

Seven-Coordinated Diaquasuccinatocadmium(II) Bidimensional Polymer: Crystal Structure and Vibrational and Thermal Behavior

E. V. Brusau, J. C. Pedregosa, and G. E. Narda¹

Area de Química General e Inorgánica "Dr. G. F. Puelles," Facultad de Química, Bioquímica y Farmacia, PID-CONICET 4929, Universidad Nacional de San Luis, Chacabuco y Pedernera, 5700 San Luis, Argentina

and

G. Echeverria and G. Punte

LANADI e IFLP, Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina

Received November 29, 1999; in revised form March 6, 2000; accepted March 10, 2000; published online June 26, 2000

Diaquasuccinatocadmium(II) has been studied by single-crystal X-ray diffraction and FTIR and Raman spectroscopies at room temperature. The structure consists of seven-coordinated Cd atoms bridged by succinate ions to form two-dimensional polymers perpendicular to the *b* axis. Hydrogen bonds embracing one of the coordination water molecule and a carboxylate residue stabilize the three-dimensional structure. The spectroscopic data are consistent with the structural model. Thermal dehydration and decomposition processes have been also investigated using TG–DTA measurements, FTIR spectroscopy, and powder X-ray diffraction analysis. A phase transition of the amorphous anhydrous compound to a stable crystalline phase was observed at 262°C. © 2000 Academic Press

1. INTRODUCTION

The binding of metal ions to the dicarboxylate residues has been the subject of particular interest because of the importance of such interactions in a wide variety of metalloproteins. Metal complexes containing dicarboxylate ions such as malonate or α -substituted malonates have been taken as models for blood and bone calcium proteins that present the modified amino acid residues γ -carboxyglutamic acid and β -carboxyaspartic acid (1, 2). Several ways of binding, which can coexist, have been observed for carboxylate groups in these compounds: monodentate and bidentate modes as well as those involving bridging interactions that yield terdentate and tetradentate forms.

Within a general research program aimed to add to the understanding of the factors that influence the ways of

binding and the formation and stability of polymeric structures of, i.e., Ca(II), Zn(II), Cd(II), and lanthanide dicarboxylates we have recently reported the vibrational and thermal behavior of calcium malonate dihydrate in connection with its crystal structure which was also revised (3).

Although Cd(II) is a toxic metal, it is usually applied as a metallic probe of Ca(II) and Zn(II) sites due to its chemical similarity. ¹¹³Cd NMR spectroscopy has been extensively used in the study of many biological systems, such as metalloenzymes (4) and metallothionein (5). The S2 site in conalbumin A (6) and the EF site of parvalbumin (7, 8) have also been investigated on the basis of ¹¹³Cd chemical shift data. Amma and co-workers (9, 10) have carried out studies of model compounds to identify the nature of such biological sites. These probes have also been applied to investigate Zn(II) sites in metal-storage proteins like thioneins and in other proteins with cysteine ligands (11). The ¹¹³Cd NMR spectroscopy is an important tool to probe metal sites because it is very sensitive to the nature of donor atoms, coordination number, and geometry. However, its use is strongly dependent on the availability of single-crystal X-ray structure data to correlate Cd(II) signals with its environment. Several Cd(II) dicarboxylates with O donor atoms have been applied for this purpose; useful information can be provided, i.e., from the crystal structures of cadmium(II) malonate monohydrate (12), tetraaquobis(malonato)dicadmium(II) (13), and diaquasuccinatocadmium(II) hemihydrate (14), that have been reported in the literature. In the malonate complexes, the coordination for Cd is seven in the first case and six and eight in the last one. Seven coordination has also been observed in the mentioned succinate complex and in cadmium diacetate dihydrate (15).

Neither the diaquasuccinatocadmium(II) structural data nor its complete vibrational assignment and thermal

¹To whom correspondence should be addressed. E-mail: gnarda@unsl.edu.ar.

analysis were found in the literature. Thus, in order to obtain greater insight into properties of the metal dicarboxylate complexes, a full description of the single-crystal X-ray study, FTIR, and Raman analysis and TG-DTA measurements of the title compound were carried out and the results are presented below.

2. EXPERIMENTAL PROCEDURES

Diaquasuccinatocadmium(II) was prepared by dissolving 1 mmol of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Baker's Analyzed) in a 50-ml aqueous solution containing 2 mmol of succinic acid (Sigma) neutralized with NaOH to pH 7, under stirring. The solution was left to evaporate slowly at room temperature. A large number of colorless prismatic single crystals, suitable for the crystallographic study, was obtained after about 10 days, and these were then filtered, washed with distilled water, and dried on P_4O_{10} . Anal. Calcd for $\text{CdC}_4\text{H}_8\text{O}_6 \cdot \text{C}$, 18.17%; H, 3.03%; O, 36.29%; Cd, 42.51%. Found: C, 19.09%; H, 4.48%; O, 38.56%; Cd, 41.33%.

Single-crystal X-ray data were taken on an automatic four-circle CAD-4 diffractometer. For data collection and cell refinement, CAD-4 software was used (16). The program SDP (17) was employed for data reduction. The structure was solved by direct methods using SHELXS86 (18) and refined by full-matrix least-squares based on F^2 using SHELXL93 (19). The structural analysis was performed with PLATON (20) and with PARST (21). The hydrogen atoms were located from the difference-Fourier syntheses. Further refinements were performed with the hydrogen atom positions riding on bound C atoms. The molecular graphics were done with ORTEP (22) and PLATON (20). Crystal data, details of data collection and structure refinement are given in Table 1. The atomic coordinates are listed in Table 2. Table 3 displays selected interatomic distances and angles.

FTIR spectra were recorded on a Nicolet PROTÉGÉ 460 spectrometer in the $4000\text{--}225\text{ cm}^{-1}$ range with 32 scans using the KBr pellet technique. Raman spectrum was 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 accumulated. 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 $10^\circ\text{C min}^{-1}$ from room temperature to 1000°C . The decomposition process was followed 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 pyrolysis residue and intermediates.

TABLE 1
Crystal Data, Data Collection, and Structure Refinement
Details for $[\text{Cd}(\text{succ})(\text{H}_2\text{O})_2]$

Empirical formula	$\text{CdC}_4\text{H}_8\text{O}_6$
Formula weight	264.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 7.110(1)\text{ Å}$ $b = 15.100(2)\text{ Å}$, $\beta = 111.340(8)^\circ$ $c = 7.1690(6)\text{ Å}$
Volume	$716.90(15)\text{ Å}^3$
Z	4
Density (calculated)	2.451 Mg/m^3
Absorption coefficient	3.027 mm^{-1}
$F(000)$	512
Crystal size	$0.3 \times 0.25 \times 0.19\text{ mm}^3$
Theta range	$1\text{--}30^\circ$
Index ranges	$-9 \leq h \leq 9$, $0 \leq k \leq 21$, $0 \leq l \leq 10$
Absorption correction	Analytical (34)
Transmission factors	$T_{\text{min}} = 0.5141$, $T_{\text{max}} = 0.6213$
No. of reflections collected	2316
No. of independent reflections	2082 [$R(\text{int}) = 0.0202$]
No. of observed reflections	1825
	$[I > 2.0\sigma(I)]$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2081/0/101
Goodness-of-fit on F^2	1.119
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0238$, $wR2 = 0.0586$
R indices (all data)	$R1 = 0.0302$, $wR2 = 0.0645$
Largest diff. peak and hole	0.92 and -0.93 e Å^{-3}

Note. Source of atomic scattering factors, Ref. (35).

X-ray powder diagrams were obtained with a Rigaku D-MAX-IIIC diffractometer using $\text{CuK}\alpha$ radiation (Ni filter) and NaCl and quartz as external calibration standards.

TABLE 2
Final Coordinates and Equivalent Isotropic Displacement
Parameters of the Non-Hydrogen Atoms (Esds in Parentheses)

Atom	x	y	z	$U_{\text{eq}} [\text{Å}^2]^a$
Cd1	0.49045(3)	0.19689(1)	0.08011(3)	0.0204(1)
O1	0.1929(3)	0.13525(14)	0.0774(3)	0.0286(6)
O1W	0.3997(4)	0.2788(2)	0.3031(5)	0.0540(10)
O2	0.4509(3)	0.04863(16)	0.2216(4)	0.0331(7)
O2W	0.4974(3)	0.12956(16)	-0.2052(3)	0.0338(7)
O3	0.1200(3)	0.17048(16)	0.4948(4)	0.0359(7)
O4	-0.1949(3)	0.19659(13)	0.3116(3)	0.0255(5)
C1	0.2705(4)	0.07010(17)	0.1862(4)	0.0200(7)
C2	0.1468(4)	0.01749(17)	0.2784(4)	0.0226(7)
C3	-0.0553(4)	0.05963(18)	0.2545(4)	0.0227(7)
C4	-0.0404(4)	0.14718(18)	0.3602(4)	0.0203(6)

^a $U_{\text{eq}} = \frac{1}{3}$ of the trace of the orthogonalized \mathbf{U} tensor.

TABLE 3^a

(a) Bond distances [Å] and angles [deg]			
Cd1–O1	2.305(2)	O1W–H11W	0.791(4)
Cd1–O1W	2.292(3)	O1W–H12W	0.892(5)
Cd1–O2	2.515(2)	O2W–H21W	0.966(3)
Cd1–O2W	2.301(2)	O2W–H22W	0.787(3)
Cd1–O4 ⁱ	2.249(2)	C1–C2	1.505(4)
Cd1–O3 ⁱⁱ	2.376(2)	C2–C3	1.523(4)
Cd1–O4 ⁱⁱ	2.487(2)	C3–C4	1.508(4)
O1–C1	1.252(3)		
O2–C1	1.256(4)		
O3–C4	1.247(4)		
O4–C4	1.267(4)		
O1–Cd1–O1W	74.53(9)		
O1–Cd1–O2	53.63(8)		
O1–Cd1–O2W	97.51(8)		
O1–Cd1–C1	26.89(8)		
O1–Cd1–O4 ⁱ	131.99(7)		
O1–Cd1–O3 ⁱⁱ	141.17(8)		
O1–Cd1–O4 ⁱⁱ	91.63(7)	H11W–O1W–H12W	109.5(5)
O1W–Cd1–O2	95.62(10)	H21W–O2W–H22W	105.2(3)
O1W–Cd1–O2W	163.99(10)		
O1W–Cd1–O4 ⁱ	86.75(10)		
O1W–Cd1–O3 ⁱⁱ	87.63(10)		
O1W–Cd1–O4 ⁱⁱ	89.22(9)		
O2–Cd1–O2W	90.40(8)		
O2–Cd1–O4 ⁱ	85.86(8)	O1–C1–O2	121.0(3)
O2–Cd1–O3 ⁱⁱ	164.76(8)	O1–C1–C2	119.5(3)
O2–Cd1–O4 ⁱⁱ	141.48(8)	O2–C1–C2	119.5(2)
O2W–Cd1–O4 ⁱⁱ	76.96(7)	C1–C2–C3	114.1(2)
O2W–Cd1–O4 ⁱ	108.53(8)	C2–C3–C4	114.8(2)
O2W–Cd1–O3 ⁱⁱ	90.45(9)	O4–C4–C3	118.8(2)
O3 ⁱⁱ –Cd1–O4 ⁱ	79.45(8)	O3–C4–O4	120.3(3)
O4 ⁱ –Cd1–O4 ⁱⁱ	132.63(7)	O3–C4–C3	120.9(3)
O3 ⁱⁱ –Cd1–O4 ⁱⁱ	53.22(8)		
(b) Selected torsional angles [deg]			
O2–C1–C2–C3	169.7(3)		
O1–C1–C2–C3	–9.4(4)		
C1–C2–C3–C4	–64.4(3)		
C2–C3–C4–O4	163.5(2)		
C2–C3–C4–O3	–17.3(4)		

(c) Selected intermolecular distances [Å] and angles [deg]
 Cd ... Cd^{iii,iv} 4.3342(7)

D–H	A	Hydrogen bonds		
		D–H	H–A	D–H ... A
O1W–H1W1 ... O2W ^{vii}		0.791(4)	2.411(4)	157.9(4)
O1W–H1W2 ... O1 ^{vii}		0.891(5)	1.762(4)	163.9(4)
O2W–H2W1 ... O2 ^v		0.966(3)	1.775(3)	166.9(2)
O2W–H2W2 ... O3 ^{vi}		0.787(3)	2.056(3)	167.8(3)

^ai, 1 + x, y, z; ii, $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; iii, $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; iv, $\frac{3}{2} + x, \frac{1}{2} - y, \frac{3}{2} + z$; v, 1 - x, -y - z; vi, x, y, z - 1; vii, $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure

Figure 1 shows that the Cd atoms are seven-coordinated to O atoms, five of them belonging to three succinate moie-

ties and the remaining ones belonging to the two crystallographically inequivalent water molecules. Two of the succinate ligands bind the Cd ions through a bidentate interaction, while the third one shows a monodentate interaction. The analysis of the geometry of the coordination polyhedra 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. This type of coordination has also been observed in the cadmium succinate mentioned above (14) and in malonates (12). The coordination distances are within the range 2.249(2)–2.515(2) Å. The oxygen atom O4, which participates in the bidentate and in the monodentate interactions, bridges two Cd atoms, at a distance of 4.3342(7) Å, through the monodentate interaction. This exhibits the shortest coordination distance, 2.249(2) Å. The inspection of the succinate geometry shows (see Table 3) that both C–C–C angle values are similar, 114.1(2)° and 114.8(2)°. The C1,O1,O2 group, which is involved in a bidentate interaction, presents its plane out of the C1,C2,C3 plane by approximately 10°, while the C4,O3,O4 group, which is involved in a bidentate as well as in a monodentate interaction, is rotated approximately 17° out of the C2,C3,C4 plane. The C–O bond distances do not present noticeable differences. The strength of the coordination of the two crystallographically inequivalent water molecules (W1 and W2) to the Cd ion, as determined from their distance to the ion, is similar. The water molecule W2 is hydrogen bonded to two oxygen atoms belonging to the

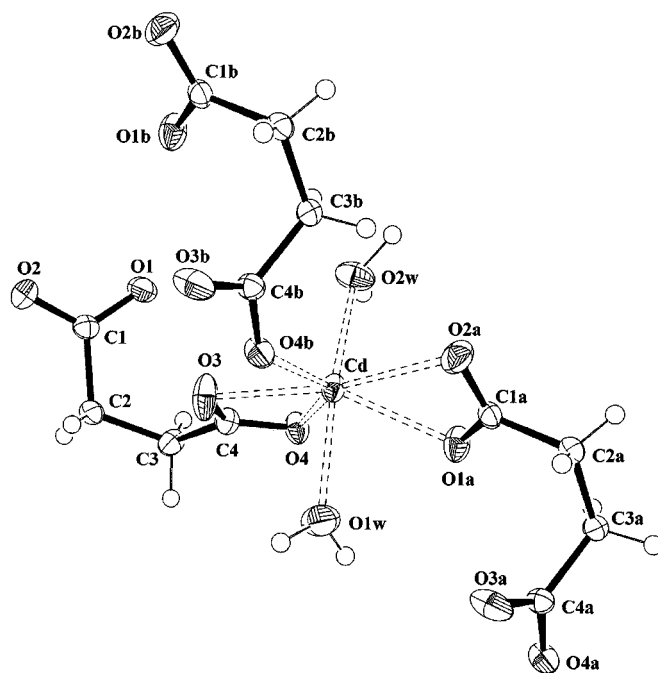


FIG. 1. ORTEP view of the Cd(II) coordination polyhedron.

succinate moiety, while the W1 water molecule is involved in one hydrogen bond with a succinate group and is weakly hydrogen bonded to W2. The difference in the strength of the hydrogen bonds involving W1 and W2 can be also assessed from the different thermal parameter of the corresponding O atoms. Table 2 shows that the U_{eq} of W1 is double the U_{eq} of W2. The structure of the title compound shows important differences with the structure of the diaquasuccinatocadmium(II) hemihydrate. In the title compound the crystal structure can be described as consistent of a bidimensional polymeric arrangement developed perpendicular to the crystallographic axis b . These (010) layers consist of two sets of chains of cadmium coordination polyhedra running approximately perpendicular. The hydrogen bonds involving the OW2 and O2 oxygen atoms link those layers of polymers stabilizing the three-dimensional structure. Figure 2 shows the corresponding molecular packing and hydrogen bonding interactions. It is reasonable to expect that its particular form of polymerization allows the compound to present a high aqueous solubility, such as other polymeric Cd(II) complexes of carboxylates (12). However, the persistence of the bidimensional polymers in the solution cannot be disregarded. Diaquasuccinatocadmium(II) hemihydrate structure consists of two crystallographically independent seven-coordinated Cd atoms bridged by succinate ions to form a three-dimensional polymer. No discussion about the interactions involving the water molecules present in its structure has been found in the literature.

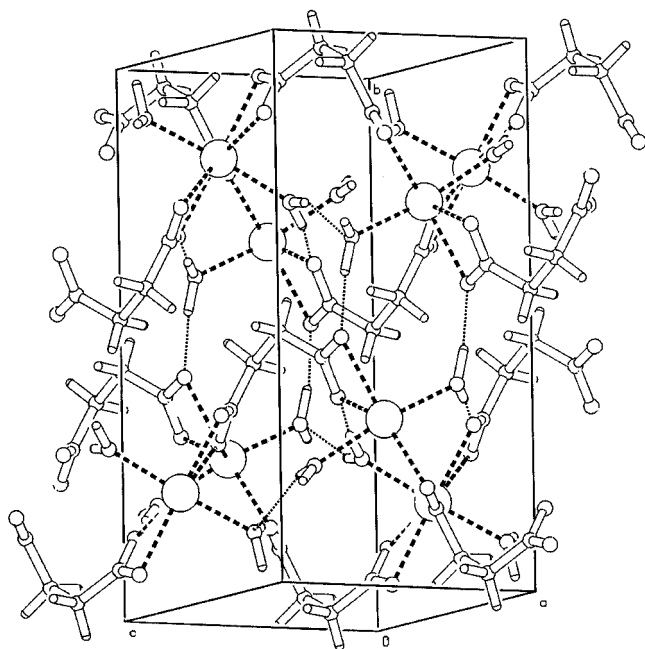


FIG. 2. Molecular packing showing the hydrogen bonds linking the bidimensional polymers.

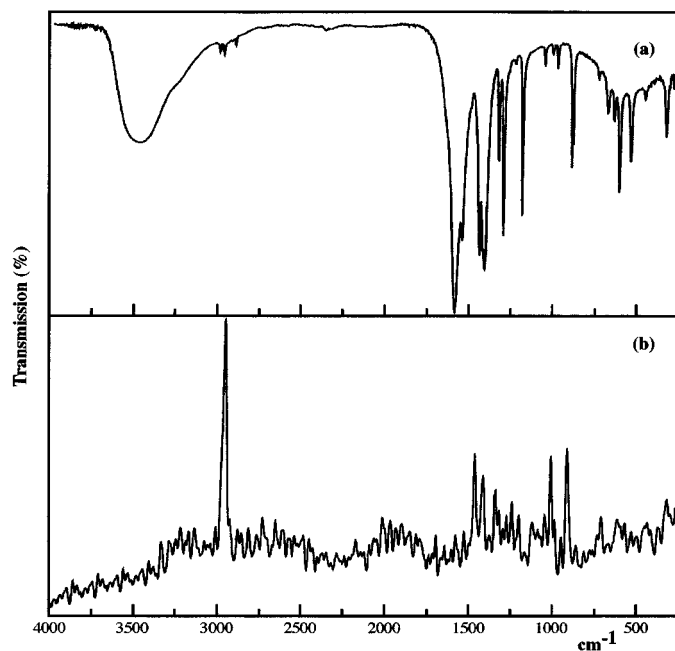


FIG. 3. (a) FTIR spectrum of $[\text{Cd}(\text{succ})(\text{H}_2\text{O})_2]$. (b) Raman spectrum of $[\text{Cd}(\text{succ})(\text{H}_2\text{O})_2]$.

3.2. Vibrational Spectra

The vibrational study has been carried out taking into account the structural characteristics outlined above. The internal vibrations can be described by means of the following building units: carboxylate groups, methylene groups and water molecules. The interpretation of its FTIR and Raman spectra is supported by their comparison with the spectroscopic data of succinic acid and related compounds found in literature (23–25). Figure 3 shows the FTIR and Raman spectra, and the proposed assignment is detailed in Table 4. Although the quality of the Raman spectrum attained was not high, it was useful for confirming the assignment of some modes, particularly the symmetric ones.

Water modes. In the FTIR spectrum appears one slightly asymmetric broad band centered at 3460 cm^{-1} , which can be assigned to $\nu(\text{OH})$. This frequency value is lower than the 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. The assignment was made taking into account the FTIR spectrum of completely dehydrated samples where no bands disappear except the OH stretching ones.

OCO group modes. Both carboxylate stretching modes appear to be split into two components, at $1585\text{--}1540$ and $1325\text{--}1300\text{ cm}^{-1}$. Coincidentally, the Raman spectrum

TABLE 4
Assignment of the Vibrational Spectra of
[Cd(succ)(H₂O)₂] (cm⁻¹)

FTIR	Raman	Assignment ^a
3460 (br)		$\nu(\text{OH})\text{W}$
2995 (w)		$\nu_{\text{as}}(\text{CH})$
2970 (w)		$\nu_{\text{as}}(\text{CH})$
2925 (sh)	2945 (s)	$\nu_{\text{s}}(\text{CH})$
2900 (w)		$\nu_{\text{s}}(\text{CH})$
1585 (vs)		$\nu_{\text{as}}(\text{OCO})$
1540 (s)		$\nu_{\text{as}}(\text{OCO})$
1440 (s)	1455 (m)	$\delta(\text{CH}_2)$
1405 (s)	1400 (m)	$\delta(\text{CH}_2)$
1325 (m)	1330 (w)	$\nu_{\text{s}}(\text{OCO})$
1300 (s)		$\nu_{\text{s}}(\text{OCO})$
1225 (vw)	1225 (w)	$\rho_{\text{w}}(\text{CH}_2)$
1185 (s)		$\nu_{\text{as}}(\text{CC})$
1055 (w)		-
1005 (vw)	995 (m)	$\nu_{\text{s}}(\text{CC})$
975 (w)		$\nu_{\text{s}}(\text{CC})$
890 (m)	895 (m)	$\rho_{\text{r}}(\text{CH}_2)$
880 (m)		$\rho_{\text{r}}(\text{CH}_2)$
730 (vw)		$\delta(\text{OCO})$
675 (w)		$\delta(\text{CC})$
635 (w)		$\rho_{\text{w}}(\text{OCO})$
605 (m)		$\rho_{\text{w}}(\text{OCO})$
535 (m)		$\pi(\text{OCO})$
450 (w)		$\rho_{\text{r}}(\text{OCO})$
325 (m)		$\delta(\text{CCO})$
280 (w)		$\nu(\text{M-O})$

^a ν_{as} , asymmetric stretching; ν_{s} , symmetric stretching; δ , deformation; ρ_{w} , wagging mode; ρ_{r} , rocking mode; π , out-of-plane deformation; br, broad; w, weak; sh, shoulder; s, strong; vs, very strong; m, medium; vw, very weak.

shows a line at 1330 cm⁻¹ assigned to the $\nu_{\text{s}}(\text{OCO})$ mode. No evidence of IR carbonyl absorption is present, in agreement with the observed C–O distances (see Table 3).

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), in accordance with the structural analysis.

A slight shift to higher frequencies can be observed for the $\nu_{\text{as}}(\text{OCO})$ as well as a shift to lower frequencies for the $\nu_{\text{s}}(\text{OCO})$ with respect to the values for ionic sodium succinate. According to a spectroscopic criterion the large $\Delta\nu$ value observed corresponds to the presence of an unsymmetrical bridging bidentate carboxylate ligands (26–28). This is consistent with the structural data description. The O3C4O4 group is involved in two binding modes that induce differences in the C–O distances larger than 2σ (see Table 3a).

The deformation modes are identified in IR at 730 cm⁻¹ [$\delta(\text{OCO})$], 635–605 cm⁻¹ [$\rho_{\text{w}}(\text{OCO})$], 535 cm⁻¹ [$\pi(\text{OCO})$], and 450 cm⁻¹ [$\rho_{\text{r}}(\text{OCO})$].

C–C modes. The IR band at 1185 cm⁻¹ is identified with the $\nu_{\text{as}}(\text{CC})$, whereas the bands at 1005 and 975 cm⁻¹ are attributed to the $\nu_{\text{s}}(\text{CC})$, this is consistent with a Raman line at 995 cm⁻¹. This mode occurs with the expected intensity in both the IR and the Raman spectra. The band at 675 cm⁻¹ in the FTIR spectrum is assigned to the $\delta(\text{CC})$ mode.

CH₂ group modes. Two sets of bands at 2995–2970 and 2925–2900 cm⁻¹ are assigned to the ν_{as} and ν_{s} modes for C–H, respectively. The latter mode is Raman active with a strongly polarized line at 2945 cm⁻¹.

Two bands at 1440 and 1405 cm⁻¹ are attributed to the bending mode of methylene; this assignment is consistent with the presence of Raman lines at 1455 and 1400 cm⁻¹. Wagging and rocking deformation modes are identified at 1225 and 890–880 cm⁻¹, respectively. The corresponding Raman lines occur at 1225 and 895 cm⁻¹.

The unlike environments of the inequivalent CH₂ groups lead to the observed splitting in their bending and rocking modes.

The band at 280 cm⁻¹ can be tentatively assigned to the Cd–O stretching mode since its intensity decreases after dehydration.

3.3. Thermal Behavior

The TG–DTA curves of cadmium succinate dihydrate are shown in Fig. 4.

The first DTA signal at 149°C corresponds to the dehydration process yielding the amorphous anhydrous compound; it occurs as a broad and asymmetric endothermic peak, indicating that water molecules are lost at different but close temperatures. This fact suggests some kind of 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.

The TG curve presents the corresponding experimental weight loss of 13.4% (theoretical, 13.6%). The loss of both water molecules could not be solved into two isolated stages even for experiments carried out at a lower heating rate (1°C min⁻¹).

A phase transition is observed at 262°C, where an exothermic peak not associated with mass change occurs. The next stage is associated with succinate ion decomposition resulting in cadmium oxide formation, confirmed by comparison of the decomposition product XRD with the JCPDS card 5-640 (29). The DTA curve shows a sharp exothermic peak at 417°C, coinciding with an experimental weight loss of 37.47% (theoretical, 37.79%).

Figure 5 shows the X-ray diffraction patterns for the initial compound, the anhydrous cadmium succinate, the sample treated at 270°C, and the final product. The later is

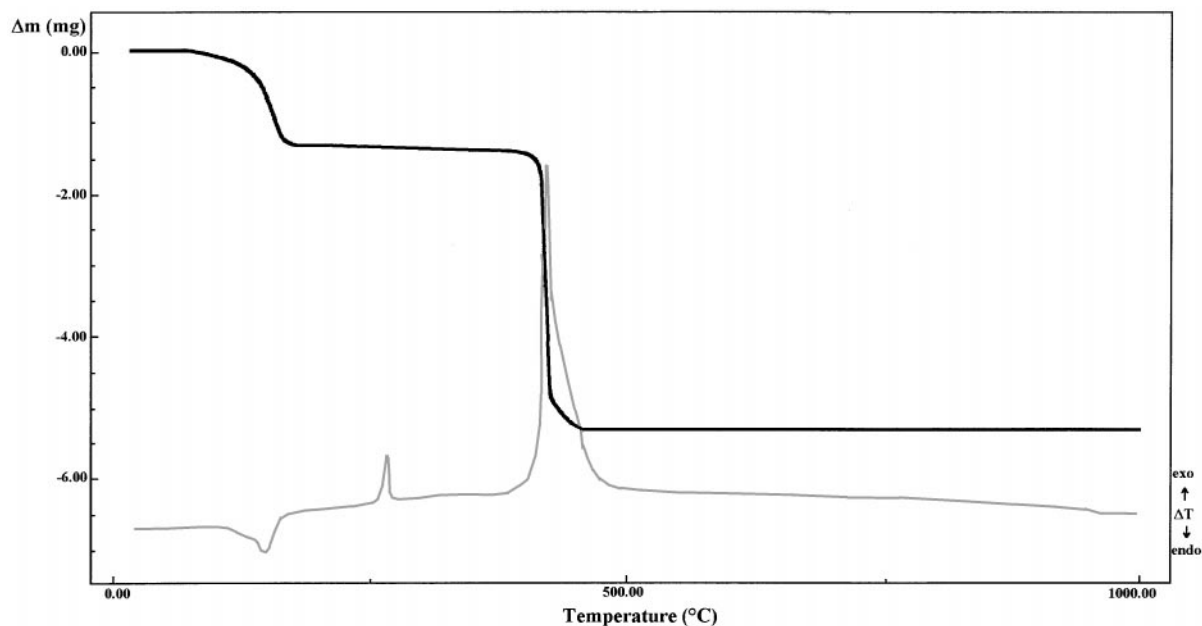


FIG. 4. TG-DTA curves of $[\text{Cd}(\text{succ})(\text{H}_2\text{O})_2]$.

stable up to 1000°C . The X-ray results indicate that the anhydrous salt is converted from amorphous to crystalline state through the exothermic process. The new phase increases its crystallinity on further heating and remains stable up to the succinate ion decomposition temperature.

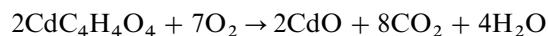
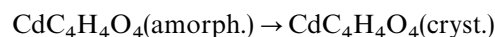
DTA measurements at 1°C min^{-1} up to 300°C showed no thermal effects on cooling to room temperature, indicating that the initial phase is not recovered. In addition, no changes are evident in the X-ray powder diagrams of this phase when the sample is kept at room temperature and dry atmosphere and measurements recorded weekly during two months.

The structural changes produced when going from the amorphous to the crystalline phase were also supported by FTIR spectrometry. No relevant modifications are observed in the vibrational behavior of these compounds in relation to $[\text{Cd}(\text{succ})(\text{H}_2\text{O})_2]$, except for the absence of the O–H water stretching modes and the relative intensification of the bands assigned to the $\rho_i(\text{CH}_2)$, $\rho_w(\text{CH}_2)$, and $\nu(\text{CC})$ modes.

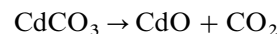
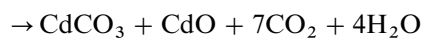
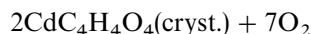
Taking into account that the Cd(II) bidimensional polymers are bonded by water molecules, it is reasonable to expect that water removal alters the coordination sphere and implies the loss of the three-dimensional structure by formation of a more stable amorphous phase which presents a less rigid structure. Several authors have performed thermal studies of various metal succinates under different experimental conditions (24, 30–32). Brzyska and Galkowska (32) have reported oxocarbonate, $\text{CdO}-\text{CdCO}_3$, an intermediate product, which further decomposes to CdO. Cadmium carbonate has not been ever detected in our X-ray

patterns. However, a change in the slope of the TG tracing is observed around 400°C which is accompanied with the broad nonsymmetric DTA peak. Besides, the FTIR spectra of samples treated at 430°C exhibit bands at 1390, 860, and 725 cm^{-1} that resemble those of the cadmium carbonate (33).

The thermal degradation course can be represented as follows:



The following reactions can also represent the last step:



4. CONCLUSIONS

This work reports the structural, vibrational, and thermal characterization of a new hydrate of cadmium succinate. Cd atoms are seven-coordinated to O atoms, five belonging to three succinate ions and the remaining ones to the two crystallographically inequivalent water molecules. Two of

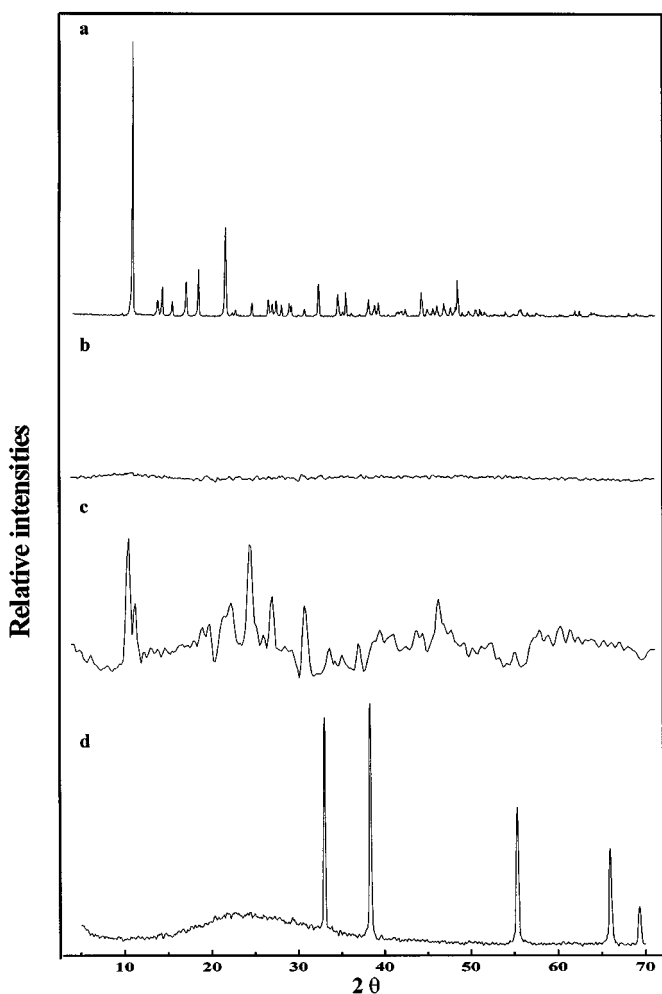


FIG. 5. DRX diagrams of (a) $[\text{Cd}(\text{succ})(\text{H}_2\text{O})_2]$, (b) $[\text{Cd}(\text{succ})]$, (c) new phase stable at 270°C , and (d) CdO , thermal decomposition final product.

the succinate ligands bind the Cd ions through a bidentate interaction, while the third one shows both bidentate and monodentate binding. These interactions yield an original bidimensional polymer. Coordination water molecules are differently involved in hydrogen bonds and link the layers of polymers stabilizing the three-dimensional structure.

The vibrational and thermal properties are in general consistent with the structural findings described above. A complete assignment of the title compound vibrational modes is proposed. The IR spectroscopic analysis allows us to confirm that the water molecules are involved in hydrogen bonds. The effect of the different types of carboxylate groups/Cd(II) interaction on the shape and position of the corresponding stretching bands is also observed in the FTIR spectrum. The dehydration process yields an amorphous compound. Transition from amorphous to crystalline phase was confirmed by X-ray patterns.

This study led to a deeper knowledge of the properties of crystalline Cd(II) dicarboxylate complexes. Taking into ac-

count the high aqueous solubility of the title compound, the present structural analysis renders additional data on Cd(II) environments potentially useful for crystal structure/ ^{113}Cd NMR spectroscopy correlations of the binding sites in biological systems, not only in solid state but also in solution.

ACKNOWLEDGMENTS

The authors thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET PID 4929), 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, 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 CONICET.

REFERENCES

1. A. Zell, H. Einspahr, and C. E. Bugg, *Biochemistry* **24**, 533 (1985).
2. D. J. Hodgson and R. O. Asplund, *Inorg. Chem.* **29**, 3612 (1990).
3. E. V. Brusau, G. E. Narda, G. Echeverría, G. Punte, and J. C. Pedregosa, *J. Solid State Chem.* **143**, 174 (1999).
4. D. B. Bailey, P. D. Ellis, and J. A. Free, *Biochemistry* **19**, 591 (1980).
5. Y. Boulanger, I. M. Armitage, K. A. Miklosy, and D. R. Winge, *J. Biol. Chem.* **257**, 13717 (1982).
6. D. B. Bailey, A. D. Cardin, W. D. Behnke, and P. D. Ellis, *J. Am. Chem. Soc.* **100**, 5236 (1978).
7. T. Drakenberg, B. Lindman, A. Cave, and J. Parello, *FEBS Lett.* **92**, 346 (1978).
8. A. Cave, J. Parello, T. Drakenberg, E. Thulin, and B. Lindman, *FEBS Lett.* **100**, 148 (1979).
9. P. F. Rodesiler, E. L. Amma, *J. Chem. Soc., Chem. Commun.* 182 (1982).
10. E. A. H. Griffith, N. G. Charles, K. Lewinski, E. L. Amma, and P. F. Rodesiler, *Inorg. Chem.* **26**, 3983 (1987).
11. I. Bertini, H. B. Gray, S. J. Lippard, and J. S. Valentine, "Bioinorganic Chemistry." University Science Books, Sausalito, CA (1994).
12. M. Post and J. Trotter, *J. Chem. Soc., Dalton Trans.* 1922 (1974).
13. K. H. Chung, E. Hong, Y. Do, and C. H. Moon, *J. Chem. Soc., Chem. Commun.* 2333 (1995).
14. E. A. H. Griffith, N. G. Charles, and E. L. Amma, *Acta Crystallogr.* **B38**, 262 (1982).
15. W. Harrison and J. Trotter, *J. Chem. Soc., Dalton Trans.* 956 (1972).
16. Enraf-Nonius CAD-4-PC, Version 1.2. Enraf-Nonius, Delft, The Netherlands (1993).
17. B. A. Frenz, "Enraf-Nonius Structure Determination Package." Enraf-Nonius, Delft, The Netherlands (1983).
18. G. M. Sheldrick, "SHELXS86, Program for the Solution of Crystal Structures." University of Göttingen, Germany (1985).
19. G. M. Sheldrick, "SHELXL93, Program for the Refinement of Crystal Structures." University of Göttingen, Germany (1993).
20. A. L. Spek, *Acta Crystallogr.* **A46**, C34 (1990).
21. M. Nardelli, PARST, *Comp. Chem.* **7**, 95 (1983).
22. C. K. Johnson, "ORTEPII. Report ORNL-5138." Oak Ridge National Laboratory, Oak Ridge, TN (1976).
23. L. J. Bellamy, "The IR spectra of complex molecules," Vol. I. Chapman and Hall, London (1975).
24. K. M. Abd El-Salaam, K.H. Halawani, and S.A. Fakiha, *Thermochim. Acta* **204**, 311 (1992).
25. Y. Suzuki, *Thermochim. Acta* **255**, 155 (1995).
26. A. Carillo, P. Vieles, and A. Banniol, *C.R. Acta Sci. Ser. C* **274**, 912 (1972).

27. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," Part B, 5th ed. J. Wiley and Sons, New York (1997).
28. G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.* **33**, 227 (1980).
29. International Center for Diffraction Data. JCPDS Data Base. Powder Diffraction File.
30. K. Nagase, H. Yokobayashi, K. Muraishi, and K. Sone, *Bull. Chem. Soc. Jpn.* **48**, 1612 (1975).
31. Y. Suzuki, K. Muraishi, and H. Ito, *Thermochim. Acta* **258**, 231 (1995).
32. W. Brzyska and B. Galkowska, *Polish J. Chem.* **72**, 498 (1998).
33. S. D. Ross, "Inorganic Infrared and Raman Spectra." Mc Graw-Hill Book Company, London (1972).
34. N. W. Alcock, *Cryst. Comput.* 271 (1970).
35. "International Tables for Crystallography," Vol. C (A. J. C. Wilson, Ed.). Kluwer Academic Publishers, Dordrecht, The Netherlands (1992).