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Short communication

Synthesis, characterization and thermal behavior of cobalt(II) 5-chloro-piridylamides complexes

Cicero B.A. Lima [a], José G.P. Espínola [b], Severino F. de Oliveira [b], Luiza N.H. Arakaki [b], Maria G. Fonseca [b,*], Claudio Airoldi [c]

[a] *Departamento de Química, FCEN, Universidade Estadual do Rio Grande do Norte, 59.633-010, Mossoró, Rio Grande do Norte, Brazil*

[b] *Departamento de Química, CCEN, Universidade Federal da Paraíba, Caixa Postal 5093, 58059-900 João Pessoa, Paraíba, Brazil*

[c] *Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970 Campinas, São Paulo, Brazil*

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Abstract

Purple cobalt(II) complexes containing 5-chloro-2-aminepyridylacetamide (CPA), 5-chloro-2-aminepyridylpropionamide (CPP) and 5-chloro-2-aminepyridylbutyramide (CPB) ligands were prepared from ethanolic solutions. The general stoichiometry CoL_2Cl_2 (L = ligand) was determined from elemental analysis data. Infrared results show monodentate CPA and CPP ligands through the aromatic nitrogen atom, CPB is bidentate through the aromatic nitrogen atom and carboxyl group. Thermogravimetric curves under nitrogen showed in the final stage all complexes presented a mixture of cobalt(II) chloride and metallic cobalt as residue. The complexes containing CPA and CPP ligands decomposed in various stages with integral loss of ligand or partial loss of the chloride. Only two steps of decomposition are seen for CPB compound.

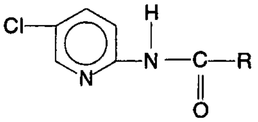
Keywords: Cobalt(II); Pyridylacetamide; Thermogravimetry; Thermal decomposition

1. Introduction

N-(2-pyridyl)acetamide coordinate through the oxygen and the heterocyclic nitrogen [1–5] with zinc group elements [6], one structural determination shows the ligand bridging two mercury atoms, using both oxygen and nitrogen basic centers [7].

N-(2-pyridyl)acetamide is expected to form a stable cobalt(II) chloride compound with a six-membered chelate ring [1,2].

This publication reports the preparation, characterization and thermal analysis of complexes with cobalt(II) chloride of three ligands (I), 5-chloro-2-aminepyridylacetamide (CPA), 5-chloro-2-aminepyridylpropionamide (CPP) and 5-chloro-2-aminepyridylbutyramide (CPB). The purpose of this investigation is to examine: (i) the effects of ring substituents and (ii) the effects on thermal stability of the amide group



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* Corresponding author.
E-mail address: mgardennia@quimica.ufpb.br (M.G. Fonseca).

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2. Experimental

2.1. Chemicals

Cobalt chloride was dehydrated by a described method [8], 2-amine-5-Cl-pyridine was distilled before use. Acetic, propionic and butyric anhydride were used without previous purification. Ethanol and acetone were previously dried [8].

2.2. Synthesis of ligands

The synthesis of the ligands involved the addition of 0.050 mol of 2-amine-5-choro-pyridine with equimolar amounts of acetic, propionic or butyric anhydride. The reaction mixture was stirred for 3 h at 298 K. Then water was added and the reaction mixture heated at 353 K for 1 h to complete the hydrolysis of residual anhydride. The acetic acid produced during the reaction was neutralized with sodium bicarbonate solution. The product was extracted from solution with chloroform. The resulting solution was crystallized twice in ethyl ether, to yield crystalline white solids. All preparations gave yield of about 60% (5.2 g).

2.3. Synthesis of cobalt complexes

Cobalt chloride (0.008 mol or 1.364 g) was dissolved in dried ethanol under stirring. To this solution was slowly added dropwise an ethanolic solution of ligand (0.0032 mol or 0.416 g). The molar ratio of cobalt:ligand was 1:2.5. After 10 min, a purple solid began to separate. The color of these complexes became more light with increasing of alkyl group of ligand. This mixture was maintained under constant stirring for 2 h to complete the reaction. Finally, the purple solid was filtered, washed with acetone, dried under vacuum at room temperature for 8 h and then stored in a desiccator over anhydrous $CaCl_2$.

2.4. Apparatus and measurements

The cobalt content for each complex was determined with an atomic spectroscopy GBC instrument model 980. The nitrogen and chloride were determined with Kjedahl and Volhard methods, respectively. Infrared spectra of ligands and complexes were recorded as Nujol mulls and KBr pellets on a BOMEM, model MB-102 spectrophotometer in the 4000–400 cm^{-1} range with a resolution of 4 cm^{-1}. The DSC curves for the complexes were obtained in a Shimadzu model DSC-50 differential thermal analyzer, at a heating rate 0.17 $K\,s^{-1}$ in a dry nitrogen atmosphere flowing at 0.83 $cm^3\,s^{-1}$. Thermogravimetric curves were obtained with a Shimadzu model TGA-50 thermobalance, at a heating rate of 4.1 $K\,s^{-1}$ in a dynamic atmosphere of dry nitrogen flowing at 0.83 $cm^3\,s^{-1}$ with samples of 3.5 ± 0.5 mg.

3. Results and discussion

All complexes were insoluble in chloroform, ethanol, acetone and 1,2-dichloroethane, but partially soluble in acetonitrile and methanol, and completely soluble in solvents with high donor properties such as dimetylsulfoxide, *N*,*N*-dimethylacetamide and *N*,*N*-dimethylformamide.

Nitrogen, chloride and cobalt elemental contents are listed in Table 1. These results are in a reasonable agreement with calculated values, except for nitrogen due to experimental limitations for quantification of aromatic nitrogen by Kjedahl method. These results suggests the general stoichiometric formula CoL_2Cl_2 for complexes.

Infrared spectroscopic data for ligands and the respective complexes with main assignments are listed in Table 2. The C=C and C=N aromatic stretching bands for the free ligands are shifted to higher frequencies, 35 cm^{-1} for $Co(CPA)_2Cl_2$ and $Co(CPP)_2Cl_2$, and 26 cm^{-1} for $Co(CPB)_2Cl_2$. This agrees with an increasing double bond character in these groups, as a consequence of coordinating to cobalt(II), through the pyridinic nitrogen atom [9,10]. The characteristic absorption of the carbonyl group (C=O), the amide I band [11–13], did not show any change for $Co(CPA)_2Cl_2$ and $Co(CPP)_2Cl_2$ as listed in Table 2. This behavior was previously observed for a similar system with an

Table 1
Percentages calculated (found) for chloride, nitrogen and cobalt for CoL_2Cl_2 (L = CPA, CPP and CPB)

CoL_2Cl_2	Chloride (%)	Nitrogen (%)	Cobalt (%)
$Co(CPA)_2Cl_2$	15.04 (15.0)	11.88 (10.2)	12.50 (12. 8)
$Co(CPP)_2Cl_2$	14.23 (14.1)	11.24 (10.2)	11.00 (11.0)
$Co(CPB)_2Cl_2$	13.44 (13.4)	10.62 (9.5)	12.90 (12.9)

Table 2
Summary of the main infrared frequencies (cm^{-1}) for ligands CPA, CPP, CPB and for the complexes of general formula CoL_2Cl_2 (L = CPA, CPP and CPB)

Compound	ν (CC, CN)	ν (CC, CN)	ν (CC, CN)	ν (CO) amide I	ν (NH)
CPA	1580	1541	1458	1664	3241
$Co(CPA)_2Cl_2$	1615	1531	1478	1665	3440
CPP	1576	1531	1455	1674	3249
$Co(CPP)_2Cl_2$	1613	1528	1477	1667	3376
CPB	1583	1526	1459	1696	3289
$Co(CPB)_2Cl_2$	1609	1524	1459	1651	3442

aromatic nitrogen donor atom [5]. In $Co(CPB)_2Cl_2$ the amide I band shifted to lower frequencies, in comparison to free ligand. In this case, the coordination apparently involves both nitrogen and oxygen atoms, suggesting the formation of a bidentate cobalt complex. The N–H aliphatic stretching is shifted to high frequency in the complexes indicating an increasing of N–H bond force and suggesting the absence of coordination of cobalt on N–H aliphatic.

Based on the infrared spectroscopic data and elemental analysis two possible distorted geometry can be adopted for complexes: $Co(CPA)Cl_2$ and $Co(CPP)_2Cl_2$ tetrahedrally coordinated and $Co(CPB)_2Cl_2$ octahedrally coordinated.

The thermogravimetric curves are presented in Figs. 1 and 2 and the results are listed in Table 3. Based on the curve profiles and the decomposition steps, the results suggested that the complexes $Co(CPA)_2Cl_2$, $Co(CPP)_2Cl_2$ and $Co(CPB)_2Cl_2$ are

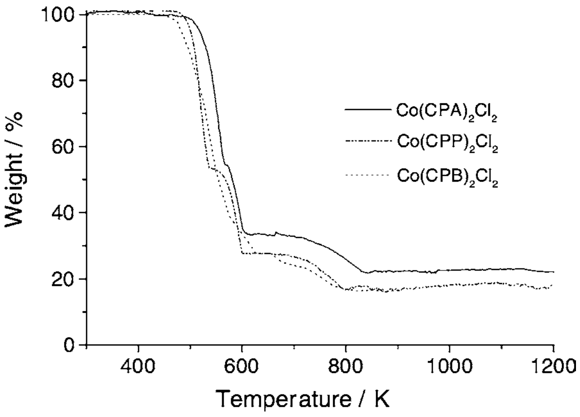
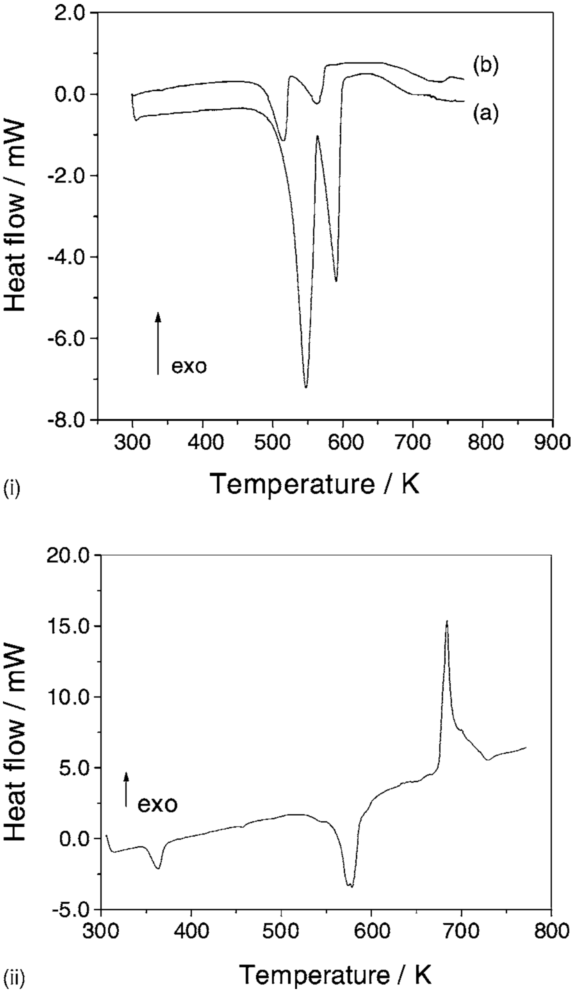


Fig. 1. Thermogravimetric curves for complexes.



(i)

(ii)

Fig. 2. DSC curves for: (i) $Co(CPA)_2Cl_2$ (a) and $Co(CPP)_2Cl_2$ (b) and (ii) $Co(CPB)_2Cl_2$ obtained at a heating rate 0.17 K s^{-1} in a dry nitrogen atmosphere.

Table 3
Thermogravimetric data for CoL_2Cl_2 (L = CPA, CPP and CPB) complexes in one (1), two (2) and third (3) steps (Stp) and residue (Res), the found weight loss in the respective range of temperature (ΔT) and enthalpy of decomposition of first step obtained by DSC data

CoL_2Cl_2	Stp	Found (%)	ΔT (K)	ΔH ($kJ\,mol^{-1}$)
$Co(CPA)_2Cl_2$	1	47.8	464–565	355.1
	2	18.7	565–640	–
	3	11.5	640–766	–
	Res	22.4	>766	–
$Co(CPP)_2Cl_2$	1	47.1	474–567	261.7
	2	24.6	567–639	–
	3	10.0	639–776	–
	Res	18.2	>776	–
$Co(CPB)_2Cl_2$	1	71.7	450–631	255.0
	2	9.8	631–734	–
	Res	18.5	>734	–

stable up to 450, 463 and 474 K, respectively. Above these temperatures, the ligands started to decompose. The mass loss values involve three consecutive stages for $Co(CPA)_2Cl_2$ and $Co(CPP)_2Cl_2$, being 48 and 49% for first, 18 and 25% for second and 10% for third mass losses. The ligand decomposition occurred in two stages for $Co(CPB)_2Cl_2$, 72 and 10%, respectively. Based on the initial temperature of decomposition, the stability of complexes follows the order: $Co(CPB)_2Cl_2 < Co(CPA)_2Cl_2 < Co(CPP)_2Cl_2$.

The first stage of decomposition of all complexes was endothermic, as illustrated by DSC curves in Figs. 1 and 2. Two endothermic peaks were detected for $Co(CPA)_2Cl_2$ and $Co(CPP)_2Cl_2$. For the $Co(CPB)_2Cl_2$ decomposition, two endothermic and one exothermic peaks were observed at 363, 578 and 683 K, respectively. Because no mass loss is associated with the first peak for $Co(CPB)_2Cl_2$, this peak must be a phase change.

The thermal stability of $Co(CPA)_2Cl_2$ and $Co(CPP)_2Cl_2$ are similar. The initial decomposition occurred at the same temperature. The enthalpies associated with the first step of decomposition of the complexes are presented in Table 3. The decomposition enthalpy decreases with the length of the alkyl group.

Acknowledgements

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