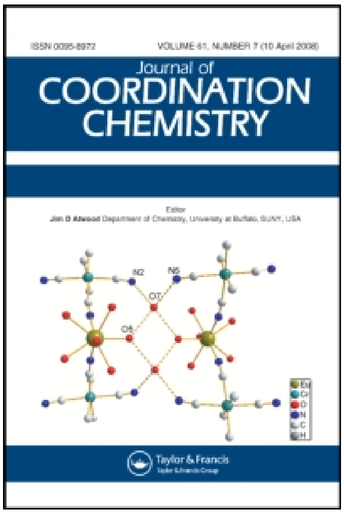

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COORDINATION BINDING MODES FOR POLYMERIC CADMIUM DICARBOXYLATE HYDRATE COMPLEXES

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To cite this Article Brusau, E. V. , Pedregosa, J. C. , Narda, G. E. , Pozzi, G. , Echeverria, G. and Punte, G.(2001) 'COORDINATION BINDING MODES FOR POLYMERIC CADMIUM DICARBOXYLATE HYDRATE COMPLEXES', Journal of Coordination Chemistry, 54: 3, 469 — 480

To link to this Article: DOI: 10.1080/00958970108022657

URL: http://dx.doi.org/10.1080/00958970108022657

J. Coord. Chem., 2001, Vol. 54, pp. 469–480
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COORDINATION BINDING MODES FOR POLYMERIC CADMIUM DICARBOXYLATE HYDRATE COMPLEXES

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(Received 14 August 2000; In final form 28 February 2001)

Single crystal X-ray crystal diffraction, IR and TGA-DTA data and searches in the Cambridge Structural Database (CSD) have been used to analyze coordination binding modes of Cd(II) in dicarboxylate complexes with anions of different length. The results, discussed in this paper, show that Cd(II) presents a range of coordination geometries. Six, seven and eight coordination with different degrees of departure from regular polyhedra are observed. The length of the ions influences the availability of donor oxygens and induces bidentate, six or four member chelating rings, and monodentate binding, which produces polymerization of different dimensionality.

Keywords: Cadmium(II) dicarboxylates; Coordination polyhedra; Vibrational behavior; Dehydration process

INTRODUCTION

Ca(II) is involved in a wide variety of metalloproteins in biological systems. In some calcium-binding proteins, modified aminoacid residues can be identified and several workers have modeled these residues by the use of malonate or α-substituted malonate ions [1, 2].

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Metallosubstitution is useful for studying metal sites in proteins and their model compounds. Usually, Cd(II) is applied as a metallic probe of Ca(II) and Zn(II) sites due to its chemical similarity [3–5]. To this end, several techniques, *i.e.*, ^{113}Cd NMR spectroscopy [6–9], are employed. However, the use of this technique is strongly dependent on the availability of single crystal X-ray structural data to correlate the spectroscopic information with the cation environment.

Several Cd(II) carboxylates have been reported in the literature *i.e.*, cadmium(II) diacetate dihydrate [10], cadmium(II) malonate monohydrate [11] and dihydrate [12], tetraaquobis(malonato)dicadmium(II) [13] and diaquasuccinatocadmium(II) hemihydrate [14]. In the acetate compound Cd is seven coordinate, whereas in the malonate complexes Cd is seven coordinate in the first two cases and six and eight in the latter. Seven coordination has also been observed in the succinate complex. The molecular packing in these compounds reveals the existence of polymeric structures of different dimensionality, geometry and packing modes.

Within a research program focused on understanding the factors that influence binding, formation and stability of polymeric structures, a structural, spectroscopic and thermal analysis of Cd(II) succinate was previously performed [15].

On this basis it was found interesting to extend this study to other dicarboxylates in order to analyze the effect of anion size and water content on the cation coordination sphere and degree of polymerization. The results for Cd(II) glutarate and adipate along with their comparison with previously reported structures of malonate [11–13] and succinate [15] are presented here.

EXPERIMENTAL

The Cd(II) compounds were prepared by dissolving 1 mmol of $Cd(NO_3)_2 \cdot 4H_2O$ (Baker's Analyzed) in a 50 mL aqueous solution containing 2 mmol of the corresponding acid (Sigma) previously neutralized with NaOH to pH 7, under stirring, except in the case of Cd(II) glutarate, where CdO (Merck) was used and the final pH was 6.

The solutions were left to evaporate slowly at room temperature. A large number of colorless prismatic single crystals, suitable for crystallographic study, was obtained after about 10 days, then filtered, washed with distilled water and dried on P_4O_{10}, in all cases. The products were then characterized by IR spectroscopy, XRD powder diagrams, TG-DTA measurements and elemental analysis. The following stoichiometries were obtained: $CdC_3H_4O_5$, $CdC_4H_8O_6$, $CdC_5H_{16}O_9$ and $CdC_6H_{12}O_6$.

A survey of Cd(II) dicarboxylates in the October 1999 Cambridge Structural Database V5.18 [16] render five Cd(II) dicarboxylate complexes. The molecular structure study of the other complexes analyzed have been previously performed for us. The details will be reported elsewhere [17]. The molecular graphics were done with ORTEP [18].

FTIR spectra were recorded on a Nicolet PROTÉGÉ 460 spectrometer in the 4000–225 cm^{-1} range with 32 scans using the KBr pellet technique. Raman spectra were scanned on a Bruker IFS 66 Fourier Transform optical bench provided with the FRA 106 Raman accessory operating with a Nd-YAG laser at 1064 nm; the scattering geometry was 180° and 50 scans were usually accummulated. Spectral resolution was 4 cm^{-1} in both cases.

TG-DTA curves were obtained with a Shimadzu TGA-50H/DTA-50 thermal analyzer apparatus using flowing oxygen at 50 mL min^{-1} at a heating rate of 10°C min^{-1}. The dehydration process was followed while heating the sample at selected and controlled temperatures in a Thermolyne 47900 furnace according to the information obtained from the thermograms. Appropriate combinations of X-ray powder diffraction and FTIR spectroscopy were used for further characterization of the anhydrous compounds.

RESULTS AND DISCUSSION

The main features of the crystal structure, the vibrational spectra essential data and the thermal dehydration process of this series of Cd(II) dicarboxylate hydrate compounds are detailed in this section. The interpretation of the FTIR and Raman spectra is supported by their comparison with the spectroscopic data of each acid and related compounds found in the literature [19–22]. Structural, vibrational and thermal data are reported in Tables I, II and III, respectively, in order to simplify comparative analysis.

Diaquasuccinatocadmium(II) [15]

Figure 1 shows that the Cd atoms are seven-coordinated to O atoms, five of them belonging to three succinate moieties and the remaining ones to the two crystallographically inequivalent water molecules. Two of the succinate ligands bind the Cd ions through a bidentate four member ring interaction, while the third one shows a monodentate interaction.

TABLE I Coordination number of Cd(II), polyhedron geometry and selected bond distances [Å]

$[Cd(C_3H_2O_4)H_2O]\cdot H_2O$[12]	$[Cd(C_3H_2O_4)H_2O]$[11]	[a]$[Cd(C_3H_2O_4)(H_2O)_2]$[13]	$[Cd(C_4H_4O_4)(H_2O)_2]$[15]	$[Cd(C_4H_4O_4)(H_2O)_2]\cdot 1/2H_2O$[14]	$[Cd(C_5H_6O_4)(H_2O)_3]\cdot 2H_2O$•	$[Cd(C_6H_8O_4)(H_2O)_2]$•
Coord. 7	Coord. 7	Coord. 8	Coord. 7	Coord. 7	Coord. 7	Coord. 6
Pentagonal	Pentagonal	Distorted	Distorted pentagonal	Pentagonal	Distorted pentagonal	Distorted
bipyramid	bipyramid	dodecahedron	bipyramid	bipyramid	bipyramid	octahedron
Cd—O1 2.546	Cd—O1 2.501(7)	Cd1—O1 2.323(4)	Cd—O1 2.305(2)	Cd1—Ow1 2.279	Cd—O1 2.524(3)	Cd1—O1 2.353(11)
Cd—O2 2.294	Cd—O2 2.330(6)	Cd1—O3 2.307(4)	Cd—O2 2.515(2)	Cd1—Ow2 2.315	Cd—O2 2.272(3)	Cd1—O2 2.317(8)
Cd—O3^{i} 2.258	Cd—O3^{i} 2.417(6)	Cd1—O4 2.775(5)	Cd—O3^{i} 2.376(2)	Cd1—O1 2.324	Cd—O3^{i} 2.713(3)	Cd1—Ow1 2.197(10)
Cd—O4^{i} 2.327	Cd—O4^{i} 2.398(7)	Cd1—O5 2.314(4)	Cd—O4^{i} 2.487(2)	Cd1—O8^{i} 2.350	Cd—O4^{i} 2.263(3)	
Cd—O1^{ii} 2.286	Cd—O1^{ii} 2.277(7)	Cd1—O6 2.775(5)	Cd—O4^{ii} 2.249(2)	Cd1—O5 2.371	Cd—Ow1 2.341(3)	Cd2—O3 2.341(13)
Cd—O3^{ii} 3.293	Cd—O3^{ii} 2.296(6)	Cd1—O8 2.310(4)	Cd—Ow1 2.292(3)	Cd1—O7^{i} 2.378	Cd—Ow2 2.307(3)	Cd2—O4 2.322(9)
Cd—Ow 2.287	Cd—Ow 2.272(7)	Cd1—Ow1 2.375(4)	Cd—Ow2 2.301(2)	Cd1—O2 2.496	Cd—Ow3 2.219(3)	Cd2—Ow2 2.246(9)
		Cd1—Ow2 2.375(4)				
				Cd2—O3^{ii} 2.286		
		Coord. 6		Cd2—Ow4 2.292		
		Octahedron		Cd2—O1 2.292		
		Cd2—O2 2.296(4)		Cd2—Ow3 2.364		
		Cd2—O4 2.225(4)		Cd2—O6 2.393		
		Cd2—Ow3 2.277(5)		Cd2—O4^{ii} 2.445		
				Cd2—O5 2.470		
		Cd3—O7 2.304(4)				
		Cd3—O6 2.219(4)				
		Cd3—Ow4 2.274(5)				

[a] There are only two crystallographically inequivalent malonate ions.
i, ii, *etc.* indicate some symmetry operation.
• Recent results.

TABLE II Assignment of the FTIR spectra of Cd(II) dicarboxylates showing the main modes frequencies of the functional groups (cm^{-1})

Assignment	$CdC_3H_2O_4 \cdot H_2O$	$[Cd(C_4H_4O_4)(H_2O)_2]$	$[Cd(C_5H_6O_4)(H_2O)_3] \cdot 2H_2O$	$[Cd(C_6H_8O_4)(H_2O)_2]$
ν(OH)	3605(m) 3525(m)	3460(br, m) 3240(sh)	3465(br, m) 3225(sh)	3460(br, m) 3240(sh)
ν_{as}(OCO)	1545(vs)	1585(vs) 1540(s)	1560(vs)	1555(vs)
ν_s(OCO)	1380(vs)	1325(m) 1300(s)	1350(m) 1315(m)	1320(m)

ν_{as}: asymmetric stretching; ν_s: symmetric stretching; br: broad; sh: shoulder; s: strong; vs: very strong; m: medium.

TABLE III DTA peaks temperature for the dehydration course of Cd(II) dicarboxylates (°C)

Compounds	*Temperatures*
$CdC_3H_2O_4 \cdot H_2O$	60
	154
$[Cd(C_4H_4O_4)(H_2O)_2]$	149
$[Cd(C_5H_6O_4)(H_2O)_3] \cdot 2H_2O$	72
$[Cd(C_6H_8O_4)(H_2O)_2]$	92
	117

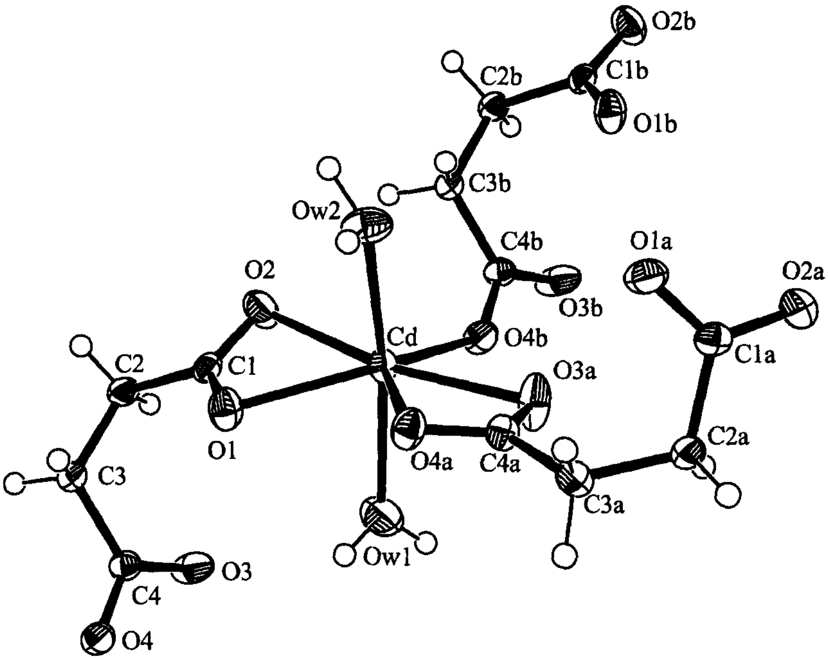

FIGURE 1 ORTEPII [18] view of the Cd(II) coordination polyhedron in diaquasuccinatocadmium(II).

Analysis of the geometry of the coordination polyhedron indicates that it can be classified as a distorted pentagonal bipyramid with the Cd and the O of the succinate ions in the equator and the O of the water molecules out of that plane.

The oxygen atom (O4b) participates in a bidentate and in a monodentate interaction and bridges two Cd atoms, which are located at a distance of 4.3342(7) Å.

In accordance with the structural analysis, the FTIR spectrum shows both carboxylate stretching modes split into two components; coincidentally the

Raman spectrum shows a line at 1330 cm^{-1} assigned to the ν_s(OCO) mode. The splitting of these modes can be attributed to the existence of two different types of interaction between the carboxylate groups of the succinate ion and Cd(II).

The coordination strength of the two crystallographically inequivalent water molecules to Cd(II), as determined from their distance to the ion, is similar. The water molecule W2 is hydrogen bonded to two O atoms belonging to the succinate moiety, while the W1 water molecule is involved in one hydrogen bond with a succinate group and is weakly hydrogen bonded to W2.

In the FTIR spectrum one slightly asymmetric broad band is assigned to ν(O—H). This band is centered at lower frequency than expected for free water stretching vibrations whereas the spectrum does not show the bending and librational modes, indicating that water molecules are tightly bound to the structure.

Thermal behavior supports the features mentioned above. Dehydration yielding the amorphous anhydrous compound is associated with an endothermic DTA signal; it occurs as a broad and asymmetric peak indicating that water molecules are lost at different but close temperatures. This fact suggests some thermal stability dependence between both molecules which is compatible with the similar strength of their coordination bonds and with the existence of a hydrogen bond linking both molecules. TG curve presents the corresponding experimental weight loss of 13.4% (theoretical, 13.6%).

Triaquaglutaratocadmium(II) Dihydrate

The crystal structure has been previously determined by Antsyshkina *et al.* [23] who did not report H atom positions. We have revisited it to get more accurate data.

Figure 2 illustrates that Cd(II) is seven-coordinated to seven O atoms, four of them belonging to the carboxylate groups and the remaining ones to water molecules. The glutarate ligands bind the Cd(II) through a bidentate interaction forming infinite chains developed along the (101) direction. These chains interact through hydrogen bonds.

The geometry of the coordination polyhedron is best described as distorted pentagonal bipyramidal with four O atoms from the glutarate ions and one from a water molecule, Ow3 approximately coplanar and the remaining water molecules located nearly axial. Cd – O3a exhibits one of the longest coordination distances, 2.713(3)Å, observed for the M—O bond in this series of cadmium dicarboxylate compounds (see Tab. I).

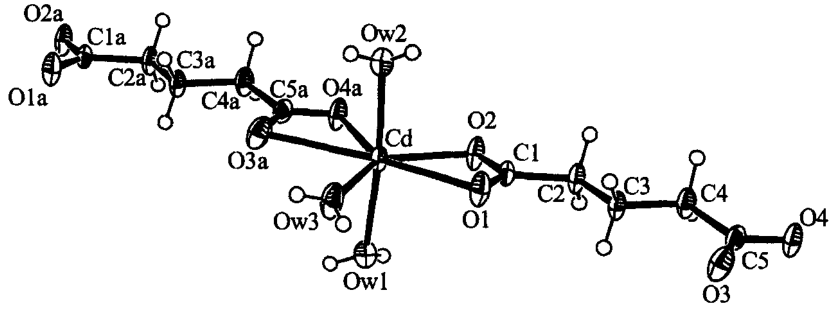

FIGURE 2 ORTEPII [18] view of the Cd(II) coordination polyhedron in triaquaglutaratocadmium(II) dihydrate.

The carboxylate group stretching modes appear in the FTIR spectrum, as a unique and very strong band for the asymmetric mode whereas the symmetric one is split into two components. This is expected for chelating OCO groups where the Cd–O distances vary quite markedly. No water modes are present except for those corresponding to the stretching ones, which exhibit a broad, asymmetric band shifted to lower frequencies in relation to free water stretching vibrations. This observation supports the existence of different kinds of water molecules: coordinated water involved in hydrogen bonding and water of hydration.

The thermal process indicates that all water molecules are lost within a wide range of temperature which starts relatively low, according to the endothermic DTA signal; this fact suggests that they are involved in different kinds of interactions. TG tracing presents the corresponding experimental weight loss of 26.9% (theoretical, 27.06%).

Diaquaadipatocadmium(II)

Structural analysis [17] reveals the presence of two inequivalent Cd(II) ions located on the C_2 axis each of which is coordinated to six O atoms, four from the adipate ions and the remaining ones from two crystallographically inequivalent water molecules. The carboxylate groups link Cd(II) ions through bidentate bonds. The coordination spheres for both Cd(II) ions are similar, the main differences are in the Cd–Ow distances. For clarity in Figure 3 only one of the two inequivalent coordination polyhedra has been included. The figure shows that the polyhedron presents a highly distorted octahedral geometry.

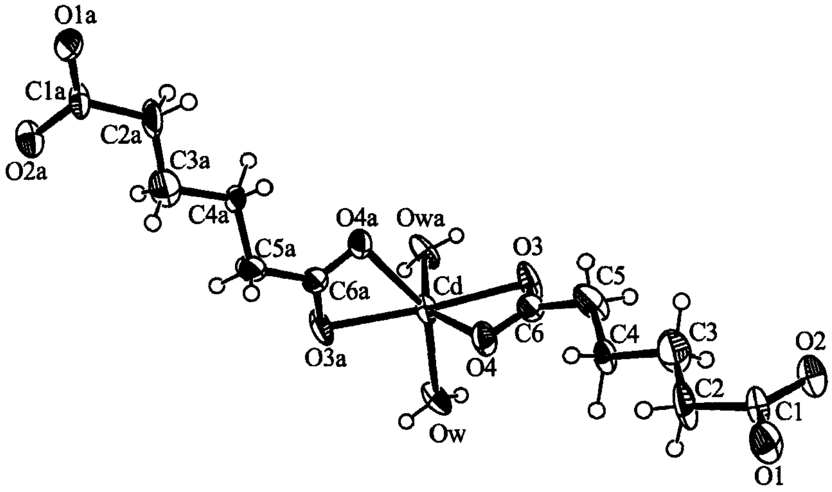

FIGURE 3 ORTEPII [18] view of one of the two inequivalent Cd(II) coordination polyhedra in diaquaadipatocadmium(II).

Both interactions from the carboxylate residues related by the C_2 axis are nearly perpendicular forming infinite corrugated chains. The structure is stabilized by a tridimensional network of hydrogen bonds, where water molecules belonging to one of the chains interact with two neighboring chains.

No splitting of carboxylate group stretching modes is observed in the FTIR spectrum, as expected from the structural data which report only bidendate coordination for the adipate ligands. A Raman line at 1310 cm^{-1}, is assigned to the ν_s(OCO) mode.

The strength of the coordination of the two crystallographically inequivalent water molecules (W1 and W2) to Cd(II), as determined from their distance to the ion, is similar, but they are involved in hydrogen bonds of different strength. This is consistent with the vibrational behavior of water molecules, *i.e.*, ν(O—H) appears as a broad, asymmetric band centered at a lower frequency in comparison with free water and no deformation mode is observed; these features indicate the presence of a strong hydrogen bond network where water molecules have distinct degrees of participation.

These facts are also in agreement with thermal data: two endothermic DTA peaks, associated with the dehydration process. TG curve shows a slightly irregular decay in this step which is accompanied by two signals in the corresponding DrTG tracing. The experimental weight loss found is 12.28% (theoretical, 12.3%).

Comparison of Cd(II) Coordination Modes and Molecular Packing

Metal-dicarboxylate interactions and the main structural features reported for the different cadmium(II)malonate hydrates and diaquasuccinatocadmium(II) are markedly different from those observed in triaquaglutaratocadmium(II) dihydrate and diaquaadipatocadmium(II). This suggests that different availability of donor oxygens induced by hydrocarbon chain length plays an important role in the binding modes and in polymerization dimensionality. When the anion hydrocarbon chain length is large and/or only two donor oxygen atoms are available, as in acetate, only unidimensional polymers are observed.

From the literature [11 – 13] we found two kinds of bidentate binding modes, four member and six member chelate rings for Cd(II) malonate compounds. Those binding modes allow the compounds to build two [13] and three-dimensional polymers [11, 12].

The diaquasuccinatocadmium(II) crystal structure consists of a two dimensional polymeric array developed perpendicular to the crystallographic axis *b*. These (010) layers contain two sets of chains of cadmium coordination polyhedra running approximately perpendicular. The hydrogen bonds link the corrugated layers of polymers stabilizing the tridimensional structure. Similar type of polymerization is observed for diaquasuccinatocadmium(II) hemihydrate, where the hydration water molecule further links successive layers and eliminates corrugation.

Triaquaglutaratocadmium(II) dihydrate and diaquaadipatocadmium(II) structures can be described as polymeric chains. Similar layer structure and packing have been observed in lithium hydrogen adipate [24], calcium glutarate monohydrate [25] and calcium adipate monohydrate [26], indicating this to be a common structural feature of long-chain dicarboxylates.

No systematic changes are observed in the FTIR spectra for the carboxylate groups stretching modes, except for a slight shift to lower frequencies for the asymmetric stretch when hydrocarbon chain length increases. The splitting of the band assigned to the symmetric OCO stretching mode in diaquasuccinatocadmium(II) and triaquaglutaratocadmium(II) dihydrate is in agreement with the unsymmetrical coordination mode found for the succinate ligand and the dispersion evidenced in the Cd—O bond distances for the glutarate complex.

In addition, the difference between the frequency values for both modes ($\Delta\nu$) is larger than the corresponding ionic values, *i.e.*, sodium salts. According to a spectroscopic criterion the $\Delta\nu$ values observed correspond to the presence of different kinds of interaction of the carboxylate ligands such as unsymmetrical bridging bidentate or chelating coordination modes [20, 27, 28].

The existence of coordinated water molecules which are in the different lattices involved in hydrogen bonding and polymerization can also be assessed from vibrational and thermal information.

The position and shape of the corresponding stretching vibration band and the absence of deformation and librational modes show the presence of tightly bound water molecules. There are no significant differences in the OH stretching zone when going from succinate to adipate; considering that all Cd—Ow bond distances of the cited complexes are in the same range, therefore coordination is the main effect that governs this feature. However, hydrogen bonding and polymerization have influence on the shape and position of the DTA signal during the dehydration process. The highest temperature is needed for the succinate compound where polyhedra interactions create a two dimensional polymer. The loss of water molecules occurs as a broad DTA peak at lower temperatures in the unidimensional polymer triaquaglutaratocadmium(II) dihydrate. The adipate complex, instead, shows two endothermic peaks and their positions account for its unidimensionality.

Acknowledgements

The authors thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET PID 4929/96), the Agencia Nacional de Promoción Científica y Tecnológica (PICT 1135- PICT 03041), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CICPBA), República Argentina, UNLP and UNSL for financial support, to Dr. E. L. Varetti for the obtainment of the Raman spectrum and Dra. E. Ferrer for thermal measurements. G. P., J. C. P. and G. E. N. are members of the CONICET.

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