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Synthesis, characterization, and investigation of the thermal behavior of Cu(II) pyrazolyl complexes

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Abstract This work reports the synthesis, characterization, and thermal behavior of three complexes of copper (II): [$CuCl_2(HPz)_4$] (**1**), [$CuCl_2(HdmPz)_4$] (**2**), and [$CuCl_2(HIPz)_4$] (**3**) (HPz = pyrazole; HdmPz = 3,5-dimethylpyrazole; HIPz = 4-iodopyrazole). The compounds were characterized by elemental analysis, infrared spectroscopy, and UV–Vis measurements. The thermal study of the compounds showed that the ligands are eliminated in 2–4 stages, yielding CuO as final residue.

Keywords Cu (II) complexes · Pyrazolyl ligands · Thermal analysis

Introduction

Pyrazoles represent an important class of ligands in coordination and organometallic chemistry [1]. The rich coordination modes of pyrazolyl type ligands arise from the existence of chemically distinct pyrrol- and pyridine-like nitrogens in a 1,2 relationship of a five-membered-ring. Metal-based compounds bearing pyrazolyl ligands have been the subject of intense research not only for their potential uses as catalysts [2], metallopharmaceuticals [3, 4], and metallomesogens, but also by their beautiful and unusual supramolecular architectures [5–11]. Particularly, we have been interested in the thermal behavior of metal-based pyrazolyl compounds [12–15] due to the possibility in obtaining unusual compounds from controlled heating [16] or to evaluate their volatility and thermal stability which are requisites of vital importance for further use of these compounds as precursors in CVD processes [17].

As a part of our ongoing studies on coordination compounds containing *N*-based ligands [18–21], this article deals with the synthesis, characterization, and investigation of the thermal behavior of the compounds [$CuCl_2(HPz)_4$] (**1**), [$CuCl_2(HdmPz)_4$] (**2**), and [$CuCl_2(HIPz)_4$] (**3**) by means of Thermogravimetry (TG) and Differential Thermal Analysis (DTA).

Experimental

Materials

The reagents commercially available were used without previous purification and all solvents were dried and kept over molecular sieves prior to use. Complex [$CuCl_2(HPz)_4$] (**1**) was prepared according to literature method [22–24].

Synthesis

*Synthesis of [$CuCl_2(HdmPz)_4$] (**2**)* 226 mg (2.35 mmols) of 3,5-dimethylpyrazole, dissolved in 5 mL of CH_3OH was added dropwise to a green solution of $CuCl_2·2H_2O$ (100 mg; 0.587 mmols) in 20 mL of the same solvent, affording a dark green solution. After stirring 1 h, the resulting solution was left to evaporate, affording a green solid. The solid was washed with methanol and vacuum-dried. Yield: 64%. The compound is soluble in chloroform, acetone, and dichloromethane.

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Table 1 Elemental analyses and melting points for complexes **1**–**3**

Complex	Melting point/°C	Carbon/%		Hydrogen/%		Nitrogen/%	
		Found	Calc.	Found	Calc.	Found	Calc.
$C_{12}N_8H_{16}Cl_2Cu$ (**1**)	132	35.5	35.4	3.80	3.96	27.3	27.5
$C_{20}N_8H_{32}Cl_2Cu$ (**2**)	198	46.5	46.3	6.35	6.22	21.7	21.6
$C_{12}N_8H_{12}I_4Cl_2Cu$ (**3**)	224	16.0	15.8	1.40	1.33	12.5	12.3

Synthesis of [$CuCl_2(HIPz)_4$] (3) A solution of 455 mg (2.35 mmols) of 4-iodopyrazole in 5 mL of CH_3OH was added dropwise to a green solution of $CuCl_2{\cdot}2H_2O$ (100 mg; 0.587 mmols) in 20 mL of CH_3OH, affording a light green suspension. After stirring 1 h, the solid was isolated by filtration, washed with methanol and vacuum-dried at room temperature. Yield: 42%. The compound is soluble in chloroform, dimethylsulfoxide, and tetrahydrofurane.

Instrumentation

Infrared spectra were recorded as KBr pellets on a Nicolet FTIR-Impact 400 spectrometer (range 4000–400 cm^{-1}). Absorptions were given as follows: very strong (vs), strong (s), medium (m), weak (w), and shoulder (sh). Electronic spectra were registered on Perkin Elmer Lambda 14P spectrophotometer (190–1100 nm) using acetone, acetonitrile, or water as solvents. C, H, and N analysis were carried out with a CE Instruments EA1110 CHNS-O microanalyzer. Melting points were determined on a MQAPF-302 apparatus. Simultaneous thermal analyses (TG-DTA) were carried out using a SDT 2960 system from TA Instruments, under dynamic flow of dry synthetic air (100 mL min^{-1}) at a heating rate of 20 °C min^{-1} using α-alumina open crucibles for sample and reference. The X-ray powder diffractograms were obtained in a Siemens D5000 diffractometer, using Cu K_α radiation ($\lambda = 1.541$ Å) and setting of 40 kV and 30 mA. The residue (CuO) was identified using ICDD bases [25].

Results and discussion

The results of the elemental analyses as well the thermogravimetric and spectroscopic data confirmed the proposed formulae for the compounds **1**–**3**. The results of the analyses and melting points are shown in Table 1.

IR spectroscopic studies

The most important IR frequencies of the copper complexes along with their assignments are presented in Table 2. The IR spectra revealed the coordination of the pyrazolyl ligands in neutral monodentate fashion by the appearance of intense νNH bands ranging from 3369 to 3260 cm^{-1}. Moreover, the observed shift of ring breathing band to lower frequencies ($\Delta\bar{\nu} \cong 28$ cm^{-1}) compared to those of the free ligands (1595–1534 cm^{-1}) also supported the monodentate character of the pyrazolyl ligands [9–11].

Table 2 Vibrational data (cm^{-1}) for compounds **1**–**3** and assignments

1	**2**	**3**	Band assignment
3260 s	3325 vs	3266 ms	νNH
3124 mw	3111 s	3147 m	νCH
–	2969 m, 2852 w	–	$\nu_{as}CH_3$, ν_sCH_3
1516 mw	1573 s	1510 w	Ring breathing
1471 mw	1469 mw	1456 mw	νring + βNH + βCH
–	1417 ms	–	$\delta_{as}CH_3$
1403 w, 1346 m	–	1393 m	νring + βring + βNH
1163 m	1167 m	1130 m	νring + βCH + βNH
1255 w	1271 m	1250 w	βCH + νring + βNH
1066 ms	1042 w		βCH
600 w	604 w	594 m	γanel + γNH

Table 3 UV–Vis spectral data[a] of complexes **1**–**3** (1.0×10^{-3} mol L^{-1})

Complex	IL transition	LMCT transition	LF transition
[$CuCl_2(HPz)_4$][b] (**1**)	213 (2750)	–	780 (2.5)
[$CuCl_2(HdmPz)_4$][c] (**2**)	–	–	827 (400)
[$CuCl_2(HIPz)_4$][d] (**3**)	235 (3000)	292 (2800)	799 (150)

[a] Absorption maximum in nm and ε in dm^3 mol^{-1} cm^{-1}; [b] in water; [c] in acetone; [d] in acetonitrile

UV–Vis spectroscopic studies

The electronic absorption data of compounds **1**–**3** together with their attributions are listed in Table 3. Very intense bands observed at 213–235 nm range were assigned to IL transition of the pyrazolyl ligands. The displacement observed of these bands when compared to those of the free ligands ($\pi \rightarrow \pi^*$ IL at 211, 216, and 227 nm for HPz, HdmPz, and HIPz, respectively) are associated with coordination effects [26]. In some cases, LMCT transitions of the type $Cl^- \rightarrow Cu(II)$ [27] were detected near 292 nm. The appearance of a broad and very low intensity band at 780–827 nm was assigned to the spin-allowed ${}^2E_g \leftarrow {}^2T_{2g}$ transition, being typical of hexacoordinated Cu(II) compounds (d^9 electronic systems) [28].

The analytical and spectroscopic results obtained for **1**–**3** suggest a distorted octahedral environment around the metallic center whose axial coordination sites are occupied by four pyrazole type ligands, whereas the chloro ions are located at the apical positions (see Fig. 1).

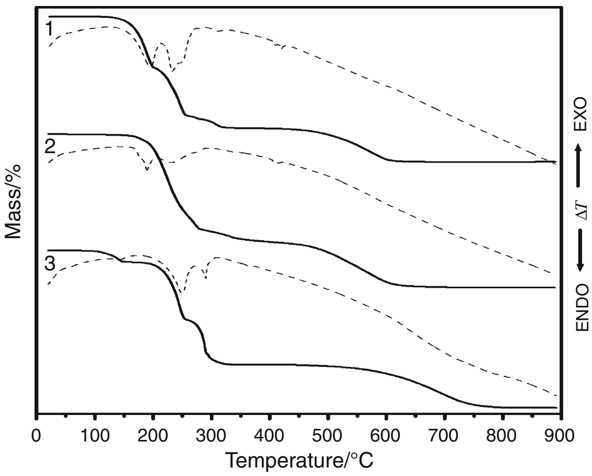


Fig. 2 TG and DTA curves of the complexes **1**–**3**

Thermogravimetric analysis

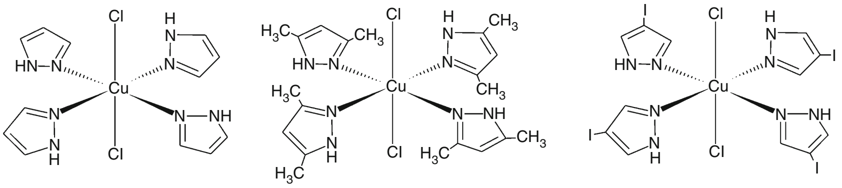
The TG and DTA curves for the compounds **1**–**3** are shown in Fig. 2. Table 4 lists the results of the thermal studies of theses complexes.

The compound $[CuCl_2(HPz)_4]$ (**1**) is thermally stable up to 107 °C. From this temperature, the compound decomposes to CuO in four steps. During the first stage (107–201 °C), it is observed an abrupt loss of 28.77% of the total weight associated with an endothermic peak at 195 °C. This mass loss is attributed, by mass calculation, to pyrolysis of 1.7 of organic ligand ($\Delta m_{calc.} = -28.54\%$). Over the temperature range of 201–265 °C, a mass loss of 26.67%, associated with an endotherm at 233 °C, which is attributed to the elimination of 1.6 HPz was observed. During the third stage of decomposition (265–329 °C), there is a loss of 6.53% of the total mass assigned, by mass calculation, to the elimination of 0.4 HPz ($\Delta m_{calc.} = -5.91\%$). At this stage, the composition of the residue remains undefined. The last mass loss ($\Delta m_4 = -18.60\%$) in the range of 329–658 °C is attributed to the thermal degradation of the material, with uptake of O_2, yielding pure CuO [25].

The decomposition of the compound $[CuCl_2(HdmPz)_4]$ (**2**) in CuO occurs in three steps. In the first stage (147–288 °C), it is observed a mass loss of 53.26% of the total weight associated with two endothermic peaks at 190 and 232 °C. According to mass calculations, it is suggested the elimination of 2.9 pyrazolyl ligand ($\Delta m_{calc.} = -53.26\%$). In the next stage of decomposition (288–363 °C), there is a mass loss of 6.28% attributed to the elimination of 0.4 HdmPz ($\Delta m_{calc.} = -6.94\%$). At this stage, as in the previous case, it is noticed a formation of a residue whose composition is unknown. In the third mass loss ($\Delta m_3 = -25.47\%$) over the range of 363–723 °C, it is suggested the degradation of the residue together with uptake O_2, affording CuO [25].

Compound **3**, $[CuCl_2(HIPz)_4]$, starts to degrade into CuO at lower temperature than **1** and **2**. Afterward, a mass loss of 6.86% of the total mass occurs over the range 83–182 °C, which is assigned by mass calculation to the elimination of 0.3 HIPz ($\Delta m_{calc.} = -6.83\%$). In the next stage (182–274 °C), there is a mass loss of 33.57% associated with an endothermic peak at 250 °C, being attributed, by mass calculation, to the elimination of 1.6 HIPz ligand ($\Delta m_{calc.} = -33.60\%$). The third mass loss ($\Delta m_{calc.} = -26.11\%$) occurs in the temperature range of 274–356 °C and is accompanied by an endothermic peak at 290 °C, which is assigned to the elimination of 1.2 HIPz ($\Delta m_{calc.} = -25.62\%$) by mass calculation. A residue of undefined composition is also generated which further degrades into CuO [25] in the last mass loss ($\Delta m_4 = -25.17\%$), over the range 356–844 °C.

Fig. 1 Proposed structures for the complexes $[CuCl_2(HPz)_4]$ (**1**), $[CuCl_2(HdmPz)_4]$ (**2**) and $[CuCl_2(HIPz)_4]$ (**3**)



1 2 3

Table 4 Thermal analysis data[a] for the compounds **1**–**3**

Complex	Step	ΔT/°C	Δm/%		DTA peak/°C		Onset point/°C
			Found	Calc.	Endo	Exo	
1	1	107–201	28.77	28.54	196	–	106.8
	2	201–265	26.67	26.56	–	233	
	3	265–329	6.53	5.91	–	–	
	4	329–658	18.60	19.40	–	–	
	Residue	–	19.39	19.56	–	–	
2	1	147–288	53.26	53.26	190 and 232	–	145.0
	2	288–363	6.28	6.94	–	–	
	3	363–723	25.47	26.78	–	–	
	Residue		14.96	15.33	–	–	
3	1	83–182	6.86	6.83	–	–	81.6
	2	182–274	33.57	33.60	250	–	
	3	274–356	26.11	25.62	290	–	
	4	356–844	25.17	25.25	–	–	
	Residue		8.27	8.74	–	–	

[a] $m_{\text{initial}} \cong 5.000$ mg

Conclusions

Synthesis, characterization, and thermal behavior of $[CuCl_2L_4]$ {L = HPz (**1**), HdmPz (**2**) and HIPz (**3**)} have been described in this work. TG studies showed that the introduction of methyl groups at the 3 and 5 positions on the pyrazolyl moiety into Cu(II) coordination compounds affects significantly their thermal stability. The compound **1**, composed by unsubstituted pyrazole, is stable up to 107 °C, whereas for the 3,5-dimethylpyrazole derivative (complex **2**), the decomposition starts at 147 °C. On the other hand, the coordination compound **3** starts to degrade at a temperature lower than the other species, probably due to the steric hindrance introduced by iodine atom at 4-position.

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