

metrical parameters for the porphyrin core are displayed in Fig. 1.* The intrinsic fourfold symmetry of the porphyrin skeleton is reflected in the small values for the e.s.d.'s of the averaged parameters.

The previously reported structure (Hoffman *et al.*, 1972) is confirmed. There is no significant difference between the room-temperature and low-temperature (122 K) geometries, but this report presents a twofold increase in accuracy for the structural parameters of this molecule.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom positions, and bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39917 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Structures and Solid-State and Solution ^{113}Cd NMR of Diaquabis(*p*-chlorobenzoato)-cadmium(II), $[\text{Cd}(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{H}_2\text{O})_2]$ (A), Diaquabis(*p*-nitrobenzoato)cadmium(II), $[\text{Cd}(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{H}_2\text{O})_2]$ (B), and Aquabis(*p*-chlorobenzoato)bis(pyridine)cadmium(II), $[\text{Cd}(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})]$ (C)

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Abstract. (A) $M_r = 459.55$, monoclinic, $C2/c$, $a = 25.904$ (9), $b = 5.371$ (2), $c = 12.049$ (7) Å, $\beta = 107.02$ (4)°, $V = 1603$ (2) Å³, $Z = 4$, $D_m = 1.89$ (2), $D_x = 1.90$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 17.1$ cm⁻¹, $F(000) = 904$, $T \sim 298$ K, $R(\text{final}) = 0.049$ for 2228 reflections. (B) $M_r = 480.66$, monoclinic, $C2/c$, $a = 26.415$ (3), $b = 5.416$ (1), $c = 12.179$ (4) Å, $\beta = 90.52$ (3)°, $V = 2514$ (3) Å³, $Z = 4$, $D_m = 1.95$ (2), $D_x = 1.96$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 14.0$ cm⁻¹, $F(000) = 952$, $T \sim 298$ K, $R(\text{final}) = 0.039$ for 2378 reflections. (C) $M_r = 599.8$, monoclinic, $C2/c$, $a = 16.908$ (7), $b = 6.058$ (2), $c = 24.547$ (2) Å, $\beta = 90.52$ (3)°, $V = 2514$ (3) Å³, $Z = 4$, $D_m = 1.59$ (2), $D_x = 1.59$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 11.1$ cm⁻¹, $F(000) = 1200$, $T \sim 298$ K, $R(\text{final}) = 0.036$ for 3681 reflections. The structures of (A) and

(B) are made up of distorted six-coordinate Cd^{II} moieties, intermediate in metal-coordination geometry between octahedral and trigonal prismatic, separated by ordinary van der Waals distances. The crystal structure of (C) is made up of seven-coordinate pentagonal bipyramidal Cd^{II} separated by ordinary van der Waals distances. The solid-state ^{113}Cd NMR of (A) and (B) consists of a single line at +24 p.p.m., relative to the Cd(ClO₄)₂ standard. The solid-state ^{113}Cd NMR of (C) and the analogous adduct of (B) consists of a single line at +30 and +29 p.p.m. respectively. The methanol solution ^{113}Cd NMR spectra of (A) and (B) consist of a single line at -51 p.p.m. and -53 p.p.m. respectively. These results for all-oxygen coordination are interpreted as the positive values arising from the distorted six-coordinate Cd^{II} and the negative values correspond to pentagonal bipyramidal seven-oxygen-coordinated metal species in solution.

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Introduction. ¹¹³Cd NMR with a chemical shift range of ~900 p.p.m. has been shown to be a sensitive probe of metal-ion sites in a wide variety of compounds, ranging from organometallic to biological macromolecules (Ellis, 1983; Rodesiler, Turner, Charles, Griffith & Amma, 1984; Armitage & Otvos, 1982). Recent developments using magic-angle spinning (MAS) of solid samples (Ackerman, Orr, Bartuska & Maciel, 1979; Cheung, Worthington, Murphy & Gerstein, 1980; Mennitt, Shatlock, Bartuska & Maciel, 1981; Murphy & Gerstein, 1981; Murphy, Stevens, Cheung, Lacelle, Gerstein & Kurtz, 1981; Fyfe, Gobbi, Hartman, Lenkinski, O'Brian, Beange & Smith, 1982; Yannoni, 1982; Lyerla, Yannoni & Fyfe, 1982; Honkonen, Doty & Ellis, 1983) have further enhanced ¹¹³Cd NMR spectroscopy as a tool. These solid-state experiments make it attractive to synthesize a wide variety of stoichiometries and coordination geometries of Cd complexes, to determine their crystal structures, and to measure the MAS solid-state ¹¹³Cd NMR as well as the ¹¹³Cd solution NMR in order to understand the role played by coordination number and coordinated atoms on the position and width of ¹¹³Cd NMR signal as well as to define differences between solid-state and solution ¹¹³Cd NMR. Ultimately we would like to utilize results from single-crystal static ¹¹³Cd NMR individual shielding tensor elements to calculate the MAS results and compare them with the experiment. Recently, we reported a summary of ¹¹³Cd NMR solution, cross-polarization magic-angle spinning (CP/MAS) solid-state ¹¹³Cd NMR results found for models of the S₂ site of concanavalin A, the EF site of parvalbumin, troponin C and calmodulin (Rodesiler & Amma, 1982; Charles, Griffith, Rodesiler & Amma, 1983). We wish to report here the details of the crystal structure analyses referred to herein as well as the details of the solution and solid-state ¹¹³Cd NMR. We discuss the geometry of these Cd complexes and its relationship to the ¹¹³Cd chemical shift and the nature of the solution and solid-state species.

Experimental. An aqueous solution containing 0.01 mol of the appropriate acid [1.57 g *p*-chlorobenzoic (Matheson, Coleman & Bell) to make (A); 1.67 g *p*-nitrobenzoic (Baker) to make (B)] was added to a solution containing 1.54 g (0.005 mol) of Cd(NO₃)₂·4H₂O (Mallinckrodt). The pH was adjusted to approximately 6 with dilute NaOH and the total volume of 300 ml was warmed gently 323 K for 15 min then allowed to evaporate slowly at ambient temperature. Diffraction-quality crystals of both carboxylate complexes were collected in 2–4 d without washing. Samples of the size required for NMR measurements were filtered by simple gravity filtration. In order to prepare the pyridine adduct each complex was dissolved in warm methanol to which excess pyridine was added. Crystals of the *p*-chlorobenzoate adduct, (C),

appeared within hours, but the *p*-nitrobenzoate adduct yielded microcrystalline material unsuitable for X-ray analysis. However, both adducts were suitable for NMR data and were filtered and washed by gravity filtration. The ¹¹³Cd solid-state NMR data with magic-angle spinning and with cross polarization were obtained at the Regional NMR Center at Colorado State University on a Nicolet NT-200 spectrometer with parameters discussed elsewhere (Charles *et al.*, 1983). The ¹¹³Cd NMR solution data were observed on either a highly modified Varian XL-100 or on a Bruker WP-400 at the University of South Carolina Regional NMR Center. Crystals of (A), (B) and (C) sealed in thin-walled capillaries, mounted on Enraf–Nonius CAD-4 diffractometer interfaced to a PDP-11/60. Crystal alignment and data collection carried out by standard techniques previously reported (Griffith, Charles & Amma, 1982). *D_m* by flotation in (A) benzene–bromofom mixtures, (B) benzene, CCl₄, HCB₃ mixtures, (C) benzene, CCl₄ mixtures. Systematic absences: (A) (B) (C) *hkl*, *h* + *k* = 2*n* + 1; *h*0*l*, *l* = 2*n* + 1 absent; faces: (A) (001̄), (001), (010̄), (010), (402̄), (402), (401), (401); (B) (001̄), (001), (100), (100), (010), (010), (401), (401), (011̄); (C) (100), (100), (010), (010), (101), (101), (104̄), (104); approximate size of crystal: (A) 0.45 × 0.14 × 0.60 mm; (B) 0.44 × 0.31 × 0.55 mm; (C) 0.62 × 0.27 × 0.60 mm; absorption correction, max. and min. transmission factors (Frenz, 1982): (A) 0.785, 0.528; (B) 0.672, 0.587; (C) 0.754, 0.667; graphite monochromator, 2θ = 12.16°; σ(*F_o*²) = [σ(*I_{raw}*)² + (0.30*I_{raw}*)²]^{1/2}/Lp and *w* = 1/σ(*F_o*)². Data considered non zero if *F*² > 4σ(*F*²); number of reflections measured in ω–2θ mode to 2θ = 60°: (A) 2761, (B) 2378, (C) 3681; number used in structure solution and refinement: (A) 2228, (B) 2289, (C) 2791; *hkl* range: (A) 0–38, 0–7, –17–16; (B) 0–36, 0–7, –16–15; (C) 0–23, 0–8, –34–34. Variable scan speed with preliminary scan speed of 4° min⁻¹ 2θ; 25 general reflections used in orientation matrix (checked ever 24 h) and used for all parameter measurements (2θ range 20–30°); 3 standard reflections monitored every 100 reflections, decay <2% *I*; standard reflections: (A) 10,2,6, 11̄,3,7, 18,2,5; (B) 733, 14,2,2̄, 12,4,4; (C) 935, 4,2,13̄, 10,2,9. Structures solved by standard heavy-atom method and refined by full-matrix least squares (Frenz, 1982), with anisotropic temperature factors, anomalous-dispersion corrections and weights based upon intensity statistics; Σ*w_i*[|*F_o*| – |*F_c*|]² minimized. Final least squares performed on Amdahl V6 (Stewart, 1979) with *f*, *f'* and *f''* for Cd²⁺, Cl⁻, all others neutral atoms from *International Tables for X-ray Crystallography* (1974). Largest shift at end of refinement (A) 0.73σ, (B) 0.08σ, (C) 0.10σ; number of variables: (A) 105, (B) 123, (C) 155; final *R* = (A) 0.049, (B) 0.039 (C) 0.036; *wR* = (A) 0.051, (B) 0.065, (C) 0.042; error of observation of unit weight = (A) 1.51, (B) 1.42, (C)

Table 1. *Positional parameters and their e.s.d.'s*

	x	y	z	$B_{eq}(\text{\AA}^2)^*$
Diaquabis(p-chlorobenzoato)Cd^{II} (A)				
Cd	0.0	0.41648 (4)	0.2500	2.42 (1)
Cl	0.22278 (3)	-0.6860 (2)	0.65227 (8)	4.92 (3)
O(1)	0.06736 (7)	0.1308 (4)	0.2850 (2)	2.77 (7)
O(2)	0.04498 (7)	0.2348 (4)	0.4418 (1)	3.02 (7)
O(3)	0.03218 (9)	0.7111 (4)	0.1601 (2)	3.68 (7)
C(1)	0.11056 (9)	-0.0906 (4)	0.4575 (2)	2.39 (7)
C(2)	0.1072 (1)	-0.1761 (7)	0.5631 (2)	3.4 (1)
C(3)	0.1421 (1)	-0.3582 (7)	0.6239 (3)	3.6 (1)
C(4)	0.1799 (1)	-0.4561 (5)	0.5757 (3)	3.18 (7)
C(5)	0.1834 (1)	-0.3789 (7)	0.4695 (3)	4.0 (1)
C(6)	0.1483 (1)	-0.1919 (7)	0.4093 (2)	3.4 (1)
C(7)	0.07234 (9)	0.1049 (4)	0.3929 (2)	2.28 (7)
Diaquabis(p-nitrobenzoato)Cd^{II} (B)				
Cd	0.5000	0.92806 (2)	0.2500	2.11 (1)
N	0.71394 (8)	-0.1549 (4)	0.6541 (2)	2.79 (7)
O(1)	0.56625 (6)	0.6416 (4)	0.2954 (1)	2.49 (6)
O(2)	0.54440 (6)	0.7422 (3)	0.4495 (1)	2.70 (6)
O(3)	0.70570 (9)	-0.2459 (4)	0.7384 (2)	4.38 (7)
O(4)	0.75064 (8)	-0.2156 (4)	0.6202 (2)	4.10 (7)
O(5)	0.53170 (8)	1.2223 (3)	0.1661 (2)	3.28 (7)
C(1)	0.6098 (1)	0.4193 (3)	0.4719 (2)	2.03 (7)
C(2)	0.60588 (9)	0.3258 (4)	0.5739 (2)	2.83 (7)
C(3)	0.6403 (1)	0.1351 (5)	0.6355 (2)	2.82 (7)
C(4)	0.6782 (1)	0.0485 (4)	0.5903 (2)	2.35 (7)
C(5)	0.6822 (1)	0.1352 (7)	0.4886 (2)	3.15 (7)
C(6)	0.64824 (9)	0.3254 (5)	0.4290 (2)	3.0 (1)
C(7)	0.57159 (8)	0.6156 (4)	0.4039 (2)	2.15 (7)
Aquabis(p-chlorobenzoato)bis(pyridine)Cd^{II} (C)				
Cd	0.0	0.10415 (3)	0.2500	2.703 (7)
O(1)	0.0562 (1)	0.0425 (3)	0.16150 (7)	4.33 (7)
O(2)	0.0339 (1)	0.3887 (2)	0.18466 (6)	3.85 (7)
Cl	0.15591 (7)	0.5329 (2)	-0.07226 (3)	7.82 (6)
N	0.1251 (1)	0.1347 (3)	0.29145 (7)	3.35 (7)
C(1)	0.0790 (1)	0.3196 (4)	0.09447 (7)	3.09 (7)
C(2)	0.1194 (2)	0.1734 (4)	0.06109 (9)	4.05 (7)
C(3)	0.1427 (2)	0.2365 (5)	0.00893 (9)	5.0 (1)
C(4)	0.1265 (2)	0.4488 (6)	-0.0082 (1)	4.7 (1)
C(5)	0.0860 (2)	0.5955 (4)	0.0240 (1)	4.7 (1)
C(6)	0.0628 (1)	0.5294 (4)	0.07610 (9)	3.54 (7)
C(7)	0.0552 (1)	0.2452 (4)	0.15052 (7)	3.05 (7)
C(8)	0.1688 (1)	0.3135 (4)	0.28261 (8)	3.81 (7)
C(9)	0.2443 (1)	0.3402 (5)	0.3042 (1)	4.3 (1)
C(10)	0.2754 (1)	0.1777 (6)	0.3360 (1)	4.7 (1)
C(11)	0.2311 (2)	-0.0033 (6)	0.3464 (1)	5.1 (1)
C(12)	0.1555 (2)	-0.0215 (5)	0.3240 (1)	4.28 (7)
O(3)	0.0	-0.2679 (4)	0.2500	6.2 (2)

$$* B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

1.40. H atoms located from difference electron density maps. H-atom coordinates refined, *B* factors constant. Final difference Fourier map qualitatively featureless; all computer programs used except final refinement were from the Enraf-Nonius *SDP* package on the PDP 11/60 (Frenz, 1982). Positional and equivalent isotropic thermal parameters of (A), (B), (C) are listed in Table 1. Table 2 contains bonded and selected non-bonded interatomic distances and angles. *ORTEP* (Johnson, 1970) drawings of isolated molecules of (A), (B), (C) are shown in Figs. 1–3, respectively.*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving hydrogen and least-squares planes data for all three compounds and unit-cell drawings of (A) and (C) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39938 (50 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. All three structures may be described as isolated molecules separated by ordinary van der Waals distances (Figs. 1–3). In the structures of the diaqua-

Table 2. *Bonded distances (Å) and angles (°) with e.s.d.'s in parentheses*

Diaquabis(p-chlorobenzoato)cadmium(II) (A)				
Cd–O(1)	2.267 (2)	C(1)–C(6)	1.385 (4)	
Cd–O(2)	2.464 (2)	C(1)–C(7)	1.496 (3)	
Cd–O(3)	2.215 (2)	C(2)–C(3)	1.386 (4)	
Cl–C(4)	1.734 (3)	C(3)–C(4)	1.380 (5)	
O(1)–C(7)	1.276 (3)	C(4)–C(5)	1.374 (5)	
O(2)–C(7)	1.257 (3)	C(5)–C(6)	1.405 (5)	
C(1)–C(2)	1.379 (4)			
O(1)–Cd–O(2)	55.34 (7)	C(2)–C(1)–C(7)	120.2 (2)	
O(1)–Cd–O(3)	101.23 (8)	C(6)–C(1)–C(7)	119.8 (2)	
O(1)–Cd–O(1')	94.89 (8)	C(1)–C(2)–C(3)	121.0 (3)	
O(1)–Cd–O(2')	91.91 (7)	C(2)–C(3)–C(4)	118.6 (3)	
O(1)–Cd–O(3')	140.51 (6)	Cl–C(4)–C(3)	118.0 (3)	
O(2)–Cd–O(3)	126.81 (6)	Cl–C(4)–C(5)	120.2 (3)	
O(2)–Cd–O(2')	133.35 (7)	C(3)–C(4)–C(5)	121.7 (3)	
O(2)–Cd–O(3')	88.07 (7)	C(4)–C(5)–C(6)	119.1 (3)	
O(3)–Cd–O(3')	88.74 (9)	C(1)–C(6)–C(5)	119.6 (3)	
Cd–O(1)–C(7)	96.1 (2)	O(1)–C(7)–O(2)	121.0 (2)	
Cd–O(2)–C(7)	87.5 (1)	O(1)–C(7)–C(1)	117.5 (2)	
C(2)–C(1)–C(6)	119.9 (2)	O(2)–C(7)–C(1)	121.5 (2)	
Diaquabis(p-nitrobenzoato)cadmium(II) (B)				
Cd–O(1)	2.255 (2)	C(1)–C(2)	1.379 (4)	
Cd–O(2)	2.502 (2)	C(1)–C(6)	1.393 (4)	
Cd–O(5)	2.213 (2)	C(1)–C(7)	1.496 (3)	
N–O(3)	1.226 (4)	C(2)–C(3)	1.403 (4)	
N–O(4)	1.226 (4)	C(3)–C(4)	1.387 (4)	
N–C(4)	1.478 (3)	C(4)–C(5)	1.363 (4)	
O(1)–C(7)	1.286 (3)	C(5)–C(6)	1.389 (4)	
O(2)–C(7)	1.257 (3)			
O(1)–Cd–O(2)	55.33 (6)	C(2)–C(1)–C(6)	120.2 (2)	
O(1)–Cd–O(5)	102.74 (7)	C(2)–C(1)–C(7)	120.5 (3)	
O(1)–Cd–O(1')	93.05 (7)	C(6)–C(1)–C(7)	119.4 (3)	
O(1)–Cd–O(2')	90.87 (6)	C(1)–C(2)–C(3)	120.7 (3)	
O(1)–Cd–O(5')	140.44 (6)	C(2)–C(3)–C(4)	117.2 (3)	
O(2)–Cd–O(5)	127.95 (5)	N–C(4)–C(3)	117.3 (2)	
O(2)–Cd–O(2')	132.55 (6)	N–C(4)–C(5)	119.5 (3)	
O(2)–Cd–O(5')	88.00 (6)	C(3)–C(4)–C(5)	123.1 (2)	
O(5)–Cd–O(5')	87.83 (7)	C(4)–C(5)–C(6)	119.0 (3)	
O(3)–N–O(4)	124.9 (2)	C(1)–C(6)–C(5)	119.8 (2)	
O(3)–N–C(4)	118.0 (2)	O(1)–C(7)–O(2)	121.6 (2)	
O(4)–N–C(4)	117.1 (2)	O(1)–C(7)–C(1)	116.8 (2)	
Cd–O(1)–C(7)	96.8 (1)	O(2)–C(7)–C(1)	121.5 (2)	
Cd–O(2)–C(7)	86.2 (1)			
Aquabis(p-chlorobenzoato)bis(pyridine)cadmium(II) (C)				
Cd–O(1)	2.408 (2)	C(1)–C(6)	1.376 (4)	
Cd–O(2)	2.428 (2)	C(1)–C(7)	1.506 (3)	
Cd–N	2.346 (2)	C(2)–C(3)	1.396 (3)	
Cd–O(3)	2.254 (3)	C(3)–C(4)	1.380 (5)	
O(1)–C(7)	1.258 (3)	C(4)–C(5)	1.374 (4)	
O(2)–C(7)	1.262 (3)	C(5)–C(6)	1.400 (4)	
Cl–C(4)	1.732 (3)	C(8)–C(9)	1.388 (3)	
N–C(8)	1.330 (3)	C(9)–C(10)	1.360 (4)	
N–C(12)	1.339 (3)	C(10)–C(11)	1.354 (5)	
C(1)–C(2)	1.390 (3)	C(11)–C(12)	1.390 (4)	
O(1)–Cd–O(2)	54.28 (6)	C(2)–C(1)–C(7)	119.0 (2)	
O(1)–Cd–N	92.39 (7)	C(6)–C(1)–C(7)	121.5 (2)	
O(1)–Cd–O(3)	81.12 (4)	C(1)–C(2)–C(3)	120.7 (3)	
O(1)–Cd–O(1')	162.15 (8)	C(2)–C(3)–C(4)	118.6 (3)	
O(1)–Cd–O(2')	143.49 (6)	Cl–C(4)–C(3)	119.6 (2)	
O(1)–Cd–N'	89.01 (7)	Cl–C(4)–C(5)	118.7 (3)	
O(2)–Cd–N	90.74 (7)	C(3)–C(4)–C(5)	121.7 (3)	
O(2)–Cd–O(3)	135.28 (4)	C(4)–C(5)–C(6)	119.0 (2)	
O(2)–Cd–O(2')	89.49 (6)	C(1)–C(6)–C(5)	120.5 (2)	
O(2)–Cd–N'	82.81 (7)	O(1)–C(7)–O(2)	122.2 (2)	
N–Cd–O(3)	94.53 (5)	O(1)–C(7)–C(1)	119.1 (2)	
N–Cd–N'	170.94 (8)	O(2)–C(7)–C(1)	118.7 (2)	
Cd–O(1)–C(7)	92.2 (1)	N–C(8)–C(9)	122.9 (2)	
Cd–O(2)–C(7)	91.2 (1)	C(8)–C(9)–C(10)	119.0 (3)	
Cd–N–C(8)	119.6 (1)	C(9)–C(10)–C(11)	118.8 (2)	
Cd–N–C(12)	122.9 (2)	C(10)–C(11)–C(12)	119.9 (3)	
C(8)–N–C(12)	117.6 (2)	N–C(12)–C(11)	121.8 (3)	
C(2)–C(1)–C(6)	119.5 (2)			

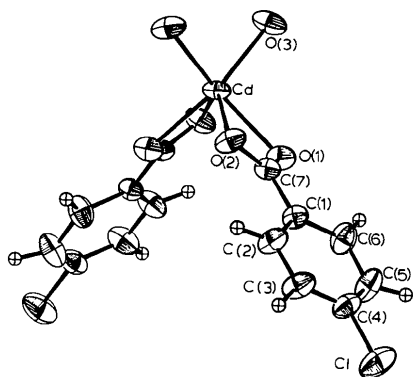


Fig. 1. An ORTEP view of an isolated molecule of diaquabis(*p*-chlorobenzoato)Cd^{II} showing the orientation of the ligands about the Cd atom. A twofold crystallographic axis of symmetry passes vertically through the Cd atom and relates the two halves of the complex (primed to unprimed). Atoms are labeled only on one half of the molecule. The ellipsoids are drawn at the 50% level and the hydrogen atoms are drawn with an arbitrary radius of 0.1 Å. The water hydrogens seem to be disordered and are not displayed.

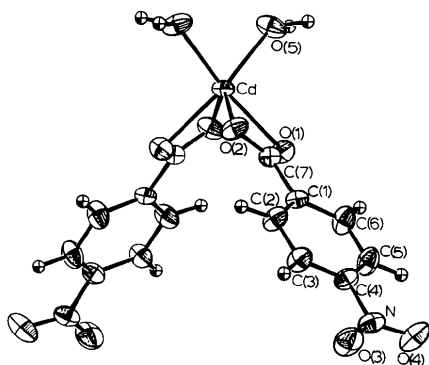


Fig. 2. An ORTEP view of an isolated molecule of diaquabis(*p*-nitrobenzoato)Cd^{II}. The water hydrogen atoms were found in this structure and are displayed. Other remarks are as in Fig. 1.

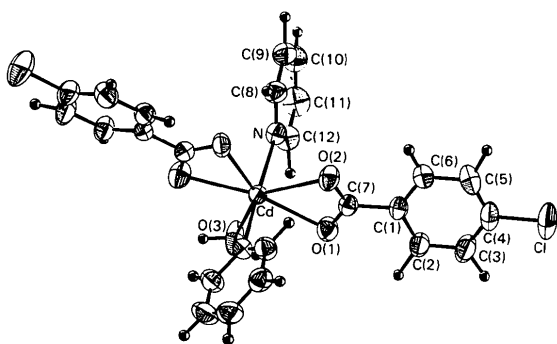


Fig. 3. An ORTEP view of an isolated molecule of aquabis(*p*-chlorobenzoato)bis(pyridine)Cd^{II}. The twofold crystallographic axis passes through Cd and O(3), relating again the two halves of the molecule (primed to unprimed). The pentagonal plane of the pentagonal bipyramid geometry about Cd is defined by O(1), O(2), the symmetry-related pair and O(3). The axial ligands are the pyridine molecules. The hydrogen atoms were located on O(3) and on the other ligands. Other general remarks from the caption of Fig. 1 apply.

bis(*p*-chlorobenzoato)Cd^{II} (*A*) and diaquabis(*p*-nitrobenzoato)Cd^{II} (*B*) the Cd atoms are required to be on a crystallographic twofold axis of symmetry. The structure of (*A*) and (*B*) may be described as a distorted irregular six-coordinate Cd²⁺, intermediate between a trigonal prism and a trigonal antiprism (octahedral) coordination. The simplest view of the coordination is to note that Cd, O(1), O(2'), O(3') and O(3), Cd, O(1'), O(2) each constitute reasonably good planes, and these two planes then form a dihedral angle of 82.1 (1)° consistent with the twofold symmetry axis and the other interatomic angles. In the trigonal-prism description vertices of four of the edges perpendicular to the threefold axis are made of oxygens from chelating carboxyl groups and the remaining two vertices are from oxygen atoms of water molecules. The crystallographic twofold axis passes through the bisector of the line between the water-molecule oxygen atoms and the Cd atom. It should be noted that the Cd—O distances for oxygens of carboxylate groups are not equal but are significantly different at 2.267 (2), Cd—O(1), and 2.464 (2) Å, Cd—O(2), for (*A*) and 2.255 (2) and 2.502 (2) Å for (*B*). These differences are also reflected in the C—O distance differences of 1.276 (3), C(7)—O(1), 1.257 (3) Å, C(7)—O(2), for (*A*) and 1.286 (3), 1.257 (3) Å for (*B*). It is somewhat surprising to note that the carboxyl group is not coplanar with the aromatic ring in (*A*) or (*B*) [dihedral angles 16.9 (1), 19.0 (1)°, respectively] and the nitro group in (*B*) is also slightly non-coplanar [6.8 (1)°] with the ring. The relatively sharp O(2)—Cd—O(1) angle of ~55° in all three structures is expected. The angles C(7)O(1)Cd and C(7)O(2)Cd in (*A*) and (*B*) of 96.1 (2), 87.5 (1) and 96.8 (1), 86.2 (1)°, respectively, along with the Cd—O distances, imply that O(1) interacts with Cd *via* an oxygen *p* orbital and lone pair, whereas O(2) interacts only poorly with a lone-pair *sp*² orbital and electron pair. It should be noted that the water molecules interact with Cd *via* only one of the lone-pair orbitals and electrons.

The structure of aquabis(*p*-chlorobenzoato)bis(pyridine)cadmium(II) (*C*) may be described by the replacement of a water molecule in (*A*) or (*B*) by pyridine and the addition of a pyridine molecule to make a seven-coordinate pentagonal bipyramid (PBP) complex with the pyridine ligands in axial positions, Fig. 3. The Cd is again on a crystallographic twofold axis as in (*A*) and (*B*) but now the twofold axis passes through the Cd and the water oxygen and relates the four carboxyl oxygen atoms in pairs. In contrast to the structures of (*A*) and (*B*), the Cd—O (carboxylate) distances are essentially the same at 2.408 (2) and 2.428 (2) Å and ~0.15 Å longer than the shortest Cd—O (carboxylate) distance of (*A*) and (*B*).

The pentagonal plane in (*C*) is planar well within experimental error and, as expected, the chelating O—Cd—O angle is about 54°. The remaining distances

and angles are the expected values. The angle between the carboxylate groups and the benzene rings is now $18.4(2)^\circ$. The nitrogen atoms of the pyridine rings clearly donate an sp^2 orbital and lone pair to the metal atom as evidenced by the Cd–N–C(10) angle of $180.5(1)^\circ$. The C(7)–O(2)–Cd and C(7)–O(1)–Cd angles are about 90° , indicating poor overlap with sp^2 lone pairs on the oxygen atoms. This lone-pair concept is supported by the equality of the C–O distances in the carboxyl groups. This structure may be viewed as a model for the coordination polyhedra of (A), (B) in solvent donor solution.

In all three of these structures, as well as other Cd²⁺ structures previously reported by us (Charles *et al.*, 1983; Griffith *et al.*, 1982; Turner, Charles & Amma, 1982) and others (Mostad & Rosenqvish, 1971; Flook, Freeman, Moore & Scudder, 1973; Boman, 1974; Harrison & Trotter, 1972), it is interesting to note that the carboxylate ligands tend to form the four-membered chelate rings with Cd, in contrast to the behavior of transition-metal carboxylates.

The distorted six-coordinate Cd^{II} carboxylate dihydrate complexes studied herein can be characterized by a ¹¹³Cd NMR CP/MAS signal deshielded at ~ 25 p.p.m. from the standard 0.1M Cd(ClO₄)₂·6H₂O D₂O solutions. This is in marked contrast to the ¹¹³Cd NMR CP/MAS results of -31 p.p.m. (shielded) for the PBP seven-coordinate Cd²⁺ in bis- μ -(*o*-hydroxybenzoato)bis(*o*-hydroxybenzoato)Cd^{II}, [Cd(H₂O)₂(CO₂-C₆H₄OH)₂]₂, (D) (Charles *et al.*, 1983), -52 p.p.m. for the seven-coordinate PBP Cd²⁺ in Cd(succinato)·H₂O (Griffith *et al.*, 1982) (E) and -58 p.p.m. (Mennitt *et al.*, 1981; Rodesiler & Amma, 1982) (F) for the irregular seven-coordinate Cd²⁺ in Cd(CH₃CO₂)₂·2H₂O (Post & Trotter, 1974). It is probably safe to say that the carboxylic-acid ligands and water molecules of hydration that yield shielded values of -30 to -50 p.p.m. correspond to higher coordination numbers than six and values of $+ \sim 25$ p.p.m. are due to the six-oxygen-coordinated Cd²⁺. The addition of pyridine to these complexes (at least to the *p*-chloro derivative) gives rise to a PBP seven-coordinate, 4-O(carboxylate), O(H₂O), 2-N(pyridine), complex with a ¹¹³Cd NMR chemical shift of $+31$ p.p.m. in the solid state. Since in the solid state the seven-oxygen-coordination PBP (D) (dimer) is at -31 p.p.m. and remains at a negative value in solution and the irregular seven-coordinate (F) is the same in the solid and solution, we interpret the ~ -50 p.p.m. value of diaqua(*p*-*x*-benzoato)Cd^{II} (where *x* = Cl or NO₂) in methanol or *N,N*-dimethylformamide solution as corresponding to an irregular CdO₇ species in solution. In going from (A), (B) to (C), in which the coordination number is increased from six to seven by replacing one of the water molecules with a pyridine nitrogen and adding an additional pyridine nitrogen, the deshielding increases by only 5–10 p.p.m. This may be interpreted

as a compromise between increasing the coordination number, which tends to give more shielded values, and replacing oxygen by pyridine, which tends toward greater deshielded values. These results are not to be interpreted as that any negative value of the ¹¹³Cd NMR chemical shift in p.p.m. (shielded) corresponds to higher coordination number, but, within the framework of these restricted geometries and ligands, negative values with only oxygen donors correspond to seven-coordinated or more oxygen atoms. Much depends upon the nature of the ligands as well as coordination number. The effect of nitrate 'bound' to metal creating a shielding of ~ 50 p.p.m. for each nitrate (Rodesiler *et al.*, 1984) is an example. Therefore, in the absence of nitrate, sulfate or similar weak oxygen donors, the negative values of -100 p.p.m. in Cd-substituted proteins is probably due to higher coordination number.

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Dihydrogen (\pm)-*trans*-1,2-Cyclohexanediaminetetraacetic Acid* Tetrachloropalladate(II) and Tetrachloroplatinate(II) Pentahydrates, [C₁₄H₂₄N₂O₈][PdCl₄].5H₂O and [C₁₄H₂₄N₂O₈][PtCl₄].5H₂O

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Abstract. [PdCl₄]²⁻ salt: $M_r = 686.7$, $P2_1/c$, $a = 12.457$ (3), $b = 11.427$ (3), $c = 18.833$ (4) Å, $\beta = 106.11$ (2)°, $V = 2575.5$ (9) Å³, $Z = 4$, $D_x = 1.77$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.18$ mm⁻¹, $F(000) = 1400$, $T = 292$ (2) K, $R = 0.040$ for 4672 observed unique reflections. Isomorphous [PtCl₄]²⁻ salt: $M_r = 775.4$, $P2_1/c$, $a = 12.499$ (3), $b = 11.371$ (3), $c = 18.885$ (5) Å, $\beta = 106.09$ (2)°, $V = 2579.0$ (11) Å³, $Z = 4$, $D_x = 2.00$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 5.98$ mm⁻¹, $F(000) = 1528$, $T = 293$ (2) K, $R = 0.048$ for 5223 observed unique reflections. The cations are *trans*-1,2-cyclohexanediaminetetraacetic acid molecules with two additional protons residing on amine nitrogen atoms. The crystals contain alternating layers of ions and water molecules parallel to the *ab* plane, with an extensive hydrogen-bonding network. The conformation of the molecule is close to that required for a six- or seven-coordinate ligand attached to a metal atom, as is usual for coordinated ethylenediaminetetraacetate-like ligands.

Introduction. The stereochemistry of complexes of ethylenediaminetetraacetic acid and related compounds has been well investigated; however, to date there have been few structures reported for uncoordinated ligands and none on a diprotonated derivative. Information on the uncoordinated *trans*-1,2-cyclohexanediamine

derivative, which exhibits marked stereoselectivity upon coordination, would be of particular interest. Here we report the structure of diprotonated racemic *trans*-1,2-cyclohexanediaminetetraacetic acid as the pentahydrated tetrachloropalladate(II) and tetrachloroplatinate(II) salts.

Experimental. Compounds prepared by mixing a solution of PdCl₂ or PtCl₂ in 2 M HCl with aqueous solution of *trans*-1,2-cyclohexanediaminetetraacetic acid. Crystals grown from hydrochloric acid, rectangular prisms, 0.15 × 0.23 × 0.25 mm for [PdCl₄]²⁻ salt, 0.21 × 0.35 × 0.46 mm for [PtCl₄]²⁻ salt. D_m not determined. Syntex P3/F diffractometer, graphite monochromator. Lattice parameters from 25 reflections for each structure ($12 < 2\theta < 25^\circ$). Empirical absorption corrections based on ψ scans; min. and max. transmission coefficient 0.546 and 0.604 ([PdCl₄]²⁻ salt), 0.453 and 0.942 ([PtCl₄]²⁻ salt). θ - 2θ scans, $\sin\theta/\lambda = 0.01$ to 0.70 Å⁻¹ ($1 \leq 2\theta \leq 60^\circ$; $\pm h, -k, -l$ for [PdCl₄]²⁻ compound; $\pm h, +k, -l$ for [PtCl₄]²⁻ compound). Three standard reflections (Pd: 800, 080, 008; Pt: 505, 060, 008) every 141 reflections (5% variation). For Pd compound, 8461 reflections measured, 7491 unique, 2819 unobserved [$I \leq 5.0\sigma(I)$]. For Pt compound, 8191 reflections measured, 7506 unique, 2283 unobserved [$I \leq 5.0\sigma(I)$]. Space group for both structures, as determined from systematic absences ($h0l, h+1 = 2n+1$ and $0k0, k = 2n+1$), unambiguous. All computer programs from SHELXTL (Sheldrick, 1981) and

* (\pm)-*trans*-N,N'-(1,2-Cyclohexylene)bis[(carboxymethyl)-ammonium].