

VIBRATIONAL SPECTRA AND ELECTROCHEMICAL BEHAVIOR OF BISPICOLINATE COPPER(II)

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Dedicated to Prof. Pedro J. Aymonino on the occasion of his 75th birthday

Abstract

The infrared and Raman spectra of the Cu(II) complex of picolinic acid (Hpic), of stoichiometry $[Cu(pic)_2] \cdot 2H_2O$ were recorded and discussed by comparison with those of the free acid on the basis of Cu(its known structural data). The electrochemical properties of the complex were investigated in dimethylformamide solutions by cyclic voltammetry. The results show that its reduction occurs through a quasi-reversible one electron process, generating a Cu(I) species.

Resumen

Se registraron los espectros de infrarrojo y Raman del complejo que forma el Cu(II) con el ácido picolínico (Hpic), de estequiometría $[Cu(pic)_2] \cdot 2H_2O$ y se los discutió por comparación con los del ácido libre y en base a sus datos estructurales, que son conocidos. Las propiedades electroquímicas del complejo se investigaron en soluciones de dimetilformamida, utilizando voltametría cíclica. Los resultados muestran que su reducción ocurre a través de un proceso cuasi reversible, involucrando un único electrón, y generando una especie de Cu(I).

Introduction

Picolinic acid (2-carboxypyridine, Figure 1), an isomer of nicotinic acid, is one of the most important chelating agents present in the human body.

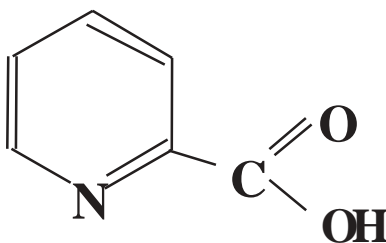


Figure 1. Schematic structure of picolinic acid.

It is generated in liver and kidneys during the catabolism of the essential amino acid tryptophan and, subsequently, transported to the pancreas. During digestion it is secreted to the intestine and is used as a complexing agent in the absorption of essential metals [1,2].

In recent years metallic complexes of picolinic acid have received increasing attention from the pharmacological point of view, as useful systems to trace element supplementation or for the design of new metallopharmaceuticals [3]. For example, at present the tris-picolinatochromium(III) complex constitutes one of the most important and popular nutritional supplements, which worldwide commercialization generates annually more than one hundred million dollars [4]. Also in the search for new drugs with insulinomimetic activity, oxovanadium (IV) and oxovanadium (V) complexes of picolinic acid and of some of its derivatives appear as very promising compounds [5-8].

In order to contribute to a better characterization of this type of metallopharmaceuticals, we have recently investigated the spectroscopic and electrochemical behavior of some Cr(III) picolinate complexes [9]. As a continuation of these studies, we have now performed a similar investigation of the Cu(II) complex of picolinic acid of stoichiometry $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$.

Experimental

Synthesis of the complex

The compound was obtained by interaction of hot diluted aqueous solutions of copper(II) acetate and potassium picolinate in a 1: 2 molar ratio. After mixing the solutions, the color changed from greenish-blue to deep blue and an abundant solid precipitate is produced. After cooling to room temperature, the solid was filtered off, washed with small portions of cold water, and finally dried in an oven at 50 °C [10]. Its purity was confirmed by elemental analysis and the crystal structure confirmed by an analysis of the x-ray powder diagram with the aid of the program POWDERCELL [11].

Spectroscopic studies

The IR spectra were recorded with a Bruker IFS 66 FTIR instrument, using the KBr pellet technique. Raman spectra were obtained with the same instrument, using the FRA 106 Raman accessory and the 1064 nm line of a Nd:YAG solid state laser for excitation.

Electrochemical measurements

Cyclic voltammograms were obtained with a PAR potentiost/galvanostat model 263A controlled by the 270/250 Software (EG&G Princeton Applied Research). A printer and a standard electrochemical three electrode cell completed the system. A glassy carbon disc was employed as working electrode. A platinum wire was used as counter electrode, while an $\text{Ag}/(10^{-3} \text{ M}) \text{AgNO}_3$ in $\text{CH}_3\text{CN}/10^{-1} \text{ M} (\text{TBA})\text{PF}_6$ was used as a reference electrode. This reference electrode was calibrated against the $[\text{Fe}(\text{C}_5\text{H}_5)_2]/[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$ redox couple, for which a potential of +0.4 V vs NHE was assumed [12,13]. All potentials reported here are referred to the NHE in volts. Ohmic drop in the solution was minimized by positive feedback [14].

The measurements were performed in dimethylformamide (DMF) solutions containing 0.1 M tetrabutylammonium hexafluorophosphate, $(\text{TBA})\text{PF}_6$, as the supporting electrolyte. The concentration of the complex was 10^{-3} M . High purity DMF (Baker, spectroscopic grade) was

dried over 4 Å molecular sieves (Merck) and used without further purification. (TBA)PF₆ was purchased from Fluka (electrochemical grade) and used as received.

Before each experiment, a cyclic voltammogram of the solution containing only the supporting electrolyte was measured. Oxygen was removed by purging the solutions with extra-pure nitrogen and a continuous gas stream was passed over the solutions during the measurements.

Results And Discussion

Structure of the complex

The complex crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$. The Cu(II) cation is located at the center of a distorted N₂O₄ octahedron, axially elongated by Jahn-Teller distortion. The equatorial positions are occupied by the two ligands coordinated through the nitrogen atom and one of the carboxylate O-atoms, in *trans* geometry. Oxygen atoms from adjacent complex units, and not involved in the primary coordination, occupy the axial positions. The crystal is built up of polymeric chains of complex molecules, joined by weak coordination bonds in the *c* direction and H-bonded zig-zag chains of intercalated H₂O molecules forming a molecular layer extended parallel to the (100) plane involving H-bonds between a carbonyl O-atom and a H₂O molecule [15].

Vibrational spectra

In order to facilitate the analysis of the IR and Raman spectra of the complex, we have also recorded the corresponding spectra of the free ligand. These spectra have been recently investigated in detail including some interesting theoretical studies [16,17]. Therefore, these spectra are not reproduced here, but we have assigned our measured spectra on the basis of this analysis complemented with the information provided by some standard references [18,19].

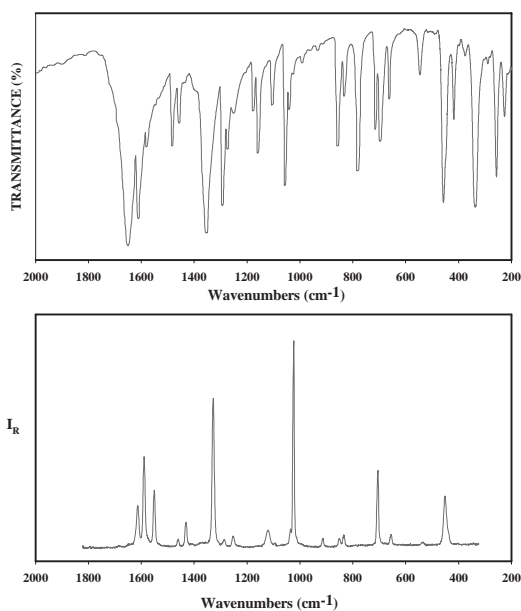


Figure 2. Vibrational spectra of $[Cu(pic)_2].2H_2O$ in the spectral range between 2000 cm^{-1} and 200 cm^{-1} : **infrared** (top); **Raman** (bottom).

The IR and Raman spectra of $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$, in the most interesting region between 2000 and 200 cm^{-1} are shown in Figure 2. The proposed assignment, together with that of the free ligand, is presented in Table 1, and is briefly commented as follows:

TABLE 1. Assignment of the vibrational spectra of picolinic acid and of the $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ complex. vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad

| Picolinic acid | | $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ | | Assignments |
|--|---------------------------------------|---|--------------------------|--|
| Infrared / cm^{-1} | Raman / cm^{-1} | Infrared / cm^{-1} | Raman / cm^{-1} | |
| 3464 w,br | | 3450 w,br 3170 w | | $\nu(\text{O-H})$ acid $\nu(\text{O-H})$ water |
| 3118m/3056w 1719 s | 3113s/3091w 1692 m | 3074s/3036m | | $\nu(\text{CH})$ $\nu(\text{C=O})$ |
| 1612vs/1600vs 1575 m | 1614m/1600s 1570 m | 1642 vs 1603s/1569w 1569 w | 1641 vw 1612m/1588s | $\nu_{\text{as}}(\text{COO}^-)$ $\nu(\text{ring})$ |
| 1459vs/1443m 1347 s | 1443 w 1358 m | 1475m/1448m | 1424 vw | $\nu(\text{C-O})$ |
| 1309 s 1294 vs | | 1389sh/1348vs 1285 s 1266 m | 1375w/1350s 1284 w | $\nu_s(\text{COO}^-)$ |
| 1251m/1203m | 1235 w | 1243 w 1168 m | 1248 w | $\delta(\text{CH})$ |
| 1158m/1088s 1048m/1009m 995 m 966 m 890w | 1163m/1086w 1037m/1011vs 993 sh | 1152s/1096 m 1047s/1031m 1015w/982w | 1122 m 1044sh/1023vs | $\delta(\text{O-H})$ acid $\gamma(\text{CH})$ |
| 837 m/825 m 801 s 767 s | 840 s 800 w | 849 s 826 m 776 w | 846 w 830 w | scis. (COO^-) $\gamma(\text{CH})$ |
| 753vs/705s 676 vs 633s/616m | | 712s/693s 660 m | 708s 660 w | $\phi(\text{CC})$ wagg. (COO^-) $\phi(\text{CC})$ |
| | | 547 m 458 vs | 536 vw 450 m | $\phi(\text{CC})$ $\rho(\text{H}_2\text{O})$ |
| 539s/499s 420vs/405s | 414 w | 418 s 376 w 338 s | 405 vw | $\nu(\text{Cu-O})$ $\nu(\text{Cu-N})$ |
| 266 vs | 271 w | 257 s 227m/186m | | |

In the spectra of the free acid some characteristic bands could be clearly identified:

a) the O-H stretching vibration, seen only as a relatively weak and somewhat broadened feature in the IR spectrum; b) The two stretching bands related to the carboxylate moiety, $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$; c) The out-of-plane OH-bending motion, observable as a mean intensity IR band. The corresponding in plane deformation apparently attains not enough intensity in our spectra; it has been recently reported as a very weak IR feature at 1370 cm^{-1} [16]. Besides, also two deformation modes of the full carboxylate group have been tentatively assigned in Table 1.

As expected, after complex formation all the bands that involve OH motions disappear and the two original carboxylate bands are transformed into the symmetric and antisymmetric stretching vibrations of the carboxylate anion. The difference between these two vibrations is equal to 294 cm^{-1} , confirming the essentially unidentate character of this group in bonding [20,21] shown by the structural analysis [15]. However, interestingly, the respective $\nu_s(\text{COO}^-)$ vibration shows some splitting evidence probably originated from the participation of one of the carboxylate O-atoms in the secondary bonding to another complex unit. The two deformational vibrations of the COO^- -group show slight frequency shifts after complex formation as can also be seen in Table 1.

The water molecules, which are not involved in metal bonding, give rise to a weak and broad IR band centered at about 3450 cm^{-1} , which can be assigned to the O-H stretching vibrations of this molecule. The position of this band suggests the formation of hydrogen bonds of medium length [22]. The corresponding deformational mode is probably overlapped by the strong $\nu_s(\text{COO}^-)$ IR band. In the lower spectral range, one deformational mode, of the hydrogen bonded water molecules, similar to a rocking motion could also be identified.

Regarding the ring vibrational modes they can roughly be assigned in the following spectral ranges [16-19]: $\nu(\text{CH})$ vibrations in the highest frequency region ($3500\text{-}3000\text{ cm}^{-1}$); skeletal ring vibration in the region between $1650\text{-}1350\text{ cm}^{-1}$; in plane $\delta(\text{CH})$ deformational modes between 1300 and 1000 cm^{-1} ; out of plane $\gamma(\text{CH})$ vibrations between 1000 and 700 cm^{-1} and out of plane $\phi(\text{CC})$ ring deformation in the $700\text{-}550\text{ cm}^{-1}$ range.

Comparing the spectra of the free acid and of the complex in the lower frequency range, it was also possible to identify the stretching vibrations of the ligand-to-metal bonds, with the $\nu(\text{Cu}-\text{O})$ mode at slightly higher energy than the corresponding $\nu(\text{Cu}-\text{N})$ mode, in a similar way as found in other picolinate complexes [9, 17, 23]. Besides, the $\nu(\text{Cu}-\text{N})$ mode is found in the same range as in $\text{Cu}(\text{II})$ complexes of nicotinic acid and nicotinamide [24].

Electrochemical behavior

The electrochemical properties of the complex were investigated by cyclic voltammetry in DMF solutions containing 0.1 M of TBAPF_6 as supporting electrolyte. Cyclic voltammograms were recorded at different scan rates (v) between 1.5 V and -2.2 V vs NHE. In this potential range only one redox couple was observed whereas at more positive or negative potential values only the solvent decomposition current was evident. The effect of the scan rate on the electrochemical response was investigated from 0.05 V/s to 5 V/s in the potential range where the complex is electroactive, ($+0.35\text{ V}$ to -1.3 V). Selected voltammograms are shown in Figures 3 and 4. As can be seen on the negative-going scan, at $v = 0.1\text{ V/s}$, a reduction peak is located at -0.69 V . Upon reversing the potential at -1.3 V the oxidative counterpart of this peak is observed at -0.59 V .

Inspection of the voltammetric data shows that at increasing scan rates, the reduction (E_{pc}) and oxidation (E_{pa}) peaks are shifted to more negative and positive

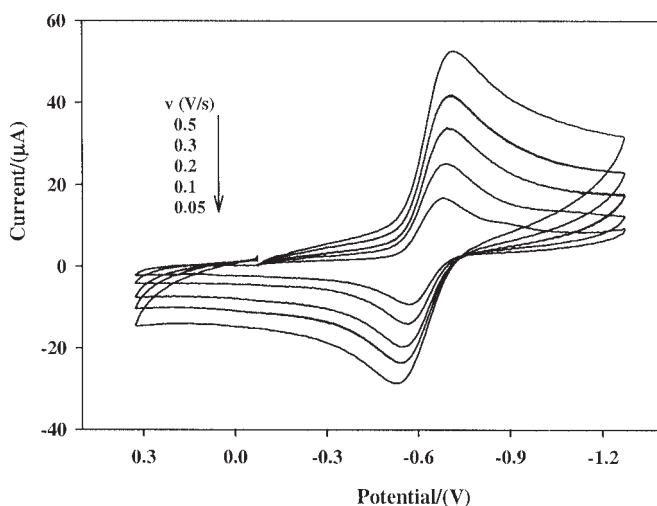


Figure 3. Cyclic voltammogram of $[Cu(pic)_2] \cdot 2H_2O$ in DMF solution, at scan rates $v \leq 0.5$ V/s.

values respectively. The separation between them, ΔE_p , exceeds the Nernstian requirement of 59 mV expected for a reversible one-electron process. This value increases from $\Delta E_p = 0.11$ V at 0.05 V/s to $\Delta E_p = 0.33$ V at 5 V/s indicating a kinetic inhibition of the electron transfer process [14, 25-27]. This behavior cannot be attributed to some uncompensated solution resistance, as the internal standard Fc/Fc⁺ couple, that shows rapid heterogeneous electron transfer in most of the solvents, gave a ΔE_p value of 73 mV (measured at $v = 0.2$ V/s). Thus, any possible uncompensated resistance is sufficiently small so that the resulting voltage drops are negligible compared to the ΔE_p values attributable to kinetic effects.

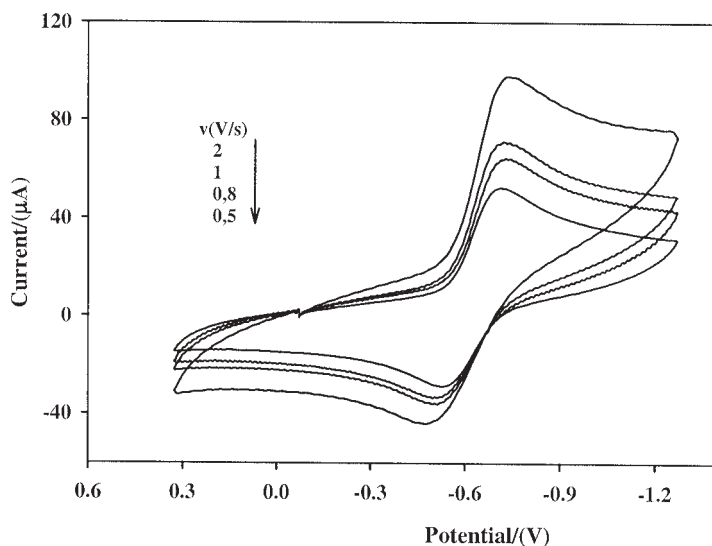


Figure 4. Cyclic voltammogram of $[Cu(pic)_2] \cdot 2H_2O$ in DMF solution, at scan rates $v \geq 0.5$ V/s.

On the other hand, and for diagnostic purposes, the ratio of anodic and cathodic current (i_{pa}/i_{pc}) was determined using the well-known empirical relation derived by Nicholson [14,27]. This ratio remains close to unity independent of the sweep rate used, giving, for this quasi-reversible process, a value of 0.5 for the charge transfer coefficient, α . The cathodic peak increases with the square root of the scan rate ($v^{1/2}$) but is not proportional to it (cf. Figure 5). The ratio $i_{pc}/v^{1/2}$ diminishes slightly from 68 to 61 $\mu\text{A s}^{1/2} \text{V}^{-1/2}$ [25-27].

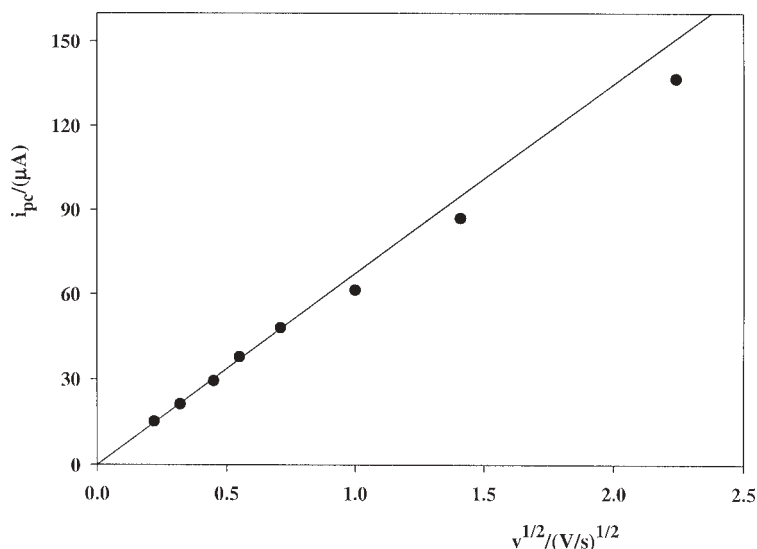
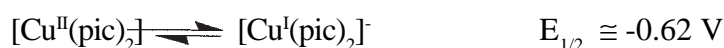


Figure 5. Dependence of the cathodic current peak on the square root of the scan rate ($v^{1/2}$).

Moreover, comparison of the cyclic voltammograms of the complex with the corresponding ligand response, under identical experimental conditions, indicates that the redox process involves only the metal ion. The cyclic voltammogram of picolinic acid at $v = 0.1 \text{ V/s}$ exhibits one reduction peak at -1.1 V and two oxidation peaks located at -0.75 and -0.2 V .

Important differences were also detected when the redox behavior of the complex was compared with those obtained in the presence of $\text{Cu}(\text{ClO}_4)_2$. The cyclic voltammogram of this compound, at $v > 0.2 \text{ V/s}$ exhibits one reduction and one oxidation peak, situated at more positive potentials than those obtained with the picolinate complex, and the process is followed by a disproportionation and the adsorption of metallic copper on the electrode (cf. also [28]). In contrast, in the case of the complex, and for all investigated scan rates, neither disproportionation nor Cu^0 adsorption on the electrode surface could be detected. Therefore, the reduction peak observed in this case can only be attributed to a one electron charge transfer from $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$.

To conclude, the experimental results prove that the reduction of $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ proceed through a quasi-reversible one electron process, generating the $\text{Cu}(\text{I})$ species, which has a life time long enough to be detected by cyclic voltammetry. The redox process can be formulated as follows:



The quasi-reversibility associated with the reduction process probably arises as a consequence of a geometry change from the originally distorted octahedral towards a distorted tetrahedral environment around the Cu(I) species.

Conclusions

The infrared and Raman spectra of the Cu(II) of picolinic acid of stoichiometry $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ were analyzed on the basis of its known crystal structure and by comparison with the spectroscopic behavior of the free ligand. The vibrational characteristics of the metal-to-ligand linkage could be fully interpreted. The electrochemical behavior of the complex was investigated by cyclic voltammetry in dimethylformamide solutions, showing that its reduction occurs through a quasi-reversible one-electron process. A value of about -0.62 V was determined for the redox couple. No evidence of disproportionation of the generated Cu(I) or for the adsorption of metallic copper on the electrode surface could be found.

Besides, a comparison with the previously investigated Cr(III) picolinate, of stoichiometry $\text{Cr}(\text{pic})_3 \cdot \text{H}_2\text{O}$, shows that the reduction of this species is more difficult and occur at a more negative potential (-1.23V) [9].

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