Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 3, 779–782

AN INVESTIGATION OF THE THERMAL BEHAVIOR OF HETEROBIMETALLIC SPECIES CONTAINING COPPER(II) AND TETRACYANOPALLADATE(II)

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Synthesis, characterization and thermal behavior of four compounds that have the general formula $[Cu\{Pd(CN)_4\}(L)_x]_n$, in which *en*=1,2-diaminoethane and *pn*=1,3-diaminopropane (*L*=*en*, *x*=1 (**I**); *L*=*pn*, *x*=1 (**II**); *L*=*en*, *x*=2 (**III**); *L*=*pn*, *x*=2 (**IV**)) were described in this work. The complexes were studied by elemental analysis, infrared spectroscopy (IR), differential thermal analysis (DTA) and thermogravimetry (TG) and the residues of the thermal decomposition were characterized by X-ray powder diffraction and found as a mixture of CuO and PdO. The stoichiometry of the compounds was established via thermogravimetric and elemental analyses and their structures were proposed as coordination polymers based on their infrared spectra. The following thermal stability sequence was found: **IV**<**I**=**II**<**III**.

Keywords: *amines, copper(II) complexes, tetracyanopalladate(II), thermal behavior*

Introduction

Due to their potential applications as molecular sieves, ion exchangers [1, 2], occlusion compounds and chemical sensors [3, 4], complexes containing cyanometallate groups, such as $[Ni(CN)_4]^{2-}$ and $[Au(CN)_2]^-$ have been widely investigated. Because of several reasons, species containing copper(II) are particularly interesting, among them the low cost of this metal, great coordination plasticity, which allows the obtaining of structures having distinct topologies [5, 6]. 1,2-diaminoethane (*en*) and 1,3-diaminopropane (*pn*) amines can coordinate themselves in the chelated form to a metallic center [7], forming 5 and 6 membered rings, respectively, which provide high stability to the complexes [6, 8]. In order to enrich scientific knowledge involving copper(II) complexes with amines and cyanometallates, the present study deals with the synthesis and thermal characterization of the compounds $[Cu\{Pd(CN)_4\}(L)_x]_n$ (*L*=*en*, *x*=1 (**I**); *L*=*pn*, *x*=1 (**II**); *L*=*en*, *x*=2 (**III**); *L*=*pn*, *x*=2 (**IV**)).

Experimental

Synthesis

The compounds were prepared by reacting 0.50 mmol of $CuCl_2\cdot 2H_2O$ in 2 mL of water and the stoichiometric amount of the amine followed by the addition of 3 mL solution containing 0.50 mmol of $K_2[Pd(CN)_4]\cdot 3H_2O$ in water [9]. The precipitates formed (**I** and **II** – blue; **III** and **IV** – violet) were washed with water and ethanol and dried in desiccator. The yields were between 80–90%. Elemental analyses data are in agreement with the proposed formulae.

Instrumentation

Quantitative analyses of C, N and H were performed on an EA 110 CHNS-O automatic analyser from CE Instruments. The infrared spectra of the compounds were recorded on a Nicolet Impact 400 spectrophotometer in the 4000–400 cm^{-1} range using KBr pellets and nujol mulls techniques.

The TG-DTA curves were recorded using a TA 2960 SDT thermobalance from TA Instruments, using sample masses of about 5 mg, α-alumina open crucibles at heating rate of 20°C min^{-1} from 30 to 900°C and synthetic dynamic air with flow at 100 mL min^{-1}. X-ray powder diffraction patterns were measured on a Siemens D-5000 X-ray diffractometer using CuK_α radiation (λ=1.541 Å) and setting of 40 kV and 20 mA.

Results and discussion

IR spectra

Infrared spectroscopy is a very useful technique to study the species containing cyano moieties, since these ligands present the ν_{CN} characteristic vibration

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1388–6150/$20.00

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Table 1 Main vibrational frequencies (cm^{-1}) of the complexes **I**–**IV**

Attribution	Complex I	II	III	IV
$\nu_{as(NH)}$	3329	3325	3337	3295
	3310	3279	3313	
$\nu_{s(NH)}$	3254	3269	3280	3261
	3263	3201	3252	3166
	3144	3128	3163	
$\nu_{as(CH)}$	2970	2991	2984	2959
	2935	2976	2959	2943
	2922	2953	2931	2937
$\nu_{s(CH)}$	2881	2891	2878	2889
		2858		
$\nu_{CN_{cyano}}$	2192	2193	2127	2123
	2176	2176		
	2149	2150		
δ_{NH_2}	1589	1587	1597	1614
		1618		1589
δ_{CH_2}	1465	1456	1456	1458
	1434			1439
$\nu_{CN_{amine}}$	1088	1045	1034	1018
	1024	1010	974	908

around 2200–2000 cm^{-1}. This vibration splits when more than one coordination mode is observed, and this information is important in the assignment of the structure of the complex [10]. Also, the coordination of the amines to the metal ion can be inferred through the analysis of their characteristic vibrations in the IR spectrum [11]. Table 1 shows the most relevant band frequencies taken from the IR spectra of **I**–**IV** complexes and their attributions as well.

The coordination of the amine to the copper(II) center is evidenced by the bands arising from the ν_{NH} and ν_{CH} stretching vibrations at 3329–3128 and 2991–2922 cm^{-1} respectively, as well as those due to the δ_{NH} and δ_{CH} angular deformations at 1618–1587 and 1465–1434 cm^{-1}, respectively. With respect to the cyanometallate groups, the appearance of three bands in the region characteristic for the ν_{CN} stretching vibration (2200–2000 cm^{-1}) in the IR spectra of **I** and **II** shows the great structural complexity of these species: the bands at lower frequencies (2149 cm^{-1} for **I** and 2150 cm^{-1} for **II**) point to terminal cyano groups, while those at higher energy indicate bridging cyano moieties, being that the more effective interaction between the cyano groups and the copper atoms gives rise to the higher frequency bands (2192 cm^{-1} for **I** and 2193 cm^{-1} for **II**), whereas the bands at 2176 cm^{-1} (for both compounds) result from weaker interactions [11]. Based on this data set, it is possible to suggest for **I** and **II** analogous structures in which the copper(II) centers are bridged by tetracyanopalladate(II) units, resulting in a one-dimensional, zig-zag polymeric structure, Fig. 1.

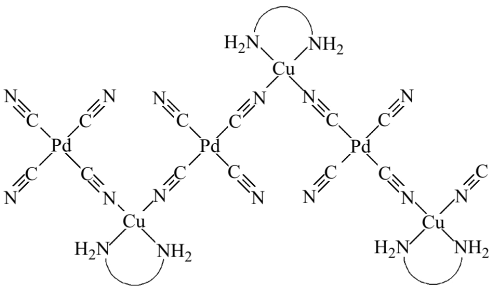

Fig. 1 Suggested structure for compounds **I** and **II**

The main difference between the spectra of **III** and **IV** in comparison with **I** and **II** is the presence of only one band for the ν_{CN} vibration. In fact, the known compound $[Cu\{Pd(CN)_4\}(en)_2]_n$ [12] is a linear coordination polymer in which the $[Cu(en)_2]^{2+}$ cations are connected by two cyano groups belonging to the $[Pd(CN)_4]^{2-}$ anions through weak coordinate bonds. This weak coordination, together with the occurrence of hydrogen bonds between the other, two non-coordinated cyano nitrogen atoms and the amino groups explains the appearance of only one band arising from this vibrational mode [12]. Thus, complex **IV** is expected to have a similar structure, as can be seen in Fig. 2.

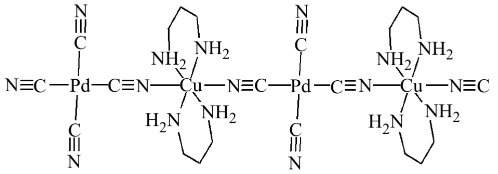

Fig. 2 Proposed structure for complex **IV**

Thermal analysis

TG and DTA curves of compounds **I**–**IV** are shown in Fig. 3. Based on the thermogravimetric data the decomposition path was suggested [13] for all complexes. As it was already mentioned, the amines *en* (1,2-diaminoethane) and *pn* (1,3-diaminopropane) form five and six membered rings, respectively, where the previous one is more stable than the latter [14]. Consequently, a higher stability was expected for compound **I** compared to **II**, which was not observed in the thermogravimetric analysis, since both start to decompose at the same temperature, 210°C. In fact, these two compounds have similar thermal behavior. Their first decomposition step is associated to the partial elimination of the amine and of the cyano groups, which is followed by a small endothermic peak in the DTA curve. The second mass loss is attributed to the elimination of the remaining cyano groups and to the burning of the diamine, which results in a strong exothermic effect. At this stage, the residue is characterized as a mixture of Pd (ASTM 05-0681) and CuO (ASTM 41-0254) [16]. Finally, both compounds undergo oxidation, forming CuO (ASTM 41-0254) and PdO (ASTM 06-0515) as

Table 2 Thermoanalytical data for the prepared compounds

Compound	Δ*T*/°C	Δ*m*/%		Residue/%		Suggested steps
		curve	theor.	curve	theor.	
I	210–405	16.32	16.91	83.68	83.09	$-0.5C_2N_2-0.5en$
	405–450	27.69	28.77	55.99	55.66	$-1.5C_2N_2-0.5en+0.5O_2$
	450–860	4.13	4.79	60.12	60.45	$+0.5O_2$
II	210–420	17.51	18.11	82.49	71.89	$-0.5C_2N_2-0.5pn$
	420–590	27.77	28.46	54.72	53.42	$-1.5C_2N_2-0.5pn+0.5O_2$
	590–800	2.96	4.60	57.68	58.01	$+0.5O_2$
III	230–295	22.22	22.87	77.78	77.13	$-1.5en$
	295–395	13.47	13.20	64.31	63.93	$-C_2N_2$
	395–435	17.26	16.76	47.05	47.17	$-0.5en-C_2N_2+0.5O_2$
	435–780	4.03	4.06	51.08	51.23	$+0.5O_2$
IV	200–245	16.89	17.55	83.11	82.45	$-pn$
	245–395	13.87	12.32	69.24	70.13	$-C_2N_2$
	395–440	25.02	26.08	44.22	44.04	$-pn-C_2N_2+0.5O_2$
	440–810	3.61	3.79	47.83	47.83	$+0.5O_2$

residue [15, 16]. In all complexes described in this paper the amines were released in two steps. It is interesting to note, when the amines are released before reaching their burning temperatures, 380°C for *en* and 350°C for *pn*, the DTA curves show very small peaks, i.e., thermal events with low intensity. On the contrary, when the temperature is higher, the burning of amines is evidenced by strong exothermic peaks. So it is supposed that in the first decomposition step the amine group is liberated as a free ligand and not as the result of the decomposition.

The first mass loss of complex **III** is attributed to the partial liberation of *en*. Subsequently, the elimination of half of the cyano groups is observed in the form of a small endothermic peak in the DTA curve. The next step is the formation of CuO (ASTM 41-0254) and Pd (ASTM 05-0681) [16] through the complete burning of the ligands. Then, this mixture oxidizes to CuO (ASTM 41-0254) and PdO (ASTM 06-0515) [14, 15] leading to the formation of oxide residue. An interesting feature concerning to the thermal decomposition of **IV** was found in the present study. Several attempts to isolate this blue compound by heating compound **IV** were carried out without success. The next step of the decomposition starts before the blue compound can be isolated. Then, we decided to reduce the amount of *pn* in the synthesis, which led to the obtaining of compound **II**, as described in the experimental section. The second step corresponds to the degradation of part of the cyano groups and the third one corresponds to the elimination of the remainder ligands resulting CuO (ASTM 41-0254) and Pd (ASTM 05-0681) [16]. The differences between the theoretical and the experimental values are due to kinetic factors, i.e., the second step begins before the first one completes. The final step involves the oxidation of Pd (ASTM 05-0681) to PdO (ASTM 06-0515) [16].

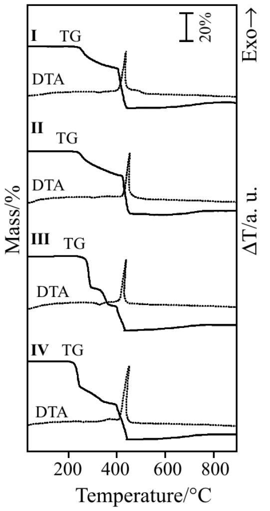

Fig. 3 TG and DTA curves for compounds **I**–**IV**

Conclusions

Synthesis, characterization and thermal behavior of four $[Cu\{Pd(CN)_4\}(L)_x]_n$, type complexes in which *en*=1,2-diaminoethane and *pn*=1,3-diaminopropane (*L*=*en*, *x*=1 (**I**); *L*=*pn*, *x*=1 (**II**); *L*=*en*, *x*=2 (**III**); *L*=*pn*, *x*=2 (**IV**)) were investigated in this work. FTIR spectra analysis of the $\nu_{CN_{cyano}}$ region indicated that all compounds consist of coordination polymers. Taking into account the initial decomposition temperatures, the following thermal stability sequence could be established: **IV**<**I**=**II**<**III**. The thermogravimetric data show that the decompositions of all complexes are consecutive, with the release of organic ligands and cyano groups leading to a mixture of CuO and PdO as final residue.

Acknowledgements

The authors wish to thank Capes, FAPESP and CNPq for their financial support.

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DOI: 10.1007/s10973-006-7858-x