PERGAMON

Polyhedron 21 (2002) 935–941

POLYHEDRON

www.elsevier.com/locate/poly

Cadmium complexation by aspartate. NMR studies and crystal structure of polymeric Cd(AspH)NO_3

Laura Gasque [a,*], Sylvain Bernès [b], Rosana Ferrari [a], Guillermo Mendoza-Díaz [c]

[a] *Departamento de Química Inorgánica, Facultad de Química, Universidad Nacional, Autónoma de México, Ciudad Universitaria, C.P. Mexico, D.F. 04510, Mexico*

[b] *Centro de Química, Instituto de Ciencias, B. Universidad Autónoma de Puebla, Apartado Postal 1613, Puebla, Pue., Mexico*

[c] *Facultad de Química, Universidad de Guanajuato, Noria Alta s/n, Guanajuato, Gto. 36050, Mexico*

Received 10 September 2001; accepted 24 January 2002

Abstract

Two cadmium compounds containing the aspartate ligand are described, with compositions Cd(AspH)NO_3 and Cd(Asp). The crystal structure of the first shows it is a two dimensional polymer in which each cadmium is coordinated to seven oxygen atoms, four from carboxylates and three from the nitrate moiety which acts both as a chelate and as a bridging ligand. For Cd(Asp), ^{111}Cd NMR studies suggests the presence of Cd–NH_2 interaction. © 2002 Published by Elsevier Science Ltd.

Keywords: Cadmium(II); Aspartate; Structures; ^{111}Cd NMR

1. Introduction

Though not as widely known to the general public as lead's, cadmium's toxicity is considerably larger [1]. As is the case with lead, the specific chemical interactions responsible for cadmium's toxicity are mostly unknown, although there has been some evidence that it mainly interferes in Zn^{2+} and Ca^{2+} sites and metabolism. The Cd uptake level is influenced by the calcium concentrations in the diet in a similar way as Lead, i.e. decreased by the increase of Ca intake [2]. The affinity that Cd^{2+} ion shows toward calcium binding sites, which are rich in aspartyl and glutamyl residues, has led to its use as a tool in studies of calcium binding sites in many systems as calbindin D_{9K} [3].

Similarities between cadmium and lead have been pointed out before, as one of several pairs of elements related by a knight's movement in the periodic table [4]. And just like lead's, classification of cadmium in the HSAB scheme has given problems, with some authors placing it among the soft acids, in agreement with Pearson's original papers [5] while others consider it borderline [6].

The behaviour of cadmium towards aminoacids has been studied both in solution and in the solid state. Stability constants for the 1:1 complexes are found to be consistently lower than for the corresponding lead complexes, usually for a little less than a logarithmic unit [7]. Several crystal structures of Cadmium–aminoacid complexes have been described [8]. The diversity of complexation modes is remarkable; from simple molecular structures with chelating aminoacid moieties, to polymeric structures where one or more of the donor groups are not coordinated to the metal.

In a recent paper, we reported two different lead complexes with aspartate, Pb(Asp) and Pb(AspH)NO_3 [9]. The X-ray structure of the latter showed it forms a three dimensional polymeric network in which each lead atom is coordinated only to oxygen atoms, from both carboxyl groups and the nitrate ion, while spectroscopic studies suggested amine group coordination in the former. Here, we present two cadmium–aspartate complexes with equivalent composition to those of lead, and discuss comparatively their structures.

---

* Corresponding author. Tel.: +52-5-622-3811; fax: +52-5-622-3724.

E-mail address: gasquel@servidor.unam.mx (L. Gasque).

PII: S0277-5387(02)00871-9

2. Experimental

Cadmium nitrate tetrahydrate and cadmium oxide were purchased from Aldrich; L-aspartic acid and L-aspartic acid monosodium salt hydrate from Sigma Chemical Co. Elemental analysis were carried out by Desert Analytics, Tucson, AZ.

2.1. *Preparation of Cd(AspH)(NO$_3$) (**I**)*

To 5 mmol of Cd(NO$_3$)$_2$·4H$_2$O dissolved in 25 ml of water, 5 mmol of NaAspH in 25 ml of water were added and pH adjusted to 4.3 with 1 M NaOH. The solution was left to stand and colourless prismatic crystals were collected after a few weeks. *Anal*. Calc. for Cd(C$_4$H$_6$N$_2$O$_7$): C, 15.68; H, 1.96; N, 9.15. Found: C, 15.63; H, 2.08; N, 8.89%.

2.2. *Preparation of Cd(Asp) (**II**)*

Five mmol AspH$_2$ were dissolved in 150 ml of warm water and to this solution 2.5 mmol finely ground CdO were added in small portions, allowing for the solid CdO to dissolve after each addition. The clear solution was evaporated with the formation of a glassy material which analysed for Cd(Asp)·1.5H$_2$O. *Anal*. Calc. for CdC$_4$H$_6$O$_{5.5}$N: C, 17.76; H, 2.96; N, 5.18. Found: C, 17.32; H, 2.81; N, 5.02%.

2.3. *Crystallography*

Single-crystal X-ray diffraction data for **1** were measured at 298 K on a Bruker P4 diffractometer using common procedures [10] and a correction for absorption effect was applied based on 50 ψ-scans with χ close to 90°. The structure was solved and refined using standard procedures [11], without restraints nor constraints. H atoms were placed on idealised positions and refined using a riding model with fixed isotropic U. The refinement of a Flack parameter [12] confirmed the absolute configuration of the enantiopure amino acid AspH to be C3-*S*. Pertinent crystal data are collected in Table 1 and complete crystallographic information is deposited as a CIF file.

2.4. *NMR spectroscopy*

The ^{111}Cd CP-MAS NMR were recorded on a VARIAN Unity-Plus 300 MHz spectrometer operating at 63.602 MHz with a 7.5 μσ pulse. A 7 mm diameter silicon nitride rotor with kel-F caps was used. The rotor spin rate was kept between 3.5 and 5 KHz for all experiments, with a delay time between 5 and 10 s and between 500 and 10 000 transients were accumulated, 1–2.5 ms of contact time for cross polarisation was used, 0.05 s of acquisition time. CdCO$_3$ was used as external reference (−30 ppm). Spectra were recorded using total side band suppression when side bands were not well removed by spinning. Processing was made using a 20–40.11 Hz of line broadening, with the exception of the compound (II) spectra, where a 530 Hz line broadening was used. ^{13}C-CP-MAS NMR were recorded on the same spectrometer operating at 75.430 MHz, acquisition time 0.05 s. Typical contact times employed were of 1.25 ms; pulse width of 8.5 μS, and delay time of 4 s. Processing was made with zero filling and a line broadening of 20.33 Hz.

Table 1
Crystal data

Empirical formula	$C_4H_6CdN_2O_7$
Formula weight	306.51
Crystal system	orthorhombic
Colour, habit	colourless, regular prism
Crystal size (mm)	0.28 × 0.22 × 0.14
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	7.1577(3)
b (Å)	7.2892(5)
c (Å)	14.9510(10)
Z	4
Absorption coefficient (mm^{-1})	2.819
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
2θ Range (°)	5.44–59.98
Reflections collected	2675
Independent reflections [a]	2276 ($R_{int} = 2.15\%$)
Transmission factors (min, max)	0.257, 0.281
Final R indices [2156 $I > 2\sigma(I)$] (%) [a]	$R_1 = 2.61$, $wR_2 = 6.74$
Final R indices [all data] (%) [a]	$R_1 = 2.81$, $wR_2 = 6.88$
Goodness-of-fit, S [a]	1.042
Data-to-parameters ratio	2276/128

[a] R_{int}, R_1, wR_2 and S are defined as follows:

$$R_{int} = \frac{\sum |F_o^2 - \langle F_o^2 \rangle|}{\sum F_o^2}, \quad R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|},$$

$$wR_2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}, \quad S = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{m - n}}.$$

Solution ^{1}H NMR was made at 299.950 MHz with a VT-Switchable broad band probe; acquisition time 2.503 s, pulse of 45° (7.5 μs). Processing was made with zero filling and a line broadening apodisation of 1 Hz. In a typical experiment 32 transients were collected. D$_2$O was used as a solvent and pD was fixed with either DCl or NaOD.

3. Results and discussion

3.1. *Crystal structure*

Relevant bond distances and angles for complex **1** are displayed in Table 2. The asymmetric unit contains one metal centre, one aspartate ligand and one nitrate ion,

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**

Bond lengths			
Cd(1)−O(1)	2.213(3)	Cd(1)−O(4)#1	2.242(2)
Cd(1)−O(2)#2	2.258(2)	Cd(1)−O(3)#3	2.273(2)
Cd(1)−O(12)	2.464(3)	Cd(1)−O(11)	2.529(3)
Cd(1)−O(11)#4	2.600(3)	C(1)−O(1)	1.254(4)
C(1)−O(2)	1.273(4)	C(4)−O(3)	1.250(4)
C(4)−O(4)	1.248(4)	N(11)−O(13)	1.219(4)
N(11)−O(12)	1.258(4)	N(11)−O(11)	1.272(4)
Bond angles			
O(1)−Cd(1)−O(4)#1	87.15(10)	O(1)−Cd(1)−O(2)#2	171.03(9)
O(4)#1−Cd(1)−O(2)#2	101.38(10)	O(1)−Cd(1)−O(3)#3	91.27(10)
O(4)#1−Cd(1)−O(3)#3	149.38(10)	O(2)#2−Cd(1)−O(3)#3	82.81(10)
O(1)−Cd(1)−O(12)	85.36(10)	O(4)#1−Cd(1)−O(12)	127.67(9)
O(2)#2−Cd(1)−O(12)	87.19(10)	O(3)#3−Cd(1)−O(12)	82.56(10)
O(1)−Cd(1)−O(11)	85.49(10)	O(4)#1−Cd(1)−O(11)	76.80(9)
O(2)#2−Cd(1)−O(11)	93.70(9)	O(3)#3−Cd(1)−O(11)	133.58(10)
O(12)−Cd(1)−O(11)	51.02(9)	O(1)−Cd(1)−O(11)#4	105.87(10)
O(4)#1−Cd(1)−O(11)#4	72.22(9)	O(2)#2−Cd(1)−O(11)#4	79.67(9)
O(3)#3−Cd(1)−O(11)#4	78.87(10)	O(12)−Cd(1)−O(11)#4	158.40(9)
O(11)−Cd(1)−O(11)#4	146.20(6)	O(1)−C(1)−O(2)	125.5(3)
O(1)−C(1)−C(2)	115.8(3)	O(2)−C(1)−C(2)	118.6(3)
O(3)−C(4)−O(4)	128.5(3)	O(3)−C(4)−C(3)	117.6(3)
O(4)−C(4)−C(3)	113.8(3)		

Symmetry transformations used to generate equivalent atoms: #1, $-x+1, y+1/2, -z+1/2$; #2, $-x, y+1/2, -z+1/2$; #3, $x-1, y, z$; #4, $-x, y-1/2, -z+1/2$.

yielding a formula similar to that of Pb(AspH)(NO$_3$) [9]. Nevertheless, the coordination geometry and the polymeric arrangement are different when substituting Pb(II) by Cd(II). As expected from the conditions of synthesis, the aspartate moiety presents two carboxylate groups while the amine function is protonated. The metal centre is seven-coordinated, with a geometry that can be described as distorted octahedral, where the sixth position is doubly occupied by two O atoms from the bidentating nitrate ion. Remaining coordination sites are occupied by one O atom from an crystallographic equivalent nitrate ion *trans* to the first one and four O atoms from 4 equiv. aspartate ligands *cis* to the nitrate moieties, as described in Fig. 1. Coordination distances span a range common for Cd(II) complexes [13], 2.213(3)–2.600(3) Å. The distortion from an ideal octahedral geometry is obvious, for example, from *trans* angles O1−Cd1−O2′ = 171.03(9)°, O3−Cd1−O4 = 149.38(10)° and from the bite *cis* angle formed by the nitrate ligand, O11−Cd1−O12 = 51.02(9)°, while remaining angles are in the range 72.22(9)°–133.58(10)°.

The complex is assembled in an original bi-dimensional polymeric network composed of perpendicularly connected chains (see Fig. 2). The main chains, running along the crystallographic *b* axis, result from the bridging character of the nitrate ion: O11 bridges 2 equiv. metallic centres, O12 is coordinated to one Cd atom and O13 is coordination-free. The different behaviour of each of these O atoms is clearly reflected in the N−O bond lengths (see Table 2), which can be compared with the N−O bond length of the free nitrate ion, 1.21 Å [14]. The 2D-polymer is formed by the connection of these chains through the α and β groups of the aspartate ligands along the *a* axis of the orthorhombic cell: O1 and O2 atoms from an aspartate ligand bridge two neighbouring Cd atoms of the previously described chain (running along the *b* axis) and the O3 and O4 atoms of the same ligand bridge two neighbouring Cd atoms of an other chain. In contrast to the iso-formula Pb complex [9], C−O bond lengths of the α and β carboxylic groups in **1** fall in a small range, 1.248(4)–1.273(4) Å. An other structural difference between Pb(AspH)(NO$_3$) and Cd(AspH)(NO$_3$) is that the polymeric connection of first one generates 18-membered rings containing three Pb ions and three AspH ligands, while for the last one the polymer includes 14-membered rings based on two Cd ions and two AspH ligands.

Moderate to weak hydrogen bonds sustain the cohesion between the 2D layers stacked along the *c* axis. The three H atoms of the ammonium group give short contacts with the three O atoms of the nitrate anion, with N−H···O separations ranging from 2.31 to 2.64 Å and angle from 118.0° to 148.3°. The carboxylic groups also participate as donor atoms in this network, with contacts N1−H1C···O2 (2.57 Å, 128.0°) and N1−H1B ···O3 (2.56 Å, 158.2°). Finally, weak contacts are directed approximately along the *c* axis, using the aliphatic groups of the asp ligand as acceptor (C2 and C3) and O atoms as donors (O1, O12 and O13). C−H··· O distances and angles ranges are characteristic of weak bonds: 2.48–2.58 Å and 136.7°–171.0°. (Table 3). These interactions are illustrated in Fig. 3.

3.2. NMR spectra

3.2.1. ^{111}Cd CP-MAS NMR spectra

Usually, ^{113}Cd is preferred since it has a slightly higher receptivity, but ^{111}Cd can also be used without an appreciable receptivity loss. As there is no primary isotope effect, results obtained on both isotopes can be directly compared [15]. As a tool for elucidating the coordination environment on the cadmium atom, a general observed trend for the Cd nuclei chemical shifts has been described [16,17]: shielding on a Cd atom is: (1) decreased when it is bonded to nitrogen (low field shift); (2) increased when bonded to oxygen (high field shift), but (3) decreased when it is part of a chelate ring. In the Cd CP-MAS spectra, distortions from octahedral symmetry are sufficient to produce large chemical shift anisotropies [18].

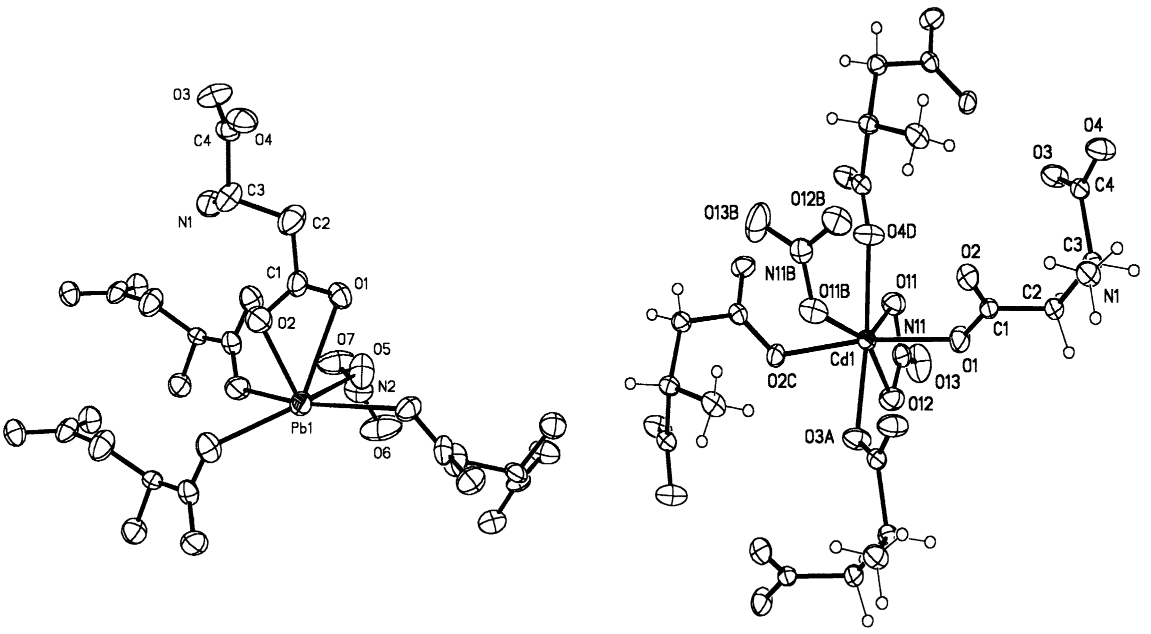


Fig. 1. The coordination environment for Cd atoms in **1** (right side) compared with the observed coordination environment in the isoformular Pb complex [9] (left side). Note that the metal centre is seven-coordinated in **1** and six-coordinated in Pb(AspH)(NO_3), leaving a large space available for a lone pair in the latter case. Thermal ellipsoids for **1** are at 50% probability level and symmetry codes used to generate equivalent atoms are the following: (A) $x-1, y, z$; (B) $-x, y-1/2, -z+1/2$, (C) $-x, y+1/2, -z+1/2$; (D) $-x+1, y+1/2; -z+1/2$.

In Cd(AspH)NO_3 (**I**), where there are seven oxygen atoms coordinated to each cadmium, an isotropic chemical shift of −78.6 ppm relative to $[Cd(H_2O)_6](ClO_4)_2$, was observed. In the latter each

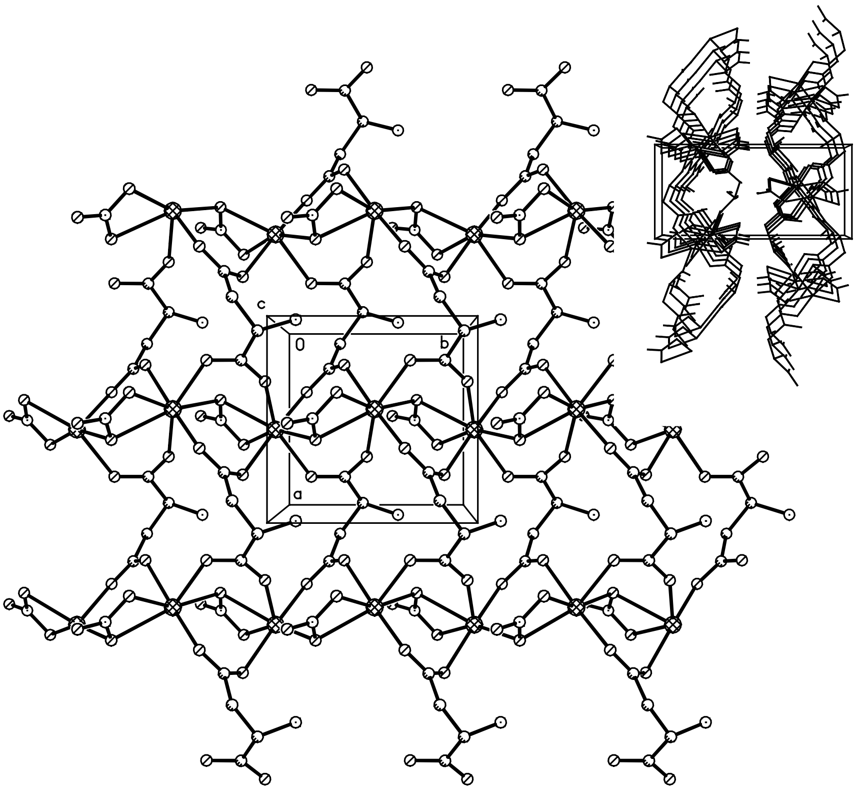


Fig. 2. The 2D polymeric layers of **1** viewed along the [001] axis. The inset shows a stick representation of two layers in a view normal to the [010] axis, i.e. as observed rotating the main figure around [100] by an angle of 90°. Note that no inter-layers contacts are observed, justifying the description of the polymer as an actual 2D framework. In both figures, H atoms are omitted for clarity.

Table 3
Hydrogen-bonds (Å and °), H···A < r (Å)+2.000 Å and D–H···A > 110°

D	H	A	Symmetry for A	D–H	H···A	D···A	D–H···A
N1	H1A	O11	$x, y-1, z$	0.890	2.462	2.985	117.96
N1	H1A	O13	$x+1/2, -y+3/2, -z$	0.890	2.561	3.139	123.24
N1	H1A	O12	$x+1/2, -y+3/2, -z$	0.890	2.637	3.320	134.26
N1	H1B	O2		0.890	2.259	2.838	122.48
N1	H1B	O3	$-x+1, y-1/2, -z+1/2$	0.890	2.559	3.401	158.19
N1	H1C	O12	$x+1, y-1, z$	0.890	2.310	3.103	148.31
N1	H1C	O2	$-x+1, y-1/2, -z+1/2$	0.890	2.568	3.193	127.95

D, donor atom; A, acceptor atom.

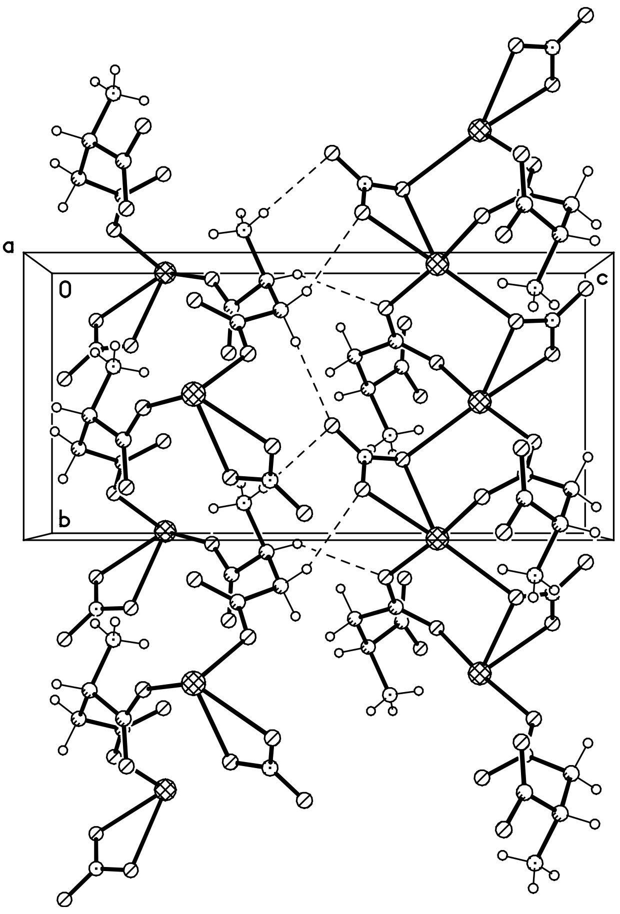


Fig. 3. Hydrogen bonding network.

Cd atom is coordinated octahedrally to six oxygen atoms from water molecules [19,20] i.e. a high field shifting is observed, as expected from the general trends mentioned above.

Nitrate chelation may be the cause of the apparent second order coupling between ^{111}Cd and ^{14}N in complex **I** as it can be seen in Fig. 4(b), together with the deconvoluted spectrum from which it is possible to see a 1:2:1 pattern, that displays a coupling constant of 125 Hz. As far as we know, there are no reported values for this second order coupling. This splitting includes the second order coupling constant and the residual splitting due to the residual dipolar interaction between ^{111}Cd and ^{14}N [21,22].

On the other hand, the spectrum for compound **II** has a very irregular, broad signal centred on 70 ppm with the highest peak in 36 ppm. This positive chemical shift is indicative of a coordination to one or more nitrogen atoms. Unfortunately, it is not possible to observe the coupling pattern between ^{111}Cd and ^{14}N. There are examples in the literature [22–26] of Cd–N environments that do not show noticeable coupling. In these cases, the observed line widths have been greater than the coupling. In complex **II**, the cadmium atom seems to be immersed in very asymmetrical site, and therefore, in spite of the spin rate used to obtain the spectrum, anisotropy could not be removed.

3.2.2. ^{13}C CP-MAS NMR spectra

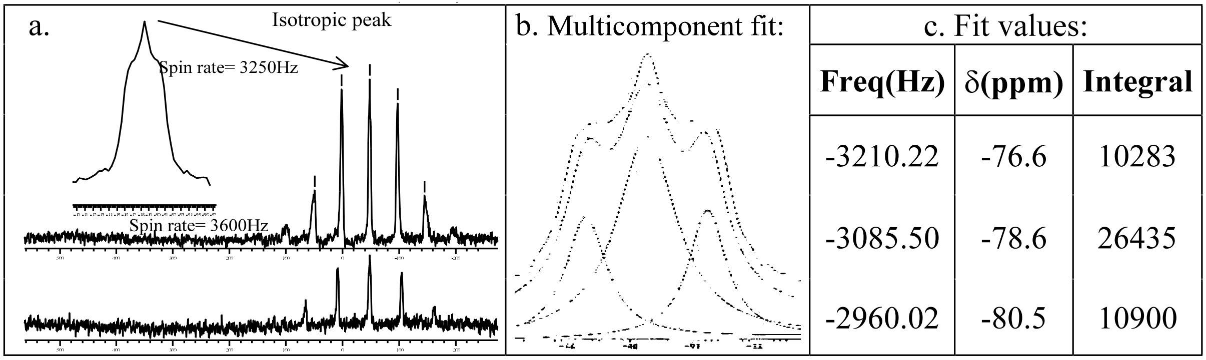
^{13}C NMR chemical shifts (ppm) are shown in Table 4. Compound **II** presents only one signal for carboxylic carbon atoms; indicating that in this compound the chemical environment for both carboxylates is quite similar. In compound **I**, however, even though both carboxylate groups are coordinated to cadmium nuclei, COOβ is involved in the strongest H-bond present in the crystal (H···O2 = 2.259 Å; N···O2 = 2.838 Å) with a H atom from the NH_3^+ group; besides, the other oxygen atom (O1) in COOβ has the strongest interaction with Cd^{2+} (shortest bond distance). Both interactions can cause a downfield shift for the COOβ carbon atom.

For compound **II**, not only the carboxylate carbon atoms show a sensible shift, but also the aliphatic ones. This could suggest the formation of a six membered chelate ring by the coordination of the amino group and the COOβ, in agreement with the observed Cd-CP-MAS data.

3.2.3. ^{1}H NMR versus pH

At a pH value close to the one used for crystallisation, the aminoacid, in presence of Cd^{2+}, develops a pattern of an ABC [27] spin system in the α-H signal (Fig. 5).

Considering the protonation state of the amine, a possible interpretation would be the formation of a chelate ring by the bonding of both carboxylate groups



Freq(Hz)	δ(ppm)	Integral
-3210.22	-76.6	10283
-3085.50	-78.6	26435
-2960.02	-80.5	10900

Fig. 4. ^{111}Cd NMR spectrum.

Table 4
^{13}C NMR chemical shifts (ppm)

Nucleus	AspH$_2$	NaAspH	Cd(AspH)NO$_3$ (**I**)	Cd(Asp) (**II**)
COOα	176.32	174.24	174.56	180.67
CH	54.11	48.9	55.16	52.23
CH$_2$	38.26	34.85	34.76	40.50
COOβ	175.25	174.24	182.75	180.67

(α and β) to cadmium. By doing so, both β hydrogen atoms would become distinguishable turning into a BC spin system rather than B$_2$.

When the amine group deprotonates, at a higher pH value, a different chelate ring is feasible due to the coordination of the amino group and the α carboxylate oxygen atom, releasing the β carboxylate and therefore, both hydrogen atoms on the CH$_2$ moiety become again indistinguishable, causing the system to return to an AB$_2$ pattern. As it has been discussed, the compound as is isolated near pH 4, has no chelate rings formed by the two carboxylates and formation of a 3D polymer is preferred.

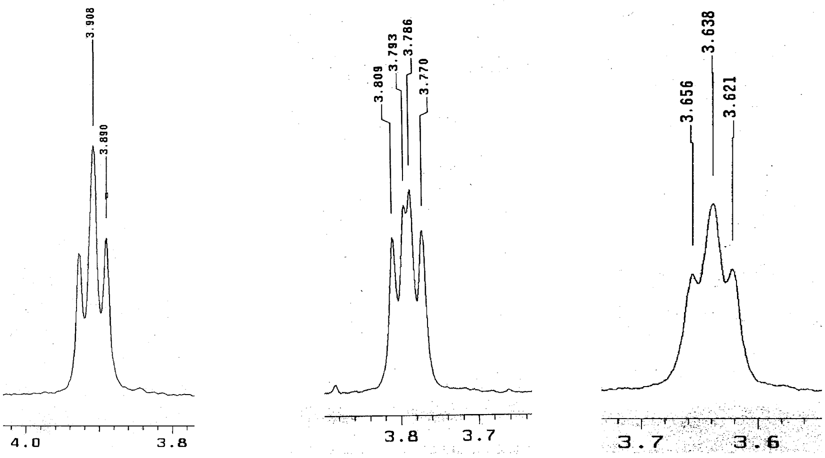
The accumulation of information on structural details of cadmium aqueous coordination chemistry—which is currently scarce—will hopefully contribute to a better understanding of this metal ion's interaction with biological molecules.

4. Supplementary material

Crystallographic data have been deposited with the CCDC. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) quoting the deposition number CCDC 169070.

Acknowledgements

S.B. is grateful to CONACyT for financial support (programa de retención, 000027).



Cd + Asp, pH=3.1 spin system AB$_2$ Cd + Asp, pH=4.2 spin system ABC Cd + Asp, pH=6.6

Fig. 5. ^{1}H NMR signal for $^{\alpha}$C–H at different pH values (Fig. 1).

References

[1] W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, Wiley, Chichester, UK, 1991.

[2] (a) P. Washko, R.J. Cousins, J. Nutr. 107 (1977) 920;
(b) P. Washko, R.J. Cousins, J. Toxicol. Environ. Health 1 (1976) 1055;
(c) A.A. Van Barneveld, C.J. Van der Hamer, Toxicol. Appl. Pharmacol. 79 (1985) 1.

[3] (a) S. Linse, W.J. Chazin, Protein Sci. 4 (1995) 1038;
(b) W. Chazin, T.D. Veenstra, Rapid Commun. Mass Spectrom. 13 (1999) 548;
(c) M. Akke, N. Skelton, J. Kordel, A.G. Palmer, W.J. Chazin, Biochemistry 32 (1993) 9832;
(d) N. Skelton, J. Koerdel, M. Akke, W.J. Chazin, J. Mol. Biol. 227 (1992) 1100;
(e) M. Akke, S. Forsén, W.J. Chazin, J. Mol. Biol. 252 (1995) 102;
(f) J. Matysik, A. Alia, G. Nachtegaal, H.J. van Gorkom, A.J. Hoff, H.J. de Groot, Biochemistry 39 (2000) 6751.

[4] M. Laing, South Afr. J. Sci. 87 (1991) 285.

[5] (a) R.G. Pearson, J. Chem. Ed. 45 (1968) 581;
(b) J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry Principles of Structure and Reactivity, fourth ed., Harper Collins, New York, 1993.

[6] (a) R.B. Martin, in: Seiler, Sigel, Sigel (Eds.), Handbook on Toxicity of Inorganic Compounds, Marcel Dekker, New York, 1988;
(b) G. Wulfsberg, Inorganic Chemistry, University Science Books, Sausalito, CA, 2000;
(c) G. Rayner-Canham, Descriptive Inorganic Chemistry, Freeman, New York, NY, 1996.

[7] A.E. Martell, R.M. Smith, Critical Stability Constants, vol. 1, Plenum, New York, 1977.

[8] (a) Y. Yukawa, Y. Inomata, T. Takeuchi, M. Simio, A. Ouchi, Bull. Chem. Soc. Jpn. 55 (1982) 335;
(b) A. Demaret, F. Abraham, Acta Crystallogr., Sect. C 43 (1987) 2067;
(c) M.Q. Ehsan, K.M.A. Malik, S.Z. Haider, J. Bangladesh Acad. Sci. 20 (1987) 175;
(d) P.J. Barrie, A. Gyani, M. Monteualli, P. O'Brian, Inorg. Chem. 32 (1993) 5262;
(e) H. Fuess, H. Bartunik, Acta Crystallogr., Sect. B 32 (1976) 2803;
(f) R.J. Flook, H.C. Freeman, C.J. Moore, M.L. Scudder, Chem. Commun. (1973) 753;
(g) D.W. Tomlin, T.M. Cooper, S.M. Cline, J.M. Hughees, W.W. Adams, Acta Crystallogr., Sect. C 53 (1997) 1815;
(h) A. Demaret, L. Abello, M. Fourati, G. Lapluye, J. Chem. Res. 354 (1978) 4339;
(i) R. Thulasidhass, J.K. Mohanarao, Curr. Sci. 49 (1980) 349;
(j) P. DeMester, D.J. Hodgson, J. Am. Chem. Soc. 99 (1977) 6884;
(k) H. Soylu, Eur. Cryst. Meeting 5 (1977) 313;
(l) I. Schaffers, D.A. Keszler, Acta Crystallogr., Sect. C 491 (1993) 156.

[9] L. Gasque, S. Bernès, R. Ferrari, C. Barbarín, M.J. Gutiérrez, G. Mendoza-Díaz, Polyhedron 19 (2000) 649.

[10] XSCANS Users Manual, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1996.

[11] G.M. Sheldrick, SHELXTL-PLUS, release 5.10, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1998; G.M. Sheldrick, SHELX-97 Users Manual, University of Göttingen, Germany, 1997.

[12] H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876.

[13] G. Wilkinson, Comprehensive Co-ordination Chemistry, vol. 5, Pergamon, Oxford, UK, 1987.

[14] P. Pascal, Noveau Traité de Chimie Minérale. Tome X. Massun ET C^{ie} Editeurs, Paris, 1956.

[15] P. Grauger, Groups 11 and 12, Copper to Mercury; in P.S. Pergostin (Ed.), Transition Metal Nuclear Magnetic Resonance, 1st ed., 293, 1991.

[16] P.G. Mennitt, M.P. Shatlock, V.J. Bartuska, G.E. Maciel, J. Phys. Chem. 85 (1981) 2087.

[17] T. Takayama, S. Ohuchida, Y. Koike, M. Watanabe, D. Hashizume, Y. Ohashi, Bull. Chem. Soc. Jpn. 69 (1996) 1579.

[18] R.S. Honkonen, P.S. Marchetti, P.D. Ellis, J. Am. Chem. Soc. 108 (1986) 912.

[19] M.F. Summers, Coord. Chem. Rev. 86 (1988) 43.

[20] B. King, Enciclopedia of Inorganic Chemistry, vol. 1, Wiley, Chichester, UK, 1995.

[21] K. Eichele, R. Wasylishen, Inorg. Chem. 33 (1994) 2766.

[22] P.J. Barrie, A. Gyanu, M. Motevalli, P. O'Brien, Inorg. Chem. 32 (1993) 3862.

[23] O.F.Z. Khan, P. O'Brien, Polyhedron 10 (1991) 325.

[24] P.S. Marchetti, S. Bank, T.W. Bell, M.A. Kennedy, P.D.J. Ellis, J. Am. Chem. Soc. 111 (1989) 2063.

[25] M.A. Kennedy, J.L. Sessler, T. Murrai, P.D. Ellis, Inorg. Chem. 29 (1990) 1050.

[26] P. DuBois Murphy, W.C. Stevens, T.T.P. Cheung, S. Lacelle, B.C. Gerstein, D.M. Kurtz, Jr., J. Am. Chem. Soc. 103 (1981) 4400.

[27] R.J. Abraham, The Analysis of High Resolution NMR Spectra, Elsevier, Amsterdam, 1971, pp. 46–83.