chloro-bridged species [13]. In fact the far-IR spectrum of **3** showed a νNi–Cl absorption at 222 cm^{-1} whereas for **3a** this band is shifted to 206 cm^{-1}. Similarly, the displacement of ν_{as}SCN band from 2077 (**4**) to 2118 cm^{-1} (**4a**) is a strong evidence of the change of the coordination mode of thiocyanate group from terminal to end-to-end fashion [12].

Thermoanalytical results

The TG and DTA curves for the complexes **1**–**4** are illustrated in Fig. 1. Table 2 lists the results of the thermal studies of these compounds together with the assignments of each decomposition stage based on mass calculation. Therefore the groups indicated at the right column of the Table 2 do not correspond necessarily to the gaseous final products of decomposition. With exception of the TG curve obtained for **3**, the

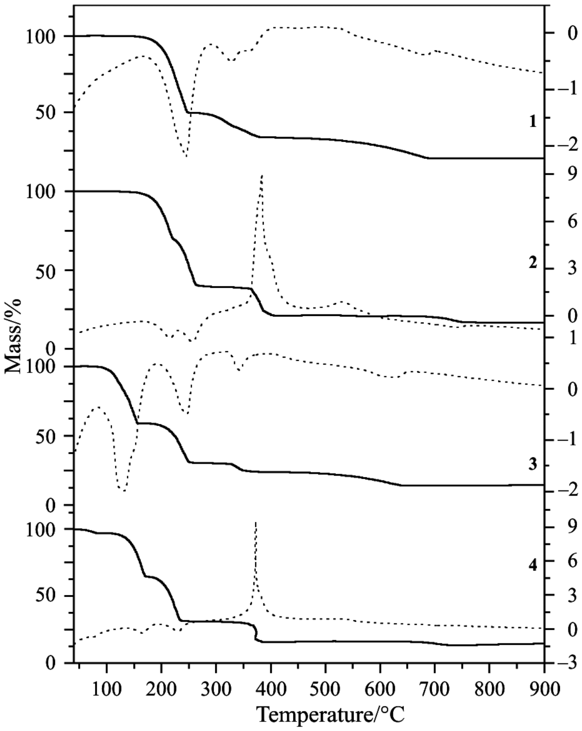

Fig. 1 —– TG and ··· – DTA curves for the complexes **1**–**4**

Table 2 Thermal analysis data for nickel(II) compounds

Complex	Step	ΔT/°C	Δm/%		DTA peaks/°C		Assignment
			obt.	calc.	endo	exo	
1	1	166–287	–49.98	–50.82	244	–	–3*HPz*
	2	287–406	–16.49	–16.94	326, 345	–	–*HPz*
	3	406–800	–13.88	–13.66	–	700	$-2Cl^-$, $+0.5O_2$
	residue		*19.65*	*18.58*			
2	1	160–216	–29.30	–30.45	208	–	–2*HPz*
	2	216–300	–31.46	–30.45	258	–	–2*HPz*
	3	300–450	–18.03	–18.81	–	384	$-NCS^-$, CN^-
	4	450–800	–4.93	–3.59	–	532, 770	$-S^{2-}$, $+0.5O_2$
	residue		*16.28*	*16.70*			
3	1	70–160	–41.04	–41.50	131	–	$-2H_2O$, –2*HdmPz*
	2	160–290	–28.71	–30.36	247	–	$-2Cl^-$, –*HdmPz*
	3	290–465	–6.74	–5.47	344	–	$-2CH_3$
	4	465–800	–9.43	–9.10	–	657	–*HPz*, $+0.5O_2$
	residue		*14.08*	*13.57*			
4	1	40–93	–2.99	–3.03	80	–	$-H_2O$
	2	93–176	–32.56	–35.32	165	–	$-H_2O$, –2*HdmPz*
	3	176–292	–33.41	–32.29	230	–	–2*HdmPz*
	4	292–505	–14.69	–14.12	–	371	$-NCS^-$, CN^-
	5	505–750	–2.81	–2.70	–	–	S^{2-}, $+0.5O_2$
	residue		*13.54*	*12.54*			

TG-DTA curves of compounds **1**, **2** and **4** showed a similar thermal degradation behavior in which the pyrazolyl ligands are firstly eliminated followed by the pyrolysis of the anionic groups together with uptake of O_2, leading to the formation of NiO residue (ASTM 78-0643) [11]. With regard to the thermal behavior of **3**, the last two stages of the decomposition probably involve the formation of a carbonaceous residue during the gradual degradation of the remaining *HdmPz* ligand. The TG-DTA curves of the isothiocyanato-complexes **2** and **4** also showed that NiS (ASTM 77-1624) [11] is formed after the release of the ligands. The following step is characterized by the oxidation of NiS to NiO (ASTM 78-0643) [11].

The analysis of TG curves also revealed the higher thermal stability of pyrazole-based systems (**1** and **2**) than those observed for $[NiX_2(HdmPz)_4]$ (**3** and **4**) probably because of the increased steric hindrance of 3,5-dimethylpyrazole. It is also worth mentioning that no stable intermediate could be isolated from the heating of **1** and **2** due to the overlapping steps.

Conclusions

The thermal behavior of $[NiCl_2(HPz)_4]$ (**1**), $[Ni(NCS)_2(HPz)_4]$ (**2**), $[NiCl_2(HdmPz)_4]\cdot 2H_2O$ (**3**) and $[Ni(NCS)_2(HdmPz)_4]\cdot 2H_2O$ (**4**) has been described in this work. TG studies showed increased stability for $[NiX_2(HL)_4]$ complexes ($X=Cl^-$, NCS^-) in the following order: *HL=HPz>HdmPz*. During the heating of the precursor samples **3** and **4** there were two pyrazole ligands released accompanied by a subsequent structural rearrangement in which the terminal X-groups changed their coordination modes to the bridging fashion, affording the coordination polymers **3a** and **4a**. Therefore, this work showed the potential use of thermal data as a tool for alternative synthetic routes of polymeric metal compounds.

Acknowledgments

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