Inorg. Chem. **2003**, *42*, 7403–7409

Inorganic Chemistry

Article

Reactivity of 2-Pyridinecarboxylic Esters with Cadmium(II) Halides: Study of ^{113}Cd NMR Solid State Spectra and Crystal Structures of Hexacoordinated Complexes $[CdI_2(C_5H_4NCOOMe)_2]$ and $[CdI_2(C_5H_4NCOOPr^n)_2]$

Ricard March, Josefina Pons,* and Josep Ros

Departament de Química, Unitat de Química Inorgànica, Universitat Autònoma de Barcelona, 08193-Bellaterra, Barcelona, Spain

William Clegg

Department of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, U.K.

Angel Álvarez-Larena and Joan Francesc Piniella

Departament de Geologia, Unitat de Cristallografia, Universitat Autònoma de Barcelona, 08193-Bellaterra, Barcelona, Spain

Jesus Sanz

Instituto de Ciencia de Materiales, Cantoblanco, Universidad Autónoma de Madrid, 28047-Madrid, Spain

Received October 23, 2002

The series of complexes $[CdX_2(C_5H_4NCOOR)]$ (X = Cl or Br; R = Me, Et, Pr^n or Pr^i) and $[CdX_2(C_5H_4NCOOR)_2]$ (X = I; R = Me, Et, Pr^n, or Pr^i) have been obtained by the addition reaction of esters of 2-pyridinecarboxylic acid to cadmium(II) halides. X-ray crystal structures of two complexes $[CdI_2(C_5H_4NCOOR)_2]$, R = Me (**10**) and R = Pr^n (**12**), have been determined. In both cases, the structure consists of discrete neutral monomeric units where the cadmium atom has a distorted octahedral coordination with $CdI_2N_2O_2$ *core,* two halides being in cis disposition. Structural information is compared with that deduced from ^{113}Cd CPMAS NMR experiments. Chemical shift anisotropies are discussed in terms of distortions produced in cadmium octahedra. The orientation of the principal axes of ^{113}Cd shielding tensor is also analyzed and related to the disposition of ligands in the structures of two analyzed compounds.

Introduction

Nowadays, considerable efforts are directed toward the study of the coordination stereochemistry of metal atoms in synthetic analogues of biological compounds.

The correlation of ^{113}Cd chemical shift parameters, deduced from solid-state NMR, with the structure of bioinorganic complexes is a fruitful approach in investigation of metal centers present in proteins.[1] ^{113}Cd NMR spectroscopy is a sensitive probe of the cadmium coordination, allowing information about the chemical bonding, conformation, and dynamics of molecules to be obtained. Environments in which ^{113}Cd is ligated by oxygen usually give rise to resonances between −100 and +150 ppm; coordination to nitrogen results in a downfield shift and resonances between +200 and +380 ppm.[2]

Unlike solution chemical shifts, solid-state NMR results can be correlated directly with structural determinations. This

---

* Author to whom correspondence should be addressed. E-mail: josefina.pons@uab.es.

(1) (a) Kidambi, S. S.; Ramamoorty, A. *Inorg. Chem.* **2003**, *42*, 2200. (b) Kidambi, S. S.; Lee, D.-K.; Ramamoorthy, A. *Inorg. Chem.* **2003**, *42*, 3142.

(2) Summers, M. F. *Coord. Chem. Rev.* **1988**, *86*, 43.

10.1021/ic0206387 CCC: $25.00

Table 1. Physical and Analytical Data for the Complexes **1**−**13**

	yield	elemental analysis[b]			conductivity[c]
complex[a]	(%)	C (%)	H (%)	N (%)	(Ω^{-1} cm^2 mol^{-1})
$[CdCl_2(C_5H_4NCOOMe)]$ **1**	92	26.3 (26.2)	2.1 (2.2)	4.5 (4.4)	42
$[CdCl_2(C_5H_4NCOOEt)]$ **2**	96	28.6 (28.7)	2.8 (2.7)	4.0 (4.2)	65
$[CdCl_2(C_5H_4NCOOPr^n)]$ **3**	90	30.7 (31.0)	3.1 (3.2)	3.9 (4.0)	54
$[CdCl_2(C_5H_4NCOOPr^i)]$ **4**	92	30.5 (31.0)	3.3 (3.2)	4.0 (4.0)	59
$[CdBr_2(C_5H_4NCOOMe)]$ **5**	99	20.6 (20.5)	1.7 (1.7)	3.4 (3.4)	38
$[CdBr_2(C_5H_4NCOOEt)]$ **6**	76	22.9 (22.7)	2.2 (2.1)	3.3 (3.3)	40
$[CdBr_2(C_5H_4NCOOPr^n)]$ **7**	84	24.8 (24.7)	2.3 (2.5)	3.1 (3.2)	41
$[CdBr_2(C_5H_4NCOOPr^i)]$ **8**	89	24.9 (24.7)	2.2 (2.5)	3.1 (3.2)	37
$[CdBr_2(C_5H_4NCOOPr^i)_2]$ **9**	80	35.8 (35.9)	3.6 (3.7)	4.5 (4.7)	28
$[CdI_2(C_5H_4NCOOMe)_2]$ **10**	69	26.4 (26.2)	2.2 (2.2)	4.4 (4.4)	21
$[CdI_2(C_5H_4NCOOEt)_2]$ **11**	55	28.8 (28.7)	2.7 (2.7)	4.2 (4.2)	22
$[CdI_2(C_5H_4NCOOPr^n)_2]$ **12**	60	30.7 (31.0)	3.1 (3.2)	3.9 (4.0)	24
$[CdI_2(C_5H_4NCOOPr^i)_2]$ **13**	67	31.2 (31.0)	3.2 (3.2)	4.0 (4.0)	20

[a] Synthesis of complexes **1**, **5**, and **10** was carried out in methanol. The rest of the reactions used ethanol as solvent. [b] Calculated analytical values are given in parentheses. [c] 10^{-3} M in methanol. The reported values for 1:1 electrolyte in methanol are 80−115 Ω^{-1} cm^2 mol^{-1}.[20]

technique has the advantage that it provides information about the three principal components of the chemical shift tensor.[3] From this analysis, we get information referring to the nature and disposition of coordinating ligands.[2]

Adducts with cadmium halides form a wide range of coordination complexes with a great deal of structural variety.[4] This is due not only to the characteristics of the ligand but also to the great variety of coordination kinds related to the d^{10} configuration of Cd(II).[5]

In our laboratory, we have carried out a systematic study of the reactivity of methyl-, ethyl-, *n*-propyl-, and *i*-propyl esters of 2-pyridinecarboxylic acid and halides of d^{10} metal ions. We have found that different structures are obtained depending on the metal, Zn(II) or Hg(II). When the metal is Zn(II), complexes are obtained with two stoichiometries, $[ZnX_2L]$ and $[ZnX_2L_2]$.[6] In contrast, if the metal ion is Hg(II), all the complexes are $[HgX_2L]$, with different degrees of nuclearity, from dimers to polymers, depending on the type of interaction Hg····X.[7]

In this work, the synthesis and the characterization of the adducts of CdX_2, X = Cl, Br, I, with methyl-, ethyl-, *n*-propyl-, and *i*-propyl esters of 2-pyridinecarboxilic acid, are presented. X-ray crystal structures of $[CdI_2(C_5H_4NCOOMe)_2]$ (**10**) and $[CdI_2(C_5H_4NCOOPr^n)_2]$ (**12**) are described and related to high-resolution ^{113}Cd NMR spectroscopic data. In particular, a confirmation of the coordination number of Cd(II) has been obtained from the analysis of chemical shift values. Stereochemical changes around cadmium have been analyzed by using chemical shift anisotropies deduced from NMR spectra.

Experimental Section

Materials and Methods. All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled by standard methods. Analyses (C, H, N) were performed in the Analysis Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in 10^{-3} M methanolic solutions employing a radiometer CDM-3 conductimeter. Infrared spectra were recorded from KBr disks on a Perkin-Elmer 2000 spectrometer in the region 4000−400 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker AC 250-Mz instrument in methanol-d_4 solutions. ^{113}Cd CPMAS spectra of solid samples were recorded on a Bruker MSL-400 spectrometer, in the case of power samples. Positive-ion atom bombardment (FAB) mass spectra were obtained with a VG Quattro quadruple mass analyzer in *p*-nitrobenzyl alcohol matrix for complexes **9** and **12**.

Preparations. The methyl-, ethyl-, *n*-propyl-, and isopropyl esters of the commercially available 2-pyridinecarboxylic acid were obtained by the usual esterification procedure in acidic medium with an excess of the corresponding alcohol.[8] In all cases, the same procedure was used in the syntheses of complexes. Solutions (4×10^{-2} M; 25 mL) of the cadmium halide were slowly added to the same volume of a solution of the ligand in 1:1, 1:2, and 1:3 M:L molar ratios. Solvents (methanol or ethanol) used in the synthesis of complexes are indicated in Table 1. The white solid formed after 10 min of being stirred was filtered off, washed with diethyl ether, and dried in vacuo.

X-ray Crystal Structure Analyses. Recrystallization of **10** in methanol and **12** in ethanol gave colorless single crystals. Crystal data and selected information on data collection and structure determination are given in Table 2. Data for **12** were collected on a Siemens SMART CCD area detector diffractometer with nitrogen gas cooling; cell parameters were refined from selected strong reflections, and intensities were integrated from a series of narrow-frame exposures (0−3° in ω), using standard Siemens SMART and SAINT software. Data for **10** were collected on an Enraf-Nonius CAD4 diffractometer at room temperature; cell parameters were refined from an initially found set of reflections, and intensities were measured by $\omega/2\theta$ scans, using standard control software. Graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) was employed in both cases. Absorption corrections were applied semiempirically, based on azimuthal scans.[9]

---

(3) (a) Mehring, M. *High-resolution NMR Spectroscopy in Solids*; Springer-Verlag: Berlin, Germany, 1983. (b) Fyfe, C. A. *Solid-state NMR for Chemists*; CFC Press: Guelph, Ontario, 1983.

(4) Tuck, D. G. *Rev. Inorg. Chem.* **1979**, *1*, 209.

(5) (a) Strasdeit, H.; Saak, W.; Pohl, S.; Driessen, W. L.; Reedjick, J. *Inorg. Chem*. **1988**, *27*, 1557. (b) Al-Inaid, S. S.; Buttrus, N. B.; Eaborn, C.; Hitchcook, P. B.; Smith, J. D.; Tabakkoli, K. *J. Chem. Soc., Chem. Commun*. **1988**, 1389.

(6) González-Duarte, P.; March, R.; Pons, J.; Clegg, W.; Cucurull-Sánchez, L.; Alvarez Larena, A.; Piniella, J. F. *Polyhedron* **1996**, *15*, 2747.

(7) (a) Alvarez-Larena, A.; Clegg, W.; Cucurull-Sánchez, L.; González-Duarte, P.; March, R.; Piniella, J. F.; Pons, J.; Solans, X. *Inorg. Chim. Acta* **1997**, *266*, 81. (b) González-Duarte, P.; Leiva, A.; March, R.; Pons, J.; Clegg, W.; Solans, X.; Alvarez-Larena, A.; Piniella, J. F. *Polyhedron* **1998**, *17*, 1591.

(8) Vogel, A. I. *Textbook of Practical Organic Chemistry*, 4th ed.; London Longman: London, 1978.

Table 2. Crystallographic Data

compound	**10**	**12**
formula	$C_{14}H_{14}CdI_2N_2O_4 \cdot 0.3MeOH$	$C_{18}H_{22}CdI_2N_2O_4$
M	650.08	696.58
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	10.124(1)	8.8997(6)
b (Å)	15.546(1)	15.3101(10)
c (Å)	12.385(1)	17.8929(11)
β (deg)	90.91(1)	102.198(2)
V (Å^3)	1949.0(3)	2383.0(3)
Z	4	4
D_c (g cm^{-3})	2.215	1.942
μ (mm^{-1})	4.308	3.530
$F(000)$	1214	1320
temp (K)	293	160
cryst size (mm^3)	0.58 × 0.18 × 0.14	0.46 × 0.40 × 0.40
θ_{max} (deg)	25.0	28.5
max indices *hkl*	12, 18, 14	11, 16, 23
measured reflns	3422	14 439
unique reflns	3422	5426
R_{int}		0.0286
transmission	0.547−0.434	0.217−0.125
weighting params *a*, *b*	0.0411, 1.017	0.0178, 3.0960
No. refined params	216	247
$R_w(F^2)$ (all data)	0.0792	0.0553
$R(F)$ (“observed” data)	0.0277	0.0231
GOF	1.076	1.176
max, min electron density (e A^{-3})	0.62, −0.47	0.72, −0.79

The structures were solved by direct methods[10] and refined by full-matrix least-squares on F^2 for all unique measured data[11] with weighting $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included with riding model constraints, and other atoms were refined anisotropically. Residuals are defined as: $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ for all data and $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $F_o^2 > 2\sigma(F_o^2)$ (for comparison with conventional refinements on F); the goodness of fit is calculated on F^2 for all data.

Atomic coordinates, complete bond lengths and angles, and displacement parameters have been deposited as Supporting Information at the Cambridge Crystallographic Data Centre.

^{113}Cd NMR Spectroscopy. ^{113}Cd CPMAS NMR spectra were recorded at 295 K with the standard cross-polarization technique.[12] Samples were spun at 4 kHz around an axis inclined 54° 44′ with respect to the field. Spectrometer frequencies used were 88.76 MHz for ^{113}Cd and 400.13 MHz for ^{1}H, respectively. The Hartman-Hann condition was obtained with radio frequency fields of 10.7 and 48.1 MHz for proton and cadmium channels. Spectra were recorded after a contact time of 4 ms and a period between accumulations of 10 s. The number of scans was 1000. Chemical shift values were referred to a 0.1 M $Cd(ClO_4)_2$ aqueous solution.

Analysis of CPMAS NMR spectra was carried out using the Bruker WINFIT program. The spinning rate and positions line widths and intensities of the components were determined with a standard, nonlinear least-squares fitting method. ^{113}Cd isotropic chemical shift values of analyzed compounds are given by the frequency positions of the sidebands that did not show change in spectra recorded at different spinning rates. However, chemical shift anisotropies (anisotropy $\Delta\sigma$ and asymmetry η) are adaptable parameters (2 ppm and 0.1, respectively) that must be determined by a trial and error procedure during the spectral analysis were carried out with the WINFIT package. Errors in isotropic chemical shift values were lower than 1 ppm; however, those estimated in $\Delta\sigma$ and η are 5 ppm. Finally, σ_{11}, σ_{22}, and σ_{33}, principal components of the shielding tensor ($\sigma_{11} > \sigma_{22} > \sigma_{33}$), were deduced from isotropic chemical shift σ_{iso}, anisotropy $\Delta\sigma$, and asymmetry η parameters.[13] In studied samples, the contribution of scalar and dipolar couplings were not considered in the spinning sideband analysis.

Results and Discussion

Synthesis and Spectroscopic Properties of the Complexes. The reaction of esters of 2-pyridinecarboxylic acid (L) with cadmium halides leads to complexes of two different formula $[CdX_2(C_5H_4NCOOR)]$ and $[CdX_2(C_5H_4NCOOR)_2]$, depending mainly on the nature of the halide ion. Thus, $CdCl_2$ gives rise to complexes of formula $[CdCl_2(C_5H_4NCOOR)]$, whereas CdI_2 always leads to complexes of formula $[CdI_2(C_5H_4NCOOR)_2]$. In both cases, this happens independently of the molar ratio M:L used. $CdBr_2$ mainly gives rise to complexes of formula $[CdBr_2(C_5H_4NCOOR)]$. In the case of $CdBr_2$ with R = isopropyl, complexes $[CdBr_2(C_5H_4NCOOPr^i)_2]$ are obtained if a 1:3 molar ratio is used. With a 1:1 or 1:2 molar ratio, the usual $[CdBr_2(C_5H_4NCOOPr^i)]$ is obtained.

^{1}H NMR spectra of complexes give evidence that trans esterification reactions have not occurred in the synthesis of the aforementioned compounds. The stoichiometries of all complexes have been established by elemental analyses (Table 1).

The mononuclear nature of complexes **9** and **12** is reflected in FAB data, the molecular ion (MH$^+$) peak being observed at *m*/*z* 603 (**9**) and 696 (**12**). The three most intense peaks can be attributed to the successive loss of one halogen atom (Br for **9** and I for **12**), then one $[CdX_2L_2]^+$, and finally one alkyl group (isopropyl for **9** and *n*-propyl for **12**). These peaks are observed at *m*/*z* 523, 358, and 315 for complex **9** and 569, 404, and 361 for complex **12**.

The conductivity measurements of the complexes are shown in Table 1. For the complexes of formula $[CdX_2(C_5H_4NCOOR_2)]$ and $[CdX_2(C_5H_4NCOOR)]$, the conductivity in methanol is high enough to assess the noncoordinated nature of the halide anion.[14] IR spectra show that in all complexes the pyridine nitrogen atom is bonded to cadmium (bands at 1350 and 650 cm^{-1}). Moreover, these IR spectra reveal a slightly different coordinative behavior of the carboxylate group in the two series, as the lowering of ν(C=O) compared to the free ligand is 28−36 cm^{-1} for $[CdX_2(C_5H_4COOR)]$ complexes whereas it is 11−22 cm^{-1} for $[CdX_2(C_5H_4NCOOR)_2]$.[15] Accordingly, it seems that the expected interaction of the carbonyl oxygen of the carboxylate group

---

(9) North, A. C. T.; Philips, P. C.; Matews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(10) Sheldrick, G. M. *SHELXS-86*: *Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1985.

(11) Sheldrick, G. M. *SHELXS-93*: *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

(12) (a) Shekar, C. S.; Lee, D.-K.; Ramamoorthy, A. *J. Magn. Reson.* **2002**, *157*, 223. (b) Pines, A.; Gibby; M. G.; Waughn, J. S. J. *J. Chem. Phys.* **1973**, *59*, 569. (c) Stejskal, E. O.; Schaefer, J.; Waugh, J. S. *J. Magn. Reson.* **1977**, *28*, 106. (c) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042.

(13) Dubois Murphy, P.; Stevens, W. C.; Cheung, T. T. P.; Lacelle, S.; Gerstein, B. C.; Kurtz, D. M., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 4400.

(14) (a) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81. (b) Thompson, L. K.; Lee, F. L.; Gabe, E. J. *Inorg. Chem.* **1988**, *27*, 39.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes **10** and **12**

	complex **10**	complex **12**		complex **10**	complex **12**
Cd−N(1)	2.359(4)	2.346(2)	Cd−N(2)	2.357(4)	2.347(2)
Cd−O(1)	2.564(4)	2.598(2)	Cd−O(3)	2.503(3)	2.519(2)
Cd−I(1)	2.776(5)	2.7886(3)	Cd−I(2)	2.7881(6)	2.7733(3)
C(6)−O(1)	1.218(6)	1.212(3)	C(15)−O(3)	1.207(5)	1.207(4)
C(6)−O(2)	1.305(6)	1.325(3)	C(15)−O(4)	1.291(6)	1.321(3)
N(1)−Cd−N(2)	145.67(12)	130.94(8)	I(1)−Cd−I(2)	111.37(2)	107.672(9)
N(2)−Cd−O(1)	84.27(12)	72.81(7)	N(1)−Cd−O(3)	84.38(12)	73.34(8)
N(2)−Cd−O(3)	68.27(11)	68.22(7)	N(1)−Cd−O(1)	67.50(12)	66.59(7)
N(2)−Cd−I(1)	98.11(9)	101.80(6)	N(1)−Cd−I(2)	99.42(9)	100.03(6)
N(2)−Cd−I(2)	100.56(9)	110.30(6)	N(1)−Cd−I(1)	100.20(9)	104.56(6)
I(2)−Cd−O(1)	158.38(8)	160.39(5)	I(1)−Cd−O(3)	157.44(8)	160.41(5)
I(2)−Cd−O(3)	89.36(8)	91.79(5)	I(1)−Cd−O(1)	88.56(8)	90.09(5)
O(3)−Cd−O(1)	72.66(11)	71.05(7)			

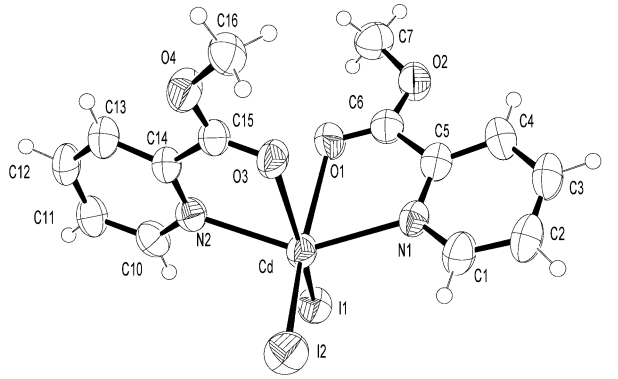

Figure 1. An ORTEP view of $[CdI_2(C_5H_4NCOOMe)_2]$ (**10**). The displacement ellipsoids enclose 50% probability.

with the cadmium atom is significantly stronger for complexes of formula $[CdX_2(C_5H_4NCOOR)]$. Single crystals have been obtained for two complexes, **10** and **12**, of formula $[CdX_2(C_5H_4NCOOR)_2]$. In these two cases, a monomeric structure has been found. All attempts to obtain single crystals for complexes with formula $[CdX_2(C_5H_4NCOOR)]$ (**1**−**8**) have been unsuccessful. Therefore, no structural information is available. Other analytical, spectroscopic, and conductivity data are not conclusive about the monomeric or polymeric nature of these complexes.

Crystal Structures of $[CdI_2(C_5H_4NCOOR)_2]$ for R = Me (10) and Pr^n (12). Recrystallization of **10** in methanol and **12** in ethanol gave colorless single crystals. The structures of complexes **10** and **12** consist of discrete neutral monomeric units where the cadmium atom is coordinated to two halides and to two picolinate ester ligands by means of the pyridine nitrogen and the carbonyl oxygen atoms. In both cases, the coordination geometry around cadmium is octahedral but severely distorted. The most relevant bond lengths and angles are given in Table 3. The molecular structures are shown in Figures 1 and 2, respectively.

The asymmetric unit is the entire molecule $[CdI_2(C_5H_4NCOOR)_2]$, which displays the halide ligands in a cis disposition. The Cd−I distances are of the same order as the sum of covalent radii (2.81 Å). The two picolinate ligands chelate the cadmium atom with Cd−N distances in good agreement with the sum of covalent radii (2.23 Å). The

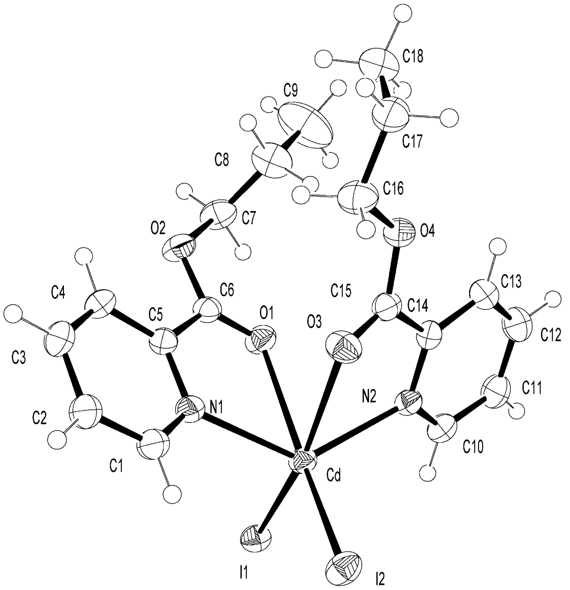

Figure 2. An ORTEP view of $[CdI_2(C_5H_4NCOOPr^n)_2]$ (**12**). The displacement ellipsoids enclose 50% probability.

Cd−O distances are significantly greater than the sum of covalent radii (2.21 Å), although they are clearly smaller than the sum of van de Waals radii (2.90 Å).[16] These long Cd−O bond distances are coherent with the IR data described above.

Distortion from ideal octahedral coordination is very significant. This distortion is mainly reflected in the N−Cd−N angle [145.67(12)° and 130.94(8)° for **10** and **12**, respectively] and in the bite angles of the chelating ligand, N−Cd−O [84.27(2)° and 92.81(7)° for **10** and **12**, respectively]. This situation is similar to that found in related octahedral Zn(II) compounds.[6] In the solid structure of complex **10**, disordered methanol molecules occupy interstitial positions.

The $CdI_2N_2O_2$ *core* is unusual in the literature. Only one structure with this *core* has been described with iodides in trans arrangement,[17] unlike the two structures here described which have iodides in cis disposition.

No structure data for cadmium complexes of esters of 2-pyridinecarboxylic acid have been reported previously, although three structures of Cd with 2-pyridinecarboxylic

---

(15) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986. (B) Paul, R. C.; Chopra, R. S.; Bhambri, R. K.; Singh, G. *J. Inorg. Nucl. Chem.* **1974**, 36.

(16) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper: New York, 1993.

(17) Pickard, J. *Z. Naturforsch., B: Chem. Sci.* **1981**, *36*, 1225.

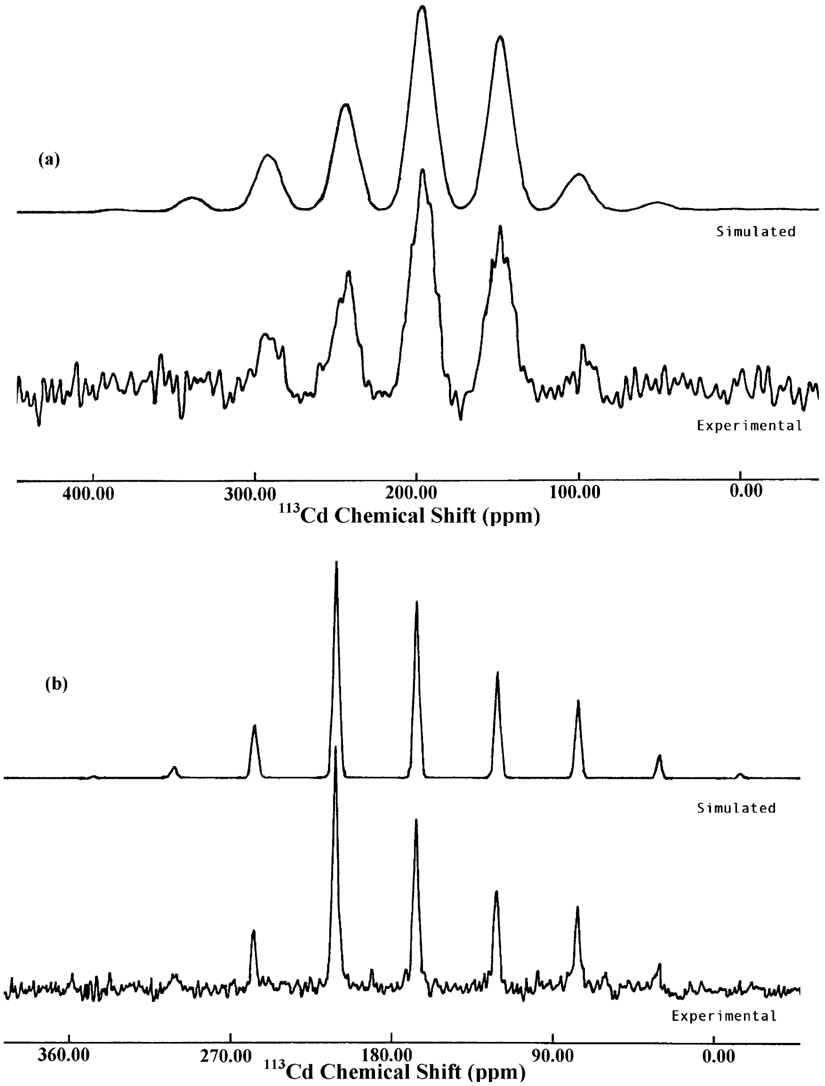

Figure 3. Experimental and simulated ^{113}Cd chemical shift NMR spectra of (a) [$CdI_2(C_5H_4NCOOMe)_2$] (**10**) and (b) [$CdI_2(C_5H_4NCOOPr^n)_2$] (**12**) complexes.

acid have been described: $\{Cd(C_5H_4NCOO)_2\}_n$, $\{Cd(C_5H_4NCOO)_2(N_3)\}_n$, and $\{Cd(C_5H_4NCOO)_2(NCS)\}_n$.[18]

Crystallographic data for complex [$CdI_2(C_5H_4NCOOMe)_2$] indicate that it is isostructural with the previously described complexes [$ZnX_2(C_5H_4NCOOMe)_2$], X = Br, I.[6]

When the Cd(II) complexes are compared with the Zn(II) complexes, it can be observed that the behavior of iodides is analogous.[6] However, for chlorides and bromides, some differences are observed between the two metals. Two stoichiometries, [$ZnCl_2L_2$] and [$ZnCl_2L$], are found; depending on the molar ratio Zn(II):L used, only complexes of stoichiometry [$CdCl_2L$] are obtained. In the case of bromide complexes, a stoichiometry [MBr_2L_2] is obtained independently of the molar ratio M:L used, except for L = $C_5H_4NCOOEt$ in the case of Zn(II) and L = $C_5H_4NCOOPr^i$ in the case of Cd(II), which lead to the formation of the complexes [$ZnBr_2(C_5H_4NCOOEt)$] and [$CdBr_2(C_5H_4NCOOPr^i)$], respectively, if a 1:1 ratio is used. The behavior of Hg(II) halides differs considerably from that found for Zn(II) and Cd(II), with only a single stoichiometry, [$HgX_2(C_5H_4NCOOR)$], being obtained in all cases.[7]

^{113}Cd NMR of [$CdI_2(C_5H_4COOR)_2$] for R = Me (10) and Pr^n (12). ^{113}Cd CPMAS NMR spectra of two analyzed complexes are given in Figure 3. Spectral simulations obtained with the WINFIT program[19] are also included in this figure. In all cases, spinning sidebands in the ^{113}Cd chemical shift spectra are separated by 45 ppm. Principal values deduced from the sideband patterns are given in Table 4, where isotropic chemical shift, anisotropy, and asymmetry parameters corresponding to each site are included.

Anisotropy parameters, 144 and −180 ppm, indicate that considerable distortions are present in both compounds. On the other hand, asymmetry parameters, 0.55 and 0.68, indicate that point symmetry of sites occupied by cadmium is low. Finally, line widths of spinning sidebands of complex **10** are higher than for complex **12**, which suggest that crystallinity of compound **12** is higher.

Isotropic values deduced for the two analyzed compounds agree with predictions based on the donator character of

---

(18) (a) Deloume, J. P.; Loiseleur, H. *Acta Crystallogr.* **1974**, *B30*, 607. (b) Mautner, F. A.; Abu-Youssef, M. A. M.; Goher, M. A. S. *Polyhedron* **1997**, *16*, 235.

(19) Massiot, D. *WINFIT*; Bruker-Franzen Analytik GmbH: Bremen, Germany, 1993.

Table 4. ^{113}Cd NMR Data for Compounds **10** and **12**

compd	σ_{iso}[a]	σ_{11}[b]	σ_{22}[b]	σ_{33}[b]	$\Delta\sigma$[c]	η[d]
10	196	291(2)	175(2)	122(3)	144	0.55
12	167	268(3)	186(2)	47(2)	−180	0.68

[a] Chemical shift (ppm) in solid state. The positive sign of values denotes lower shielding than that of external 0.1 M $Cd(ClO_4)_2$ at 0 ppm. [b] Principal components of the shielding tensors. [c] $\Delta\sigma = \sigma_{33} - 1/2(\sigma_{11} + \sigma_{22})$ ($\Delta\sigma < 0$); $\Delta\sigma = \sigma_{11} - 1/2(\sigma_{33} + \sigma_{22})$ ($\Delta\sigma > 0$). [d] $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{iso})$ ($\Delta\sigma < 0$); $\eta = (\sigma_{22} - \sigma_{33})/(\sigma_{iso})$ ($\Delta\sigma > 0$).

atoms bound to cadmium atoms. According to these predictions, deshielding increases when going from oxygen to iodine and finally to nitrogen. In accordance with these ideas, isotropic chemical shift values deduced for $I_2N_2O_2$ octahedral in the two analyzed complexes (167, 196 ppm) are higher than those reported for O6 octahedral (10 ppm)[20] and lower than those associated with N6 octahedral (230 ppm).[21]

The shielding tensor parameters, anisotropy and asymmetry, have been correlated to the disposition of ligands around Cd cations.[22] As expected, in absence of appropriated symmetry elements at cadmium sites (point symmetry 1), asymmetry parameters are important (0.55 and 0.68). On the other hand, values deduced for anisotropy parameters agree with the severe distortions detected in the octahedron around the Cd. These values result from the existence of three different atoms around Cd cations. Finally, the chelate character of picolinate ester ligands causes the N−Cd−N angle to depart considerably from 180°.

Finally, an analysis of the orientation of the three orthogonal principal axes of the chemical shift tensor, with respect to the molecular framework, has been undertaken. This study was based on two main criteria relative to the influence of the stereochemistry around cadmium on shielding tensor individual components. These criteria are: (1) that the shielding effects of a given M−L bond are maximal in the directions perpendicular to the M−L vector and (2) that nitrogen is the most deshielding atom.[23]

On the basis of the above ideas, the principal σ_{33} axis should be disposed perpendicular to the plane that contains atoms with the lowest deshielding character, i.e., oxygen and iodide atoms.[24] On the other hand, the line perpendicular to the plane defined by Cd and the two nitrogen atoms must be ascribed to the σ_{11} axis (the highest principal value). Finally, the σ_{22} axis, located at the intersection of the two previously mentioned planes, will coincide with the pseudobinary axis[25] (Figure 4).

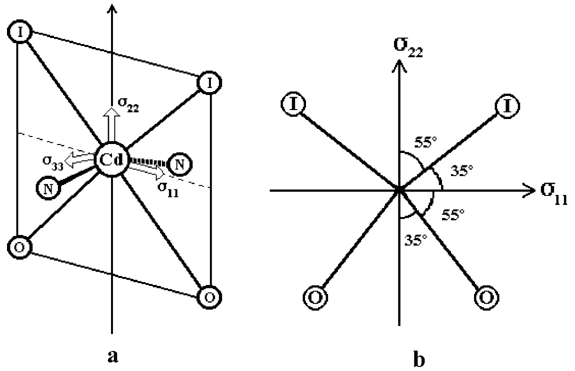

Figure 4. (a) Proposed orientation of the shielding tensor in $CdI_2N_2O_2$ polyhedron. (b) Disposition of σ_{11} and σ_{22} axes in the mean square plane CdI_2O_2.

Following the previous assignment, the σ_{11} axis would be inclined 55° and 35° with respect to Cd−O and Cd−I directions. In a parallel way, angles formed by σ_{22} with these axes would be 35° and 55°. Taking into account the above angles, the σ_{11} values will be more affected by Cd−O and σ_{22} by Cd−I bonds.

These ideas enable us to compare the principal values measured in the two analyzed complexes. For σ_{33} values, the lower value detected in complex **12** ($\sigma_{33} = 47$ ppm) with respect to complex **10** (122 ppm) must be associated with the decrease of the Cd−O distances. As indicated above, the σ_{11} values are mainly determined by the Cd−N distances, which are similar in the two compounds. Therefore, differences found in σ_{11} values between two compounds must be related to the differences between Cd−O distances, similar to what has been described for $\Delta\sigma_{33}$.

Concerning σ_{22} values, differences between the two complexes are small, in agreement to similar Cd−N and Cd−I distances deduced from structural determinations and the lower contribution of Cd−O bonds to the σ_{22} parameter deduced from NMR considerations. The σ_{22} value of **10** is lower than the σ_{22} value of **12,** a fact attributed to the smaller angles between Cd−N bonds and the plane orthogonal to σ_{22} axis in **10**.

Conclusions

The addition reaction of esters of 2-pyridinecarboxylic acid to Cd(II) halides leads to two types of complexes: $[CdX_2(C_5H_4NCOOR)]$ and $[CdX_2(C_5H_4NCOOR)_2]$. These products mainly depend on the nature of the halide. This dependence of stoichiometry on the nature of the halide contrasts with the other Cd(II) complexes previously described.

Analytical, spectroscopic, and conductivity data for both types of synthesized complexes $[CdX_2(C_5H_4NCOOR)]$ and $[CdX_2(C_5H_4NCOOR)_2]$ are coherent with tetrahedral and octahedral environments of the metal atom, respectively. This assumption has been confirmed for $[CdX_2(C_5H_4NCOOR)_2]$ complexes by the X-ray structures of compounds **10** and **12**. In both complexes, the pyridine ester molecule acts as a bidentate ligand. The chelate character of pyridine ester ligands and the bulk of iodides make the N−Cd−N bonds depart considerably from the octahedral configuration by introducing strong distortions in $CdI_2O_2N_2$ coordination.

---

(20) (a) Mennitt, P. G.; Shatlock, M. P.; Bartuska, V. J.; Macial, G. E. *J. Phys. Chem.* **1981**, *85*, 2087. (b) Honkonen, R. S.; Ellis, P. D. *J. Am. Chem. Soc.* **1984**, *106*, 5488.

(21) (a) Summers, M. F. *Coord. Chem. Rev.* **1988**, *86*, 43. (b) Reger, D. L.; Myers, S. M.; Mason, S. S.; Darensbourg, D. J.; Holtcamp, M. W.; Reibenspies, J. H.; Lipton, A. S.; Ellis, P. D. *J. Am. Chem. Soc.* **1995**, *117*, 10998.

(22) (a) Srikanth, K.; Ramamoorthy, A. *J. Phys. Chem. A* **2002**, *106*, 10363. (b) Barrie, P. J.; Gyani, A.; Montevalli, M.; O'Brien, P.; *Inorg. Chem.* **1993**, *32*, 3862. (c) Marchetti, P. S.; Ellis, P. D.; Bryant, R. G. J. *J. Am. Chem. Soc.* **1985**, *107*, 8191. (d) Wen, H.; Wilkins, C. J. *Z. Anorg. Allg. Chem.* **1992**, *615*, 143.

(23) Honkonen, R. S.; Marchetti, P. S.; Ellis, P. D. *J. Am. Chem. Soc.* **1986**, *108*, 912.

(24) Rivera, E.; Ellis, P. D. *Inorg. Chem.* **1992**, *31*, 2096.

(25) Lipton, A. S.; Mason, S. S.; Myers, S. M.; Reger, D. L.; Ellis, P. D. *Inorg. Chem.* **1996**, *35*, 7111.

In the analysis, the ^{113}Cd NMR shielding tensor of two monomeric Cd complexes (compounds **10** and **12**) has also been analyzed. It was deduced that the principal axis σ_{33} is disposed perpendicularly to the plane formed by the two oxygen atoms and the two iodide atoms, but σ_{11} is perpendicular to the plane defined by Cd and the two nitrogen atoms. The σ_{11} and σ_{22} values are mainly influenced by the Cd−N bonds and the σ_{33} by the Cd−O bonds. As the Cd−N (and Cd−I) bonds are similar in two analyzed complexes, differences observed in σ values are mainly due to differences in Cd−O bonds. According to this fact, the σ_{33} value is the one that changes more in analyzed compounds.

Acknowledgment. The authors thank MCYT (BQU 2000-0238) for financial support. R.M. is grateful for a grant from the Ministerio de Educación y Ciencia. We are grateful to Dr. Joan Sola for useful discussions and analysis of the ^{113}Cd NMR.

Supporting Information Available: Four crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.ac.org.

IC0206387