

Vibrational Spectra of Copper(II) Complexes of L-Proline

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SUMMARY. The infrared and Raman spectra of the Cu(II) complexes of L-proline (L-pro) [Cu(L-pro)₂]₂.5H₂O and [Cu(L-pro)(H₂O)Cl] were recorded and analyzed in relation to its structural peculiarities and by comparison with the spectra of the free amino acid. The electronic spectra of both complexes are also briefly discussed.

RESUMEN. "Espectros Vibracionales de Complejos de Cobre(II) con L-Prolina". Se registraron los espectros de infrarrojo y Raman de los complejos de Cu(II) con L-prolina (L-pro) [Cu(L-pro)₂]₂.5H₂O y [Cu(L-pro)(H₂O)Cl] y se los analizó en relación a sus peculiaridades estructurales y por comparación con los espectros del amino ácido libre. También los espectros electrónicos de ambos complejos se discuten brevemente.

INTRODUCTION

Copper(II) complexes of amino acids present important pharmacological interest as several of them show a wide spectrum of effects, including anti-inflammatory, antiulcer, anticonvulsant and even anti-tumoral activity ¹⁻⁵. It has also been established that these complexes often present a higher pharmacologically activity than that of its active free ligands ¹⁻³.

During the last years we have performed systematic studies on the physicochemical properties of copper(II) complexes of amino acids and small peptides ⁶⁻¹⁴ and, as a continuation of them, we have now investigated the vibrational spectroscopic behavior of two simple complexes of Cu(II) with the amino acid L-proline (Fig. 1), namely [Cu(L-pro)₂]₂.5H₂O and [Cu(L-pro)(H₂O)Cl].

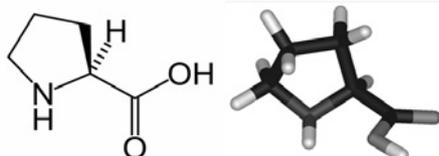


Figure 1. Schematic structure of L-proline.

MATERIALS AND METHODS

L-proline was purchased from Sigma, whereas all the other reagents were analytical grade products from Merck. They were used as supplied. The complex of composition [Cu(L-pro)₂]₂.5H₂O was prepared by reaction of L-proline (0.02 mol) with a slight excess (0.012 mol) of Cu(CO₃).Cu(OH)₂.H₂O, suspended in 50 ml of water. The mixture was heated over a water bath, with continuous stirring, during 1 h. The excess of basic carbonate was separated by filtration and the remaining blue solution was slowly evaporated at room temperature. After a few days, blue crystals of the compound were obtained. They were separated by filtration, washed with small amounts of cold water and dried in air ¹⁵. Analytical results: Found: C, 35.55; H, 6.35; N, 8.24. Calculated for Cu₂C₂₀H₄₂N₄O₁₃ (MW: 673.66): C, 35.62; H, 6.23; N, 8.31%.

The second complex, of stoichiometry [Cu(L-pro)(H₂O)Cl], was obtained by mixing 0.01 mol of CuCl₂.2H₂O and 0.01 mol of L-proline in 40 ml of water. Well formed blue crystals were obtained from the solution by keeping it in a desiccator containing acetone, after 2-3 weeks ¹⁶.

KEY WORDS: Copper(II) complexes, Electronic spectra, IR spectra, L-proline, Raman spectra.

PALABRAS CLAVE: Complejos de cobre(II); Espectros electrónicos, Espectros IR, Espectros Raman, L-prolina.

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Analytical results: Found: C, 25.90; H, 4.42; N, 5.90. Calculated for $\text{CuC}_5\text{H}_{10}\text{NO}_3\text{Cl}$ (MW:231.14): C, 26.00; H, 4.35; N, 6.00%.

Infrared spectra were recorded in the spectral range between 4000 and 400 cm^{-1} with a Bruker IFS 66 FTIR instrument, using the KBr pellet technique. Raman spectra were obtained with the FRA 106 Raman accessory of the same instrument. The 1064 nm line of a solid state Nd : YAG laser was used for excitation.

The UV-visible spectrum of $[\text{Cu}(\text{L-pro})_2]_2 \cdot 5\text{H}_2\text{O}$ was recorded as a Nujol mull, employing a Spectronic 3000 spectrophotometer. For $[\text{Cu}(\text{L-pro})(\text{H}_2\text{O})\text{Cl}]$ electronic spectroscopic data were available ¹⁶.

RESULTS AND DISCUSSION

Structure of the complexes

The $[\text{Cu}(\text{L-pro})_2]_2 \cdot 5\text{H}_2\text{O}$ complex belongs to the monoclinic $P2_1$ crystal system with $Z = 2$. It possesses two chemically different complex molecules, both with the Cu(II) ion in a N_2O_2 planar coordination. One of the complex units has one water molecule in an apical position whereas the other one has water molecules in each of the two apical positions ¹⁵.

The second complex, $[\text{Cu}(\text{L-pro})(\text{H}_2\text{O})\text{Cl}]$, also crystallized in the monoclinic $P2_1$ space group with $Z = 2$. The structure consists of a one-dimensional polymer chain bridged by the carboxylate group of proline. Each Cu(II) ion is in square pyramidal environment, surrounded in the plane by the chloride anion, the water molecule, the N-atom of proline and one of the carboxylic O-atoms of the same amino acid, whereas the second O-atom of this grouping interacts with a second Cu(II) ion. The apical position is occupied by a carboxylic O-atom from another proline residue. The polymer chains are arranged parallel to the b axis and the Cu(II) ions in the chain, which are bridged by carboxylates, are related by a 2_1 axis ¹⁶.

Vibrational spectra

In order to facilitate the spectroscopic assignment of the two complexes, we have investigated first the IR and Raman spectra of free L-proline. The proposed assignment is shown in Table 1 and is based on results of an older, partially incomplete, IR and Raman study ¹⁷ complemented with some most recent theoretical calculations for the free amino acid ¹⁸ and its zwitterion ¹⁹ as well as in some general standard references ^{20,21}. In the solid state, L-proline is evidently present in its zwitterionic form and,

therefore, the N-H moiety must be protonated, generating a NH_2^+ group whereas the acid group remains in the anionic COO^- form. Some important and interesting aspects of this assignment are briefly discussed, as follows:

a) The two NH_2^+ stretching vibrations appear as a unique very strong and relatively broad IR band, and they are absent in the Raman spectrum. The unexpectedly high energy of this band is probably a consequence of the fact that the NH_2^+ group is a part of a relatively constrained ring system. The theoretical calculations performed for the zwitterion show also the coincidence of the two expected stretching modes, at an even higher frequency (*ca.* 3515 cm^{-1}) ¹⁹.

b) The deformational modes of the NH_2^+ moiety are relatively weak in both the IR and Raman spectra and also appear at higher frequencies as compared to the NH_3^+ bending modes in other amino acids ¹⁹.

c) The assignment of the two carboxylate stretching vibrations is straightforward, although the antisymmetric stretching is probably mixed, to some extent with NH_2^+ deformational modes ¹⁹. On the other hand, some deformational modes of the OCO-moiety, in part mixed with other vibrations, could also be identified in the lower frequency range.

d) An important number of vibrations related to the CH_2 groups could also be assigned. In these assignments we have applied the same general criteria, as those employed in the assignment of the vibrational spectra of pyrrolidine, i.e. $\delta_{\text{sciss}}(\text{CH}_2) > \tau(\text{CH}_2) > \delta_{\text{w}}(\text{CH}_2) > \rho(\text{CH}_2)$ ²². A similar ordering was also proposed in the case of bis(pyrrolidinium)-chloride-hexachloroantimonate, $[(\text{C}_4\text{H}_8\text{NH}_2^+)_2\text{SbCl}_6^- \text{Cl}^-]$ ²³. From the presented assignment it becomes clear that in the region below 1000 cm^{-1} the CH_2 bending vibrations show important mixing with ring modes.

e) One interesting feature is the presence of a sharp and medium intensity Raman line at 1492 cm^{-1} which has not IR counterpart. This band seems to be very characteristic as it is also found in the Raman spectra of the two complexes and has been assigned to a ring stretching mode (cf. also ²⁴).

On the basis of the known structural data, it is possible to extend these assignments to the IR and Raman spectra of both investigated Cu(II) complexes.

The IR spectrum of $[\text{Cu}(\text{L-pro})_2]_2 \cdot 5\text{H}_2\text{O}$ is shown in Fig. 2 whereas the corresponding Raman spectrum, in the most interesting spectral

Infrared (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
3417 vs		$\nu(\text{NH}_2^+)$
3062 s	3005 vs	$\nu(\text{CH}_2)$
2985 s	2985 s	$\nu(\text{CH})$
	2949 s, 2890 m	$\nu(\text{CH}_2)$
2760 m, 2360 w		combinations and/or overtones
1624 vs	1615 w	$\nu_{\text{as}}(\text{COO}^-)$
1565 w	1544 w	$\delta(\text{NH}_2^+)$
	1492 m	ν_{ring}
1447 w	1454 s	$\delta_{\text{sciss}}(\text{CH}_2)$
1408 s	1373 s	$\nu_{\text{s}}(\text{COO}^-)$
1330 w	1332 vw	$\tau(\text{CH}_2)$
1288 sh	1286 m	$\tau(\text{CH}_2) + \delta_{\text{w}}(\text{CH}_2) + \delta(\text{CH})$
	1269 m, 1211 s	$\delta_{\text{w}}(\text{CH}_2) + \tau(\text{NH}_2^+)$
1169 m	1174 m	$\delta_{\text{w}}(\text{CH}_2)$
1088 w	1083 w	$\rho(\text{CH}_2) + \delta(\text{CH})$
1043 m	1049 s, 1034 s	$\nu(\text{CC}) + \text{ring modes}$
995 w	992 m	$\nu(\text{CCN}) + \nu(\text{CC}) + \rho(\text{NH}_2^+)$
947 w, 921 sh	950 m, 917 s	$\rho(\text{CH}_2) + \nu(\text{CC})$
	902 s, 893 w	$\rho(\text{NH}_2^+) + \rho(\text{CH}_2)$
847 m	837 s	$\rho(\text{NH}_2) + \nu(\text{CN})$
783 m	788 w	$\rho(\text{NH}_2) + \nu(\text{CC})$
679 s	675 w	$\rho(\text{COO}^-) + \delta(\text{COO}^-) + \nu(\text{CN})$
630 w	640 m, 578 w	$\delta(\text{COO}^-) + \nu(\text{CC})$
459 m	450 s	$\rho(\text{COO}^-) + \delta(\text{COO}^-) + \rho(\text{CC})$
	372 w, 317 w	$\delta(\text{CC})$

Table 1. Assignment of the vibrational spectra of L-proline; **vs:** very strong; **s:** strong; **m:** medium; **w:** weak; **vw:** very weak; **sh:** shoulder.

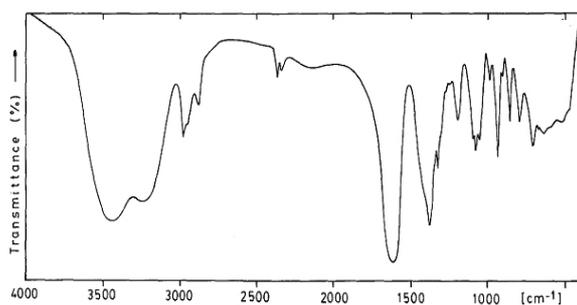


Figure 2. FTIR spectrum of $[\text{Cu}(\text{L-pro})_2]_2 \cdot 5\text{H}_2\text{O}$ in the spectral range between 4000 and 400 cm^{-1} .

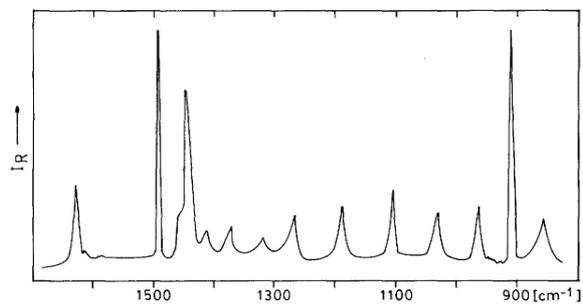


Figure 3. FT-Raman spectrum of $[\text{Cu}(\text{L-pro})_2]_2 \cdot 5\text{H}_2\text{O}$ in the spectral range between 1700 and 800 cm^{-1} .

range, is presented in Fig. 3. The proposed assignment is shown in Table 2 and briefly commented, as follows:

a) In the complex the amino group is present as NH moiety and, therefore, deformational modes of the NH_2^+ group are absent in both spectra. The stretching vibration of the NH group is observed again at a relatively high frequency. This behavior is supported by the mentioned theoretical study which gives scaled values above 3600 cm^{-1} for the two possible conformers of the amino acid¹⁸. Besides, in a matrix isolation study, in which L-proline is trapped in its molecular form and presents two

different conformations, the N-H stretching vibrations are found at 3393 and 3369 cm^{-1} for each of the two conformers²⁵.

b) The IR spectrum presents a very strong band related to the OH stretching vibration of the water molecules. The corresponding deformational modes probably contribute to the broadening of the strong carboxylate band centered at 1610 cm^{-1} . The position of the $\nu(\text{OH})$ vibration suggests the participation of the H_2O molecules in hydrogen bonds of intermediate strength²⁶. Besides, one of the librational modes of bonded water has tentatively been assigned in Table 2.

Infrared (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
3429 vs,br		$\nu(\text{N-H})$
3332 vs		$\nu(\text{O-H}) \text{H}_2\text{O}$
2976 m	2984 s	$\nu(\text{CH})$
2946 sh	2927 s	$\nu(\text{CH}_2)$
2875 w	2881 s	$\nu(\text{CH}_2)$
2360 w, 2339 w		combinations and/or overtones
1610 vs	1630 m	$\nu_{\text{as}}(\text{COO}^-)$
	1492 vs	ν_{ring}
1443 sh	1455 sh	$\delta_{\text{sciss}}(\text{CH}_2)$
1375 vs	1450 vs	$\nu_{\text{s}}(\text{COO}^-)$
	1414 w, 1372 w	$\delta_{\text{sciss}}(\text{CH}_2)$
1321 w	1323 w	$\tau(\text{CH}_2)$
	1269 m	$\tau(\text{CH}_2) + \delta_{\text{w}}(\text{CH}_2) + \delta(\text{CH})$
1192 m	1190 m	$\delta_{\text{w}}(\text{CH}_2)$
1092 w	1102 m	$\rho(\text{CH}_2) + \delta(\text{CH})$
	1037	$\nu(\text{CC}) + \text{ring modes}$
1074 s		$\nu(\text{CC}) + \text{ring modes}$
1044 w		$\nu(\text{CC}) + \text{ring modes}$
984 w	973 m	$\nu(\text{CCN}) + \nu(\text{CC})$
933 s	919 s	$\rho(\text{CH}_2) + \nu(\text{CC})$
905 w		$\rho(\text{CH}_2)$
856 s	855 m	$\rho(\text{CH}_2) + \nu(\text{CN})$
793 s	795 w	$\rho(\text{CH}_2) + \nu(\text{CC})$
708 s	690 w	$\rho(\text{COO}^-) + \delta(\text{COO}^-) + \nu(\text{CN})$
632 m	636 m	$\rho(\text{H}_2\text{O}) (?)$
615 m	590 w	$\delta(\text{COO}^-) + \nu(\text{CC})$
	517 m, 470 w	see text

Table 2. Assignment of the vibrational spectra of $[\text{Cu}(\text{L-pro})_2]_2 \cdot 5\text{H}_2\text{O}$; **vs:** very strong; **s:** strong; **m:** medium; **w:** weak; **br:** broad; **sh:** shoulder.

c) The carboxylate stretching vibrations of L-proline show only small shifts after coordination, suffering small displacements to lower frequencies. Interestingly, the energy difference between both vibrations ($\Delta = 235 \text{ cm}^{-1}$, from IR data) clearly supports the participation of this group in monodentate binding²⁷⁻²⁹.

d) Most of the CH_2 vibrations, as well as skeletal modes and carboxylate deformations suffer only small energy and intensity changes in the complex, in comparison to values found in the "free" amino acid. Besides, the characteristic ring stretching vibration of L-proline (1492 cm^{-1} in the Raman spectrum) remains exactly at the same position in the complex (cf. Fig. 3).

e) The presence of two chemically different complex molecules in the investigated solid has, apparently, scarce effect over the general spectroscopic behavior.

f) It was not possible to identify bands related to metal-to-ligand vibrations although by comparison with the spectroscopic behavior of other $\text{Cu}(\text{II})$ complexes of amino acids⁶, the weak Raman band observed at 470 cm^{-1} may be, eventually, related to a Cu-N motion.

Regarding $[\text{Cu}(\text{L-pro})(\text{H}_2\text{O})\text{Cl}]$, its IR spectrum in the medium spectral region is shown in Fig. 4. The Raman spectrum of this complex was relatively poor and the greatest part of the spectrum was conformed by relatively weak and not well defined lines. Therefore, in Table 3 we have only performed the assignment of the IR

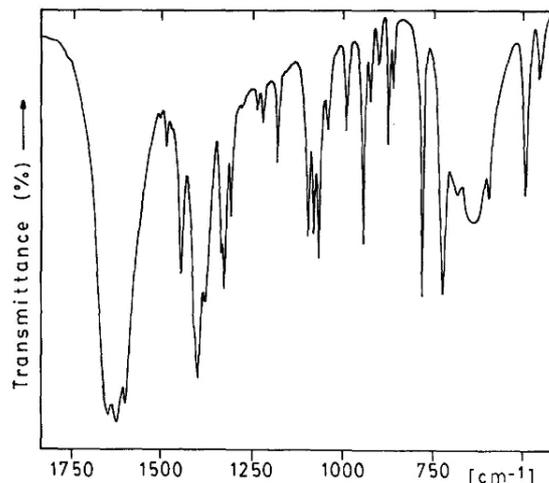


Figure 4. FTIR spectrum of $[\text{Cu}(\text{L-pro})(\text{H}_2\text{O})\text{Cl}]$ in the spectral range between 2000 and 900 cm^{-1} .

Infrared (cm ⁻¹)	Assignment
3448 vs	v(N-H)
3353 s, 3234 vs	v(O-H) H ₂ O
2991 vs	v(CH)
2964 m, 2953 vs	v(CH ₂)
2896 w, 2853 w	v(CH ₂)
2285 w	combination and/or overtone
1639 w, 1618 vs, 1594 w	v _{as} (COO ⁻) + δ(H ₂ O)
1439 s	δ _{sciss} (CH ₂)
1406 sh, 1392 vs, 1368 w	v _s (COO ⁻)
1329 sh, 1318 m	τ(CH ₂)
1302 m	τ(CH ₂) + δ _w (CH ₂) + δ(CH)
1230 w, 1209 w	δ _w (CH ₂)
1173 m	δ _w (CH ₂) + ρ(CH ₂) + δ(CH)
1090 s, 1074 s	ρ(CH ₂) + δ(CH)
1062 s, 1034 w	v(CC) + ring modes
987 m	v(CCN) + v(CC)
939 s	ρ(CH ₂) + v(CC)
921 w, 897 w, 848 w	ρ(CH ₂) + v(CN) + v(CC)
777 v	ρ(CH ₂) + v(CC)
719 vs, 675 w	ρ(COO ⁻) + δ(COO ⁻) + v(CN)
633 m	ρ(H ₂ O) (?)
591 w	δ(COO ⁻) + v(CC)
494 s, 453 w	ρ(COO ⁻) + δ(COO ⁻) + ρ(CC)

Table 3. Assignment of the IR spectrum of [Cu(L-pro)(H₂O)Cl]; **vs**: very strong; **s**: strong; **m**: medium; **w**: weak; **br**: broad; **sh**: shoulder.

spectrum, which is briefly discussed, as follows:

a) Also in this complex the NH stretching vibration is the highest energy band as it is in the complex described before and lies even somewhat higher than in [Cu(L-pro)₂]₂.5H₂O.

b) The water stretching vibrations are clearly separated into two strong components while the δ(H₂O) mode contributes to the splitting observed in the v_{as}(COO⁻) region. A librational mode of the bonded water could also be identified.

c) The region related to the CH and CH₂ stretching vibrations is very rich in bands. Also in the Raman spectrum a strong band multiplet is seen in this spectral region, with components at 3020, 2991, 2925, 2897 and 2866 cm⁻¹.

d) Most of the deformational modes were found in similar ranges as in the "free" ligand. The commented ring stretching mode is also present in the Raman spectrum of this complex, again at 1492 cm⁻¹, and is the strongest signal observed in this spectrum.

e) Similar as in the other complex, in this case the carboxylate bands only show very weak changes after coordination and the energy difference between both stretching modes is also similar (Δ = 226 cm⁻¹), despite the fact that in this case the carboxylate group acts as a bridg-

ing ligand whereas in [Cu(L-pro)₂]₂.5H₂O it is monodentate. This somewhat unexpected behavior can be understood on the basis of the available structural information. The two C-O distances within the carboxylate groups are markedly different, generating a highly unsymmetrical bridge: the C-O bond belonging to the O-atom linked to the square-planar coordination sphere of Cu(II) is equal to 1.948(3) Å while the other one, involving the O-atom which occupies the apical position of the second Cu(II) cation, is equal to 2.286(5) Å¹⁶. This fact implies that also in this case the carboxylate group may be considered as "pseudo-monodentate" and such a situation often generates unusually high Δ-values²⁸.

f) Bands related to metal-to-ligand vibrations, like Cu-O, Cu-N, or Cu-Cl modes, could not be identified. Only in the Raman spectrum we could detect a weak band at 265 cm⁻¹, which can probably be related to a Cu-Cl vibration (bands related to these modes are usually expected to lie between 400 and 200 cm⁻¹²⁷).

Electronic spectra

It was interesting to compare the electronic spectra of the two complexes. The diffuse reflectance spectrum of [Cu(L-pro)(H₂O)Cl] shows

one band located at 749 nm¹⁶, whereas the spectrum of [Cu(L-pro)₂]₂.5H₂O, measured by us, shows a relatively broad band centered at 678 nm with a shoulder located at 625 nm.

We have analyzed the positions of these bands with the simple calculations discussed in the theoretical model of Prenesti *et al.*^{30,31}. For the chloride ligand in [Cu(L-pro)(H₂O)Cl], we have used the same coefficient as for the aqua ligand, taking into account its relative closeness in the spectrochemical series³², and adding the suggested mean value of 36 nm for the incorporation of one axial carboxylate O-atom to the square coordination sphere³¹. The obtained value of 752 nm is in excellent agreement with the experimental one.

For [Cu(L-pro)₂]₂.5H₂O it can be assumed that the shoulder found at 625 nm may be originated in the pyramidal [Cu(N₂O₂)(H₂O)] moiety, while the main band, at 678 nm, is related to the octahedral [Cu(N₂O₂)(H₂O)₂] unit, taking into account that usually, in Cu(II) complexes, the electronic band shifts to higher energy as the coordination decreases from six to five or to four³². In this case, the calculations with the mentioned theoretical model^{30,31} gave a value of 622 nm, which lies nearer to the value of the measured shoulder.

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REFERENCES

- Sorenson, J.R.J. (1976) *J. Med. Chem.* **19**: 135-48.
- Sorenson, J.R.J. (1982) *"Metal Ions in Biological Systems"* (H. Sigel, Ed.), M. Dekker, New York, Vol. **14**, pp. 77-124.
- Baran, E.J. (1985) *Acta Farm. Bonaerense* **4**: 125-33.
- Farrell, N. (1989) *"Transition Metal Complexes as Drugs and Chemotherapeutic Agents"*, Kluwer, Dordrecht.
- Baran, E.J. (2004) *Mini Rev. Med. Chem.* **4**: 1-9.
- Cuevas, A., I. Viera, M.H. Torre, E. Kremer, S.B. Etcheverry & E.J. Baran (1998) *Acta Farm. Bonaerense* **17**: 213-8.
- Cuevas, A., I. Viera, M.H. Torre, E. Kremer, S.B. Etcheverry & E.J. Baran (1999) *Afinidad* **56**: 263-5.
- Baran, E.J., C.C. Wagner, M.H. Torre, E. Kremer & P. Kögerler (2000) *Acta Farm. Bonaerense* **19**: 231-4.
- Wagner, C.C. & E.J. Baran (2002) *Acta Farm. Bonaerense* **21**: 287-90.
- Wagner, C.C. & E.J. Baran (2004) *Acta Farm. Bonaerense* **23**: 339-42.
- Viera, I., M.H. Torre, O.E. Piro, E.E. Castellano & E.J. Baran (2005) *J. Inorg. Biochem.* **99**: 1250-4.
- Baran, E.J. (2005) *Z. Naturforsch.* **60b**: 663-6.
- Baran, E.J., I. Viera & M.H. Torre (2007) *Spectrochim. Acta* **A66**: 114-7.
- Facchin, G., E. Kremer, E.J. Baran, E.E., Castellano, O.E. Piro, J. Ellena, A.J. Costa-Filho & M.H. Torre (2006) *Polyhedron* **25**: 2597-604.
- Sartoris, R.P., L. Ortigoza, N.M.C. Casado, R. Calvo, E.E. Castellano & O.E. Piro (1999) *Inorg. Chem.* **38**: 3598-604.
- Yukawa, Y. (1992) *J. Chem. Soc. Dalton Trans.* 3217-21.
- Herlinger, A.W. & T.V. Long (1970) *J. Am. Chem. Soc.* **92**: 6481-6.
- Tarakeshwar, P. & S. Manogaran (1996) *J. Mol. Struct. (Theochem)* **365**: 167-81.
- Tarakeshwar, P. & S. Manogaran (1997) *J. Mol. Struct. (Theochem)* **417**: 255-63.
- Lin-Vien, D., N.B. Colthup, W.G. Fateley & J.C. Grasselli (1991) *"The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules"* Academic Press; San Diego.
- Smith, B. (1999) *"Infrared Spectral Interpretation"* CRC-Press; Boca Raton.
- Evans, J.C. & J.C. Wahr (1959) *J. Chem. Phys.* **31**: 655-62.
- Bednarska-Bolek, B., R. Jakubas, G. Bator & J. Baran (2002) *J. Mol. Struct.* **614**: 151-7.
- Jenkins, A.L., R.L. Larsen & T.B. Williams (2005) *Spectrochim. Acta* **A61**: 1585-94.
- Reva, I.D., S.G. Stepanian, A.M. Plokhonichenko, E.D. Radchenko, G.G. Sheina & Yu.P. Blagoi (1994) *J. Mol. Struct.* **318**: 1-13.
- Siebert, H. (1966) *"Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie"*, Springer, Berlin.
- K. Nakamoto (1997) *"Infrared and Raman Spectra of Inorganic and Coordination Compounds"*, 5th Edit., Part B, Wiley, New York.
- Deacon, G.B. & R.J. Phillips (1980) *Coord. Chem. Rev.* **33**: 227-50.
- Zelenák, V., Z. Vargová & K. Györyová (2007) *Spectrochim. Acta* **A66**: 262-72.
- Prenesti, E., P.G. Daniele, M. Prencipi & G. Ostacoli (1999) *Polyhedron* **18**: 3233-41.
- Prenesti, E., P.G. Daniele, S. Berto & S. Toso (2006) *Polyhedron* **25**: 2815-23.
- Lever, A.B.P. (1984) *"Inorganic Electronic Spectroscopy"*, 2nd Edit., Elsevier, Amsterdam.