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Pentagonal-Bipyramid Geometry and ^{113}Cd NMR Chemical Shifts: Crystal Structures and Solution and Solid-State ^{113}Cd NMR of Bis(μ-*o*-hydroxybenzoato)bis(*o*-hydroxybenzoato)tetraaquodicadmium(II) and Tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II)

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Bis(μ-*o*-hydroxybenzoato)bis(*o*-hydroxybenzoato)tetraaquodicadmium(II) (I) and tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II) (II) have been shown by X-ray diffraction to consist of pentagonal-bipyramidal seven-coordinate Cd(II). In the former, the coordination sphere is made up of five carboxyl oxygen atoms in the equatorial plane (one bridging) and two oxygen atoms of water molecules in the axial positions. The latter has four carboxyl oxygen atoms and one pyridine nitrogen atom in the equatorial plane and two axial pyridine nitrogen atoms to complete the coordination sphere. The solid-state MAS ^{113}Cd NMR chemical shifts of these compounds are -31 and $+61$ ppm, respectively. The ^{113}Cd NMR chemical shifts of these and other Cd-containing compounds are correlated with the number of lone pairs that are directed toward the Cd atom. The shielded chemical shifts of a number of Cd model compounds as well as Cd-containing macromolecules are discussed. Crystal data (I): $a = 7.747$ (3) Å, $b = 12.455$ (3) Å, $c = 15.725$ (7) Å, $\beta = 96.23$ (3)°, $Z = 4$, $P2_1/a$, $\rho_{\text{obsd}} = 1.83$ (2) g/cm^3, $\rho_{\text{calcd}} = 1.86$ g/cm^3, NO = 5058, NV = 208, $R_F = 0.028$. Crystal data (II): $a = 10.187$ (4) Å, $b = 14.846$ (5) Å, $c = 17.965$ (5) Å, $\beta = 93.79$ (3)°, $Z = 4$, $P2_1/n$, $\rho_{\text{obsd}} = 1.54$ (2) g/cm^3, $\rho_{\text{calcd}} = 1.53$ g/cm^3, NO = 4944, NV = 428, $R_F = 0.029$. For both I and II, structures were refined by full-matrix least squares with anisotropic temperature factors and absorption corrections.

Introduction

^{113}Cd NMR with a chemical shift range of ~900 ppm has been shown to be a sensitive probe of metal ion sites in a wide variety of compounds, ranging from organometallic to biological macromolecules.[1-34] Recent developments using magic angle spinning (MAS) of solid samples[35-37] have further enhanced ^{113}Cd NMR spectroscopy as a tool. Of particular importance for this report is the fact that the ^{113}Cd chemical shifts for Cd in the S_2 site of concanavalin A[13] and the EF site of parvalbumin,[12,17] calmodulin,[28] and troponin C[19] have been found to be at ~-100 ppm (more shielded than the aqueous 0.1 M $Cd(ClO_4)_2$ standard), and until recently there has been no explanation of this behavior in terms of model compounds.[33] As part of a program involving the synthesis, ^{113}Cd solution NMR measurement, ^{113}Cd CP/MAS solid NMR observations, and the single-crystal X-ray structure determination of models of biological macromolecular sites containing cadmium, we have synthesized a series of pentagonal-bipyramidal seven-coordinate Cd complexes. We report here on two of them and discuss their relationship to the above mentioned shielded enzymatic sites and to the negative chemical shifts in general. We reported earlier the preliminary results[33] on some of these, and here we give the structural details as well as as the ^{113}Cd NMR spectral details and attempt a more rational description of the results.

Experimental Section

Bis[diaquobis(*o*-hydroxybenzoato)cadmium(II)] (I). A 250-mL solution containing 3.6 g (0.02 mol) of acetylsalicylic acid (Mallinckrodt) and 1.54 g (0.01 mol) of $Cd(NO_3)_2 \cdot 4H_2O$ (Fisher) was brought to pH ~6 with ammonium hydroxide and heated gently (~60 °C) for 30 min. Hydrolysis and complexation proceeded smoothly, and crystals suitable for diffraction studies were isolated.

Tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II) (II). Crystals of bis[diaquobis(*o*-hydroxybenzoato)cadmium(II)] were dissolved in methanol containing an excess of pyridine (Baker). Crystals of the product appeared in 3–5 days and were isolated for diffraction studies or filtered and air-dried for the ^{113}Cd NMR studies.

NMR Data. The ^{113}Cd NMR methanol or DMF solution data were collected on a highly modified XL-100-15 spectrometer described earlier[3] or on a Bruker WP200 spectrometer. Natural-abundance ^{113}Cd was used throughout. The solution spectra were measured over a concentration range of 35–105 mM. A small concentration de-

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Table I. Cell Data, Data Collection, and Refinement Parameters

(a) Bis[bis(*o*-hydroxybenzoato)cadmium(II) dihydrate]

$a = 7.747$ (3) Å $b = 12.455$ (3) Å $c = 15.725$ (7) Å
$\beta = 96.23$ (3)° $\rho_{obsd} = 1.83$ (2) g/cm³ $\rho_{calcd} = 1.86$ g/cm³
$Z = 4$ fw = 422.66

λ(Mo Kα) = 0.710 73 Å
graphite monochromator used; $2\theta = 6.1°$
space group $P2_1/a$
$h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$ absent
size of crystal: 0.20 × 0.20 × 0.50 mm
$\mu = 14.8$ cm^{-1}
faces of the form {001}, {010}, {100}, [101], [101]
abs cor made; max/min transmissn factors 0.765/0.485
P factor = 0.030 in $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PI_{raw})^2]^{1/2}/Lp$ and $w = 1/\sigma(F_o)^2$
data considered nonzero if $F^2 > 4\sigma(F^2)$
6614 independent hkl's measd in ω–2θ mode to $2\theta = 70°$
5058 reflcns used to solve and refine structure
variable scan speed with preliminary scan speed of 4°/min in 2θ
25 reflcns used in orientation matrix (checked every 24 h)
3 std reflcns monitored every 100 reflcns; decay less than 2% I
room temp ~18 °C
structure refined by full-matrix least squares, including anisotropic temperature factors and anomalous dispersion corrections with weights based upon intensity statistics; function minimized = $\Sigma_i w_i[|F_{oi}| - |F_{ci}|]^2$
largest shift at end of refinement: 0.55σ
final least squares performed on Amdahl V6 (f's from ref 41)
no. of variables: 208
final $R = 0.028$, weighted $R = 0.042$
error of observn of unit wt: 1.27

(b) Tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II)

$a = 10.187$ (4) Å $b = 14.846$ (5) Å $c = 17.965$ (5) Å
$\beta = 93.79$ (3)° $\rho_{obsd} = 1.54$ (2) g/cm³ $\rho_{calcd} = 1.53$ g/cm³
$Z = 4$ fw = 623.9

λ(Mo Kα) = 0.710 73 Å
graphite monochromator used; $2\theta = 6.1°$
space group $P2_1/n$
$h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$ absent
size of crystal: 0.20 × 0.25 × 0.30 mm
$\mu = 8.5$ cm^{-1}
faces of the form {001}, {100}, {011}
abs cor made; max/min transmissn factors 0.855/0.789
P factor = 0.030 in $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PI_{raw})^2]^{1/2}/Lp$ and $w = 1/\sigma(F_o)^2$
data considered nonzero if $F^2 > 4\sigma(F^2)$
8171 independent hkl's measd in ω–2θ mode
4944 reflcns used to solve and refine structure
variable scan speed with preliminary scan speed of 4°/min in 2θ
25 reflcns used in orientation matrix (checked every 24 h)
3 std reflcns monitored every 100 reflcns; decay less than 2% I
room temp ~18 °C
structure refined by full-matrix least squares, including anisotropic temp factors and anomalous dispersion corrections with weights based upon intensity statistics; function minimized = $\Sigma_i w_i[|F_{oi}| - |F_{ci}|]^2$
largest shift at end of refinement; 1.57σ
final least squares performed on Amdahl V6 (f's from ref 41)
no. of variables: 428
final $R = 0.029$, weighted $R = 0.033$
error of observn of unit wt: 0.92

pendence of ~3 ppm was observed. A typical peak width at peak half-height was found to be 20 Hz. The external standard was a 0.1 M aqueous $Cd(ClO_4)_2$ solution.

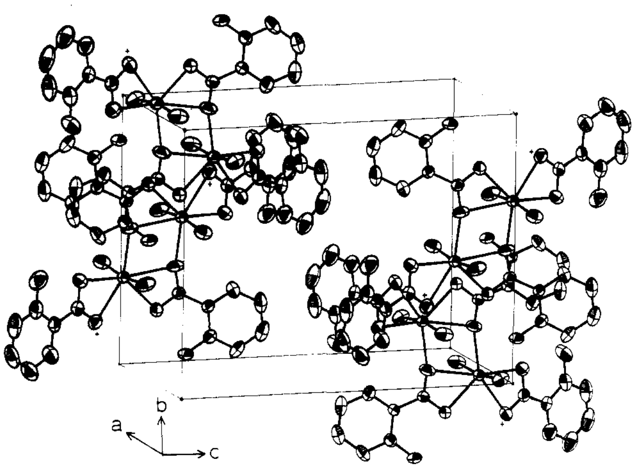

Figure 1. ORTEP drawing of the contents of the unit cell of I. The origin is in the left front corner with axes as indicated. The + in the upper left center of the unit cell identifies an oxygen involved in intermolecular hydrogen bonding to a water molecule translated back one unit cell from that nearest to the +.

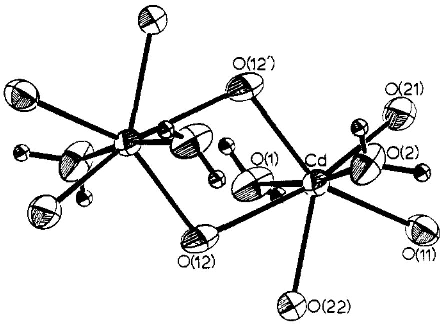

Figure 2. ORTEP drawing of the details of the environment of the Cd atom showing only the oxygen atoms and the water molecules in the coordination polyhedron. The orientation of the water molecules is readily apparent, and the direction of the lone-pair orbitals is easily seen.

Solid-state ^{113}Cd NMR spectra were obtained from ca. 0.5-g samples containing the natural-abundance ^{113}Cd nuclide on a modified Bruker WP200 or on a NT200 spectrometer at 44.42 MHz (4.7 T) by using cross-polarization (CP) and magic-angle-spinning (MAS) techniques. The contact time was 4 ms, the ^{1}H 90 °C spin-locking time was 5 ms, and the recycle time was 4 s. Rotor speeds of approximately 4 kHz were employed. A "solid solution" (finely dispersed mixture) of "concentration" 0.1 M $[Cd(H_2O)_6](ClO_4)_2$ in Al_2O_3 was used as an external standard.

The ^{113}Cd NMR results are shown in Table V.

X-ray Data. Crystals of both I and II were sealed into thin walled-capillaries and mounted on an Enraf-Nonius CAD-4 diffractometer interfaced to a PDP-11/40. Crystal alignment and data collection were carried out by standard techniques previously reported.[38] Details are found in Table I.

Solution and Refinement of Crystal Structures. The crystal structures of I and II were solved by standard heavy-atom methods[39] and refined by full-matrix least squares, including anisotropic temperature factors. Final refinement was completed on the Amdahl V6 with X-RAY 79[40] using anomalous dispersion corrections with scattering factors f, $\Delta f'$, $\Delta f''$ from ref 41. Absorption corrections were made. See Table I for details. Hydrogen atoms were located from difference maps for I and II. For I, they were included in the refinement with

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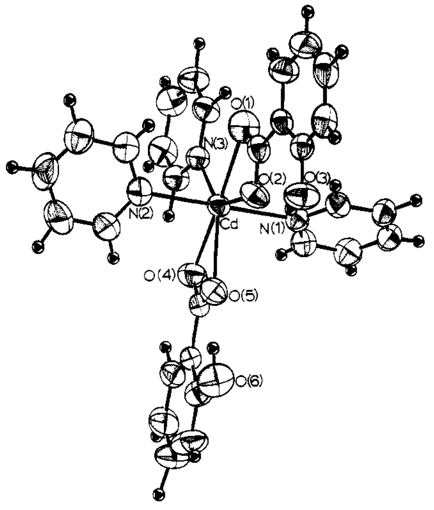

Figure 3. ORTEP drawing of the molecule of tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II) (II). The pentagonal plane of the PBP is defined by O(1), O(2), O(5), O(4), and N(3) whereas the axial ligands are N(1) and N(2). The notation is consistent with the tables and is as follows: O(4), O(5) are bonded to C(14), which is bonded to C(8), numbering then proceeding in a clockwise fashion toward O(6) for C(9), ..., C(13); O(1), O(2) are bonded to C(7), which is bonded to C(1), numbering then proceeding in a counterclockwise fashion toward O(3) for C(2), ..., C(6); from N(3) numbering is in a clockwise fashion for C(25), ..., C(29), from N(2) in a clockwise fashion for C(20), ..., C(24), and from N(1) in a counterclockwise fashion away from O(3) for C(15), ..., C(19). The ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level and those of the hydrogen atoms at an arbitrary radius of 0.1 Å.

a fixed value of positional and thermal parameters. For II, the hydrogen positional parameters were varied but B's were held constant. The final R factors were 0.028 and 0.029, respectively. See Table I. Tables of F_o and F_c have been deposited as supplementary material, along with the anisotropic thermal parameters. Positional and equivalent isotropic thermal parameters of both I and II are listed in Table II, but hydrogen atom coordinates have been deposited as supplementary material. Table III contains the bonded and selected nonbonded interatomic distances and angles. Table IV lists some important least-squares planes. ORTEP[42] drawings of the contents of the unit cell of I, details of the water molecules in the coordination sphere of I, and an isolated molecule of II are shown in Figures 1-3, respectively. Isolated dimers of I and the packing diagram of II have been deposited as supplementary material. A preliminary report of I[43] did not include the modern corrections as above or sufficient information for our studies; furthermore, we have a different interpretation of the hydrogen-bonding scheme, and consequently our results for I are included here along with those of II.

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B_{equiv}, Å^2
(a) Bis[bis(*o*-hydroxybenzoato)cadmium(II) dihydrate]				
Cd	0.00177 (1)	0.10559 (0)	0.08777 (0)	2.166 (6)
O(1)	0.2940 (2)	0.09439 (9)	0.0747 (1)	3.87 (7)
O(2)	−0.2823 (2)	0.0857 (1)	0.1000 (1)	3.76 (7)
O(11)	0.0444 (2)	0.2620 (1)	0.17989 (8)	3.25 (6)
O(21)	0.0837 (2)	0.1013 (1)	0.23420 (9)	3.85 (7)
O(31)	0.2247 (3)	0.0720 (2)	0.3877 (1)	5.5 (1)
O(12)	−0.0091 (2)	0.0756 (1)	−0.07218 (9)	3.74 (7)
O(22)	−0.0196 (2)	0.23622 (9)	−0.01752 (7)	3.12 (6)
O(32)	0.0097 (2)	0.40373 (9)	−0.1046 (1)	3.65 (7)
C(11)	0.1681 (2)	0.2479 (2)	0.3255 (1)	2.86 (7)
C(21)	0.2334 (3)	0.1794 (2)	0.3931 (1)	3.74 (7)
C(31)	0.3078 (3)	0.2266 (3)	0.4696 (1)	5.4 (1)
C(41)	0.3186 (4)	0.3340 (3)	0.4788 (2)	5.7 (2)
C(51)	0.2490 (5)	0.4011 (2)	0.4133 (2)	5.7 (1)
C(61)	0.1799 (3)	0.3576 (2)	0.3378 (1)	4.28 (7)
C(71)	0.0932 (2)	0.2015 (1)	0.2430 (1)	2.74 (7)
C(12)	0.0339 (2)	0.2260 (1)	−0.16275 (9)	2.26 (5)
C(22)	0.0394 (2)	0.3379 (1)	−0.1704 (1)	2.72 (6)
C(32)	0.0791 (3)	0.3850 (2)	−0.2469 (1)	3.77 (7)
C(42)	0.1098 (3)	0.3206 (2)	−0.3138 (1)	4.3 (1)
C(52)	0.1066 (3)	0.2105 (2)	−0.3078 (1)	4.4 (1)
C(62)	0.0673 (3)	0.1625 (2)	−0.2319 (1)	3.31 (7)
C(72)	−0.0013 (2)	0.1756 (1)	−0.08095 (8)	2.29 (6)
(b) Tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II)				
Cd	0.24913 (1)	0.48003 (1)	0.67816 (0)	3.071 (7)
O(1)	0.3843 (1)	0.5832 (1)	0.7620 (1)	5.25 (7)
O(2)	0.4726 (2)	0.4597 (1)	0.72129 (9)	4.43 (7)
O(3)	0.7164 (2)	0.4281 (1)	0.7456 (1)	5.70 (7)
O(4)	0.0945 (2)	0.3983 (1)	0.59495 (9)	4.81 (7)
O(5)	0.2806 (2)	0.3289 (1)	0.62328 (9)	4.71 (7)
O(6)	0.3298 (2)	0.1781 (1)	0.5625 (1)	6.3 (1)
N(1)	0.3259 (2)	0.5499 (1)	0.5705 (1)	3.49 (7)
N(2)	0.1709 (2)	0.4116 (1)	0.7853 (1)	4.07 (7)
N(3)	0.0844 (2)	0.5898 (1)	0.68497 (9)	3.32 (7)
C(1)	0.6091 (2)	0.5549 (2)	0.7981 (1)	3.09 (7)
C(2)	0.7203 (2)	0.5023 (1)	0.7898 (1)	3.49 (7)
C(3)	0.8402 (2)	0.5261 (2)	0.8260 (2)	4.5 (1)
C(4)	0.8494 (3)	0.5991 (2)	0.8707 (1)	5.5 (1)
C(5)	0.7406 (3)	0.6517 (2)	0.8804 (2)	5.8 (1)
C(6)	0.6217 (2)	0.6297 (2)	0.8444 (1)	4.7 (1)
C(7)	0.4808 (2)	0.5320 (2)	0.7587 (1)	3.8 (1)
C(8)	0.1275 (2)	0.2567 (1)	0.5385 (1)	3.05 (7)
C(9)	0.2087 (3)	0.1836 (2)	0.5282 (1)	4.4 (1)
C(10)	0.1627 (4)	0.1133 (2)	0.4808 (2)	6.5 (2)
C(11)	0.0415 (4)	0.1163 (2)	0.4465 (2)	6.5 (2)
C(12)	−0.0405 (3)	0.1889 (2)	0.4561 (2)	6.0 (1)
C(13)	0.0018 (2)	0.2580 (2)	0.5012 (1)	4.1 (1)
C(14)	0.1689 (2)	0.3327 (1)	0.5882 (1)	3.40 (7)
C(15)	0.2489 (2)	0.5564 (2)	0.5075 (1)	4.1 (1)
C(16)	0.2883 (3)	0.5943 (2)	0.4435 (1)	4.8 (1)
C(17)	0.4145 (3)	0.6285 (2)	0.4425 (1)	4.6 (1)
C(18)	0.4955 (2)	0.6236 (2)	0.5068 (1)	4.3 (1)
C(19)	0.4487 (2)	0.5834 (2)	0.5688 (1)	3.81 (7)
C(20)	0.1026 (3)	0.3348 (2)	0.7801 (2)	5.9 (1)
C(21)	0.0419 (4)	0.2998 (2)	0.8406 (2)	7.4 (2)
C(22)	0.0559 (3)	0.3433 (2)	0.9080 (2)	6.6 (2)
C(23)	0.1272 (3)	0.4191 (2)	0.9137 (2)	5.7 (1)
C(24)	0.1832 (2)	0.4523 (2)	0.8509 (2)	4.5 (1)
C(25)	−0.0367 (2)	0.5768 (2)	0.6519 (1)	4.0 (1)
C(26)	−0.1363 (2)	0.6388 (2)	0.6557 (2)	4.9 (1)
C(27)	−0.1131 (3)	0.7178 (2)	0.6944 (2)	5.2 (1)
C(28)	0.0098 (3)	0.7320 (2)	0.7285 (2)	5.0 (1)
C(29)	0.1055 (2)	0.6667 (2)	0.7222 (1)	4.2 (1)

Discussion

The crystal structure of I may be described as essentially isolated asymmetrically bridged dimers of diaquobis(*o*-hydroxybenzoato)cadmium(II) (Figure 1). The center of the dimer corresponds to a crystallographic center of symmetry; the dimer is formed by a bridging oxygen [O(12), O(12′)] of a carboxylato group with a Cd-Cd distance of 3.715 (2) Å. The OH groups of the salicylic acid [O(31), O(32)] are internally hydrogen bonded to the carboxyl groups. The molecular packing (Figure 1) is such that most of the intramolecular interaction is solely that of van der Waals forces except that H(22) (Figure 2) of water molecule O(2) is hydrogen bonded to O(11) of the dimer immediately below and, correspondingly, the other half of the dimer is hydrogen bonded to a corresponding oxygen atom immediately above. The coordination polyhedron of each Cd is an approximate pentagonal-bipyramidal[45] geometry (PBP) with the five carboxyl

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[42] Johnson, C. K. "ORTEP II", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1970.

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[44] Turner, R. W.; Charles, N. G.; Amma, E. L. *Cryst. Struc. Commun.* **1982**, *11*, 241-245.

[45] Pentagonal bipyramid geometry (PBP) has been observed previously for Cd; see: (a) Mostad, A.; Rosenquist, E. *Acta Chem. Scand.* **1971**, *25*, 147-157. (b) Post, M. L.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1922-1925. (c) Flooh, R. J.; Freeman, H. C.; Moore, C. J.; Scudder, M. L. *J. Chem. Soc., Chem. Commun.* **1973**, 753-754.

Table III. Bonded Distances (Å) and Angles (deg) with Esd's in Parentheses

		(a) Bis[bis(*o*-hydroxybenzoato)cadmium(II) dihydrate]			
Cd–O(1)	2.300 (2)	C(21)–O(31)	1.342 (3)	C(12)–C(22)	1.401 (2)
Cd–O(2)	2.243 (2)	C(31)–C(41)	1.347 (5)	C(12)–C(62)	1.392 (3)
Cd–O(11)	2.429 (1)	O(1)–H(1,1)	0.865 (1)	C(12)–C(72)	1.484 (2)
Cd–O(21)	2.322 (2)	O(1)–H(1,2)	0.862 (2)	C(22)–C(32)	1.401 (3)
Cd–O(12)	2.535 (2)	O(2)–H(2,1)	0.825 (2)	C(22)–O(32)	1.360 (2)
Cd–O(12′)	2.271 (2)	O(2)–H(2,2)	1.029 (2)	C(32)–C(42)	1.363 (3)
Cd–O(22)	2.314 (1)	C(41)–C(51)	1.388 (4)	C(42)–C(52)	1.375 (4)
C(11)–C(21)	1.413 (3)	C(51)–C(61)	1.363 (4)	C(52)–C(62)	1.398 (3)
C(11)–C(61)	1.382 (3)	C(71)–O(11)	1.271 (2)	C(72)–O(12)	1.256 (2)
C(11)–C(71)	1.480 (2)	C(71)–O(21)	1.257 (2)	C(72)–O(22)	1.271 (2)
C(21)–C(31)	1.404 (3)				
O(1)–Cd–O(2)	170.17 (9)	O(12′)–Cd–O(22)	128.45 (6)	C(22)–C(32)–C(42)	119.3 (2)
O(1)–Cd–O(11)	91.76 (5)	C(21)–C(11)–C(61)	118.6 (2)	C(32)–C(42)–C(52)	121.8 (2)
O(1)–Cd–O(21)	85.50 (7)	C(21)–C(11)–C(71)	119.9 (2)	C(42)–C(52)–C(62)	119.5 (2)
O(1)–Cd–O(12)	80.19 (6)	C(61)–C(11)–C(71)	121.4 (2)	C(12)–C(62)–C(52)	120.0 (2)
O(1)–Cd–O(12′)	83.88 (5)	C(11)–C(21)–C(31)	118.2 (2)	C(12)–C(72)–O(12)	122.1 (1)
O(1)–Cd–O(22)	88.46 (6)	C(11)–C(21)–O(31)	122.9 (2)	C(12)–C(72)–O(22)	118.4 (1)
O(2)–Cd–O(11)	96.24 (6)	C(31)–C(21)–O(31)	119.0 (2)	O(12)–C(72)–O(22)	119.5 (1)
O(2)–Cd–O(21)	94.45 (7)	C(21)–C(31)–C(41)	121.5 (2)	Cd–O(11)–C(71)	90.0 (1)
O(2)–Cd–O(12)	98.11 (6)	C(31)–C(41)–C(51)	120.3 (2)	Cd–O(21)–C(71)	95.3 (1)
O(2)–Cd–O(12′)	86.33 (6)	C(41)–C(51)–C(61)	119.4 (2)	Cd–O(12)–C(72)	88.0 (1)
O(2)–Cd–O(22)	98.30 (6)	C(11)–C(61)–C(51)	121.9 (2)	Cd–O(12)–Cd′	104.79 (6)
O(11)–Cd–O(21)	54.69 (4)	C(11)–C(71)–O(11)	120.6 (2)	Cd′–O(12)–C(72)	166.4 (1)
O(11)–Cd–O(12)	134.26 (5)	C(11)–C(71)–O(21)	119.8 (2)	Cd–O(22)–C(72)	97.9 (1)
O(11)–Cd–O(12′)	149.09 (4)	O(11)–C(71)–O(21)	119.6 (2)	Cd–O(1)–H(1,1)	118.3 (1)
O(11)–Cd–O(22)	81.79 (4)	C(22)–C(12)–C(62)	119.2 (2)	Cd–O(1)–H(1,2)	112.8 (1)
O(21)–Cd–O(12)	163.08 (8)	C(22)–C(12)–C(72)	120.4 (1)	H(1,1)–O(1)–H(1,2)	108.5 (2)
O(21)–Cd–O(12′)	94.42 (4)	C(62)–C(12)–C(72)	120.3 (2)	Cd–O(2)–H(2,1)	122.5 (1)
O(21)–Cd–O(22)	135.74 (3)	C(12)–C(22)–C(32)	120.1 (2)	Cd–O(2)–H(2,2)	112.3 (1)
O(12)–Cd–O(12′)	75.21 (6)	C(12)–C(22)–O(32)	121.7 (2)	H(2,1)–O(2)–H(2,2)	108.2 (2)
O(12)–Cd–O(22)	53.27 (5)	C(32)–C(22)–O(32)	118.2 (2)		
O(21)–H(31a)	1.755 (2)	O(22)–H(32a)	1.703 (1)	O(11)–H(2,2)[a]	1.744 (1)
		(b) Tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II)			
Cd–O(1)	2.497 (2)	C(2)–O(3)	1.356 (3)	C(17)–C(18)	1.375 (4)
Cd–O(2)	2.375 (2)	C(3)–C(4)	1.349 (4)	C(18)–C(19)	1.377 (4)
Cd–O(4)	2.424 (2)	C(4)–C(5)	1.377 (4)	C(19)–N(1)	1.348 (3)
Cd–O(5)	2.481 (2)	C(5)–C(6)	1.374 (4)	N(2)–C(20)	1.335 (4)
Cd–N(1)	2.372 (2)	C(6)–C(1)	1.389 (3)	C(20)–C(21)	1.386 (5)
Cd–N(2)	2.360 (2)	C(8)–C(9)	1.386 (3)	C(21)–C(22)	1.372 (5)
Cd–N(3)	2.350 (2)	C(9)–C(10)	1.406 (4)	C(22)–C(23)	1.339 (5)
O(1)–C(7)	1.248 (3)	C(9)–O(6)	1.345 (3)	C(23)–C(24)	1.387 (4)
O(2)–C(7)	1.266 (3)	C(10)–C(11)	1.345 (5)	C(24)–N(2)	1.324 (3)
O(4)–C(14)	1.246 (3)	C(11)–C(12)	1.382 (5)	N(3)–C(25)	1.347 (3)
O(5)–C(14)	1.266 (3)	C(12)–C(13)	1.359 (4)	C(25)–C(26)	1.375 (4)
C(7)–C(1)	1.484 (3)	C(13)–C(8)	1.407 (3)	C(26)–C(27)	1.377 (4)
C(14)–C(8)	1.481 (3)	N(1)–C(15)	1.336 (3)	C(27)–C(28)	1.373 (4)
C(1)–C(2)	1.392 (3)	C(15)–C(16)	1.364 (4)	C(28)–C(29)	1.386 (4)
C(2)–C(3)	1.391 (3)	C(16)–C(17)	1.384 (4)	C(29)–N(3)	1.333 (3)
O(1)–Cd–O(2)	53.36 (6)	Cd–N(1)–C(15)	121.0 (2)	C(9)–C(8)–C(13)	118.6 (2)
O(1)–Cd–O(4)	171.39 (8)	Cd–N(1)–C(19)	122.4 (1)	C(9)–C(8)–C(14)	122.0 (2)
O(1)–Cd–O(5)	135.57 (5)	C(15)–N(1)–C(19)	116.6 (2)	C(13)–C(8)–C(14)	119.4 (2)
O(1)–Cd–N(1)	91.47 (6)	Cd–N(2)–C(20)	120.8 (2)	C(8)–C(9)–O(6)	121.6 (2)
O(1)–Cd–N(2)	88.52 (6)	Cd–N(2)–C(24)	120.8 (2)	C(8)–C(9)–C(10)	119.0 (2)
O(1)–Cd–N(3)	84.82 (6)	C(20)–N(2)–C(24)	118.1 (2)	C(10)–C(9)–O(6)	119.4 (2)
O(2)–Cd–O(4)	135.00 (5)	Cd–N(3)–C(25)	120.9 (1)	C(9)–C(10)–C(11)	120.8 (3)
O(2)–Cd–O(5)	82.41 (5)	Cd–N(3)–C(29)	121.9 (1)	C(10)–C(11)–C(12)	120.8 (3)
O(2)–Cd–N(1)	87.78 (6)	C(25)–N(3)–C(29)	117.1 (2)	C(11)–C(12)–C(13)	119.5 (3)
O(2)–Cd–N(2)	92.69 (6)	O(1)–C(7)–O(2)	121.2 (2)	C(12)–C(13)–C(8)	121.1 (2)
O(2)–Cd–N(3)	138.08 (7)	O(1)–C(7)–C(1)	120.7 (2)	N(1)–C(15)–C(16)	123.7 (2)
O(4)–Cd–O(5)	52.99 (5)	O(2)–C(7)–C(1)	118.2 (2)	C(15)–C(16)–C(17)	119.1 (2)
O(4)–Cd–N(1)	87.20 (6)	O(4)–C(14)–O(5)	121.2 (2)	C(16)–C(17)–C(18)	118.4 (2)
O(4)–Cd–N(2)	92.72 (7)	O(4)–C(14)–C(8)	120.3 (2)	C(17)–C(18)–C(19)	118.8 (2)
O(4)–Cd–N(3)	86.69 (6)	O(5)–C(14)–C(8)	118.5 (2)	C(18)–C(19)–N(1)	123.4 (2)
O(5)–Cd–N(1)	90.71 (6)	C(2)–C(1)–C(6)	118.0 (2)	N(2)–C(20)–C(21)	121.4 (3)
O(5)–Cd–N(2)	89.71 (6)	C(2)–C(1)–C(7)	121.2 (2)	C(20)–C(21)–C(22)	119.4 (3)
O(5)–Cd–N(3)	139.51 (3)	C(6)–C(1)–C(7)	120.8 (2)	C(21)–C(22)–C(23)	119.1 (3)
N(1)–Cd–N(2)	179.40 (7)	C(1)–C(2)–C(3)	120.1 (2)	C(22)–C(23)–C(24)	119.1 (3)
N(1)–Cd–N(3)	90.83 (7)	C(1)–C(2)–O(3)	121.7 (2)	C(23)–C(24)–N(2)	122.8 (3)
N(2)–Cd–N(3)	88.58 (6)	C(3)–C(2)–O(3)	118.1 (2)	N(3)–C(25)–C(26)	122.7 (2)
Cd–O(1)–C(7)	90.1 (1)	C(2)–C(3)–C(4)	120.5 (2)	C(25)–C(26)–C(27)	119.5 (2)
Cd–O(2)–C(7)	95.3 (1)	C(3)–C(4)–C(5)	120.4 (2)	C(26)–C(27)–C(28)	118.5 (2)
Cd–O(4)–C(14)	94.4 (1)	C(4)–C(5)–C(6)	119.8 (3)	C(27)–C(28)–C(29)	118.8 (2)
Cd–O(5)–C(14)	91.3 (1)	C(5)–C(6)–C(1)	121.1 (2)	C(28)–C(29)–N(3)	123.3 (2)
C(17)–N(1)–Cd	178.8 (7)	C(22)–N(2)–Cd	173.8 (2)	C(27)–N(3)–Cd	179.0 (6)

[a] Through symmetry operation $^1/_2 + x$, $^1/_2 - y$, z.

oxygen atoms in the equatorial plane, two of which are bridging oxygen atoms, O(12) and O(12′). The two water oxygens are in the axial position of each Cd. The Cd–O–H angles of 112.3 (1)–122.5 (2)° clearly indicate that one of the lone-pair orbitals of the water oxygen atoms is almost directly pointed toward the Cd atom.

We wish to propose the following simple qualitative model as a step toward understanding the ^{113}Cd isotopic chemical shifts, and we shall discuss structural details in terms of this model. We assume that the K(4d^{10}) $^1S_0$ electronic configuration and state of Cd^{2+} represent the most shielded ^{113}Cd nucleus from its chemical environment. Any chemical bonding to Cd^{2+} would then deshield this nucleus by removing electrons from these filled shells via orbital mixing with outer metal orbitals and ligand orbitals of appropriate symmetry.[46] On this basis, it is not surprising that there exist more shielded values of the ^{113}Cd chemical shift than of the standard, $[Cd(H_2O)_6](ClO_4)_2$, 0.1 M aqueous solution in which probably six oxygen lone pairs[47] are pointed toward Cd. With this in mind, it is clear that the chemical shift may be positive or negative and not necessarily dependent upon coordination number or Cd–O distance, but rather upon the number of ligand lone-pair electrons in orbitals pointing in the direction of the metal and the ability of these ligands to donate electron pairs.

It is particular significance to the ^{113}Cd NMR results to notice that the Cd–O–C angles in I vary from 88.0 (1) to 97.9 (1)° and, except for one side of the bridging oxygen, the Cd′–O(12)–C(72) angle, which is 166.4 (1)°, the angles are all less than 100° (Figure 1; Table III). If one considers the oxygen of the carboxyl group as sp^2 hybridized,[48] then the C–O–(lone pair) angle would be 120°. The carboxyl groups are coplanar (Figures 1 and 3; Table IV) with the Cd(II), but the aromatic rings are tipped by ~20° to this plane. This means that none of the lone-pair orbitals of the carboxyl groups are pointed toward the Cd(II) atoms (in fact they are somewhat out of the plane), and of the seven ligands only the water molecule lone pairs are pointed directly toward Cd(II). Therefore, it is no surprise that in I the ^{113}Cd signal is deshielded relative to $Cd(H_2O)_6(ClO_4)_2$,[49] in which presumably six lone pairs are pointed toward Cd (−31 ppm compared to O); vide supra. A situation similar to that of I exists in the structure of diaquobis(succinato)cadmium(II)[38] (IV), which is also PBP and has a chemical shift value of −52 ppm. The geometry about O(12) also implies that Cd′ (Figure 2; related by a center of symmetry to Cd) can interact with two lone pairs albeit their orientation is not favorable, but Cd can interact with only one lone pair of O(12) in an unfavorable orientation. This leads to a Cd–O(12′) distance of 2.271 (2) Å and a Cd–O(12) distance of 2.535 (2) Å. The five oxygens form a reasonable plane with a maximum deviation of 0.12 Å, and Cd is slightly (0.18 Å) displaced toward O(2). Since the chelating ring contains only four atoms, it is not surprising that the O–Cd–O angles are relatively sharp at ~54°. These two very acute angles in the equatorial plane no doublt contribute to the formation of the pentagonal plane of the pentagonal bipyramid. The total spread of Cd–O distances is from 2.243 (2) to 2.535 (2) Å, very similar to those values found for IV.[38] Note that protons on the two water molecules on each Cd point in the same direction away from Cd. It is not clear whether this is due to the hydrogen bonding or some more subtle factor. The remaining distances and angles are the expected values.

The structure of II may be thought of as derived from I by pyridine replacement of the water molecules and pyridine displacement of the bridging oxygen of the dimer. The PBP geometry is retained with one equatorial and two axial pyridine ligands (Figure 3). The molecular packing indicates only normal van der Waals forces between molecules. The Cd–O distances are much more uniform (2.375 (2)–2.497 (2) Å) than in I. The Cd–N distances are also fairly uniform with a variation between 2.350 (2) and 2.372 (2) Å. As in I, the O–Cd–O angles are relatively sharp at ~53°. It is clear from Figure 2 and Table IIIb, where C(*y*)–N(*x*)–Cd ~ 180° and C(*y*) is across the ring from the nitrogen, that the pyridine nitrogen atom lone pairs are directed toward the metal. Again, as in I, it is clear from the Cd–O–C angles of ~93° that none of the carboxyl oxygen lone-pair orbitals are directed toward the Cd. The solid-state CP/MAS ^{113}Cd shift (this will not be confused by solvent effects) should be more deshielded in II than that in I, +61 ppm, for three reasons: (1) Three lone pairs are now directed toward Cd. (2) The lone-pair orbitals of the carboxyl groups are now in the equatorial plane [compare angles between planes 1–5 and 2–5 for I and between planes 2–3 and 4–5 for II (Tables III and IV)]. (3) Nitrogen atoms are more deshielding than oxygen.

Aquobis(*p*-aminobenzoato)cadmium(II) (III) is also PBP seven-coordinated with four equatorial carboxylate oxygen atoms, one water oxygen atom, and two axial nitrogen atoms. However, in this case the nitrogen atoms are donating π electrons to the Cd. Therefore, one would expect this also to be deshielded relative to $Cd(H_2O)_6{}^{2+}$ but not as much as II (+33 ppm compared to +61 ppm). Unfortunately in III a disorder in the water oxygens precluded a location of the protons on the water molecule.[44]

In a previous communication[33] we had attributed the more shielded values of the chemical shift of ^{113}Cd to higher coordination numbers. That may still be the case but only indirectly because the higher coordination numbers tend to develop situations where many lone pairs are pointed in directions other than toward Cd; i.e., the less directed the chemical bonding the more shielded is the ^{113}Cd nucleus relative to $Cd(H_2O)_6{}^{2+}$.[47] The single greatest structural drawback to the understanding of the more shielded ^{113}Cd chemical shifts at this time is the lack of knowledge of proton atomic positions since most of the current examples are hydrates of various sorts and the location of the protons indicates the lone-pair directions. With the above model, one would expect the following to be isotropically shielded relative to the $Cd(H_2O)_6{}^{2+}$ standard (experimental values in parentheses): $3CdSO_4{\cdot}8H_2O$ (−58, −45 ppm);[36,37] $Cd(Ac)_2{\cdot}2H_2O$ (−46 ppm);[36] $CaCd(Ac)_4{\cdot}6H_2O$ (−14 ppm);[36] $Cd(NO_3)_2{\cdot}4H_2O$ (−100 ppm).[36] Each of these has some water molecules in the coordination sphere, but there are always less than six. Beyond this, it depends upon the orientation of the lone pairs and the utilization of the lone pairs of the other "ligands". Certainly one would expect little directed valence from $SO_4{}^{2-}$ ions, and the shielded values for an octahedron composed of two oxygen atoms from H_2O and four oxygens from $SO_4{}^{2-}$ should be large, i.e. more negative than those of I. $Cd(Ac)_2{\cdot}H_2O$[50] appears to have two water molecules contributing two electron pairs to Cd, but not much else directed toward Cd. In spite of being

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(46) This is not a new concept, but rather a restatement of the Pauling electroneutrality principle. When an electron donor donates electron pairs, electron density must flow out of inner orbitals to maintain charge. In modern terminology, the molecular orbitals arising from the closed-shell metal orbitals are mostly metal in character and those involving outer metal orbitals and ligands are mostly ligand in character.

(47) The crystal structure of $[Cd(H_2O)_6](ClO_4)_2$[49] is disordered in the water molecules and may in fact not have six lone pairs pointed toward the metal, and the Cd^{2+} Tutton salt[55] might be a better reference point. However, the proton positions in this structure have only been inferred from the Mg^{2+} salt.

(48) Although this is a very simple description, it is borne out by experimental observations; see e.g.: Bernard, M.; Coppens, P.; De Lucia, M. L.; Stevens, E. D. *Inorg. Chem.* **1980**, *19*, 1924–1930.

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(50) Harrison, W.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1972**, 956–960.

Table IV

Least-Squares Planes ($Px + Qy + Rz = S$)

	planes	max dev, Å	dev out of plane, Å	
	$[(C_6H_4OHCOO)_2Cd\cdot 2H_2O]_2$			
I	aromatic ring 1, C(*n*1)	0.020 (1)	O(31)	0.04 (1)
II	aromatic ring 2, C(*n*2)	0.006 (5)	O(32)	0.01 (1)
III	O(12), C(72), C(12), O(22)	0.009 (3)	...	...
IV	O(11), O(21), C(71), C(11)	0.01 (1)		
V	O(12), O(22), O(11), O(21), O(12′)	0.12 (3)	Cd	−0.18 (3)
	$(C_5H_5N)_3(C_6H_4OHCOO)_2Cd$			
I	ring 1, C(1)···C(6)	0.008 (3)	O(3)	0.005 (3)
II	ring 2, C(8)···C(13)	0.004 (3)	O(6)	0.01 (1)
III	ring 3, N(1)···C(19)	0.007 (3)	...	
IV	ring 4, N(2)···C(24)	0.013 (3)	...	
V	ring 5, N(3)···C(29)	0.002 (3)	...	
VI	O(4), O(5), O(2), O(1), N(3)	0.09 (2)	...	
VII	O(4), C(14), O(5), Cd	0.014 (4)	...	
VIII	O(1), O(2), C(7), Cd	0.006 (3)	...	
IX	O(4), O(5), C(14), C(8)···C(13)	0.034 (4)	...	
X	O(1), O(2), C(7), C(1)···C(6)	0.077 (3)	...	

Angles between Planes, deg

$[(C_6H_4OHCOO)_2Cd\cdot H_2O]_2$				$(C_5H_5N)_3(C_6H_4OHCOO)_2Cd$	
I-IV	3.57 (3)	I-V	17.9 (1)	VII-IX	2.22 (2)
II-III	3.58 (3)	II-V	22.3 (1)	VIII-X	4.03 (3)

Table V. ^{113}Cd NMR Chemical Shifts (ppm)[a]

compd	soln	solid CP/MAS	coord no.; geometry
bis[diaquobis(*o*-hydroxybenzoato)cadmium(II)][b] (I)	−57 (MeOH)	−31	7 (O); PBP[b]
tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II)[b] (II)	−5 (MeOH)[c]	+61	3 (N), 4 (O); PBP[b]
aquobis(*p*-aminobenzoato)cadmium(II)[d] (III)	−49 (MeOH)[e]	+33	5 (O), 2 (N); PBP
diaquobis(succinato)cadmium(II)[f] (IV)		−52[b,g]	7 (O); PBP

[a] Relative to a 0.1 M $Cd(ClO_4)_2$ aqueous solution reference. [b] This work. [c] This value is probably representative of an intermediate species between I and II since II precipitates in the NMR tube. [d] Reference 44. [e] Reference 33. [f] Reference 38. [g] Because of loss of water coordinated to Cd during the spinning of the sample, this result is from static experiments. We are indebted to R. S. Honkonen for his help in these experiments.

described as a distorted seven-oxygen-coordinated Cd, the ^{113}Cd chemical shift is approximately the same as that of I. $CaCd(Ac)_4\cdot 6H_2O$ has been described as eight-oxygen-coordinated,[51] but this is possibly a misnomer since two cadmium–oxygen distances are 2.677 (8) Å! Nevertheless, the M–O–C angles are such that as many as four electron pairs may be pointed toward Cd; i.e., the isotropic chemical shift should be between that of I (−31 ppm) and that of standard. $Cd(NO_3)\cdot 4H_2O$ is more difficult to explain (−100 ppm)[36] on the basis of above postulates. Although the coordination sphere is that of eight oxygens,[52] four from nitrate groups and four from water molecules, the Cd–O distances to the oxygen of nitrate are long as 2.438 (9) and 2.590 (11) Å when compared to Cd–O distances of 2.290 (4) and 2.299 (4) Å found in bis(tetramethylthiourea)bis(nitrato)cadmium(II) and the covalent radii sum of 2.14 Å. However, they are more comparable to the distances of 2.34 (4)–2.43 (1) Å found in $(2,2'\text{-bpy})_2Cd(NO_3)_2\cdot 0.5H_2O$.[53] When the $Cd\text{–}O(NO_3)$ distances are long empirically, each nitrate group systematically contributes ~60 ppm toward more shielded values within a fixed geometry.[53] The −100 ppm value for $Cd(NO_3)_2.4H_2O$ can be rationalized on that basis. Clearly, a more careful analysis is needed in which the amount of covalent bonding from each carboxyl group is carefully considered compared to water molecule contribution and to nitrate contributions.

The methanol solution ^{113}Cd chemical shifts are very similar for I and III. These results can be understood in terms of the solvent breaking the bridge bonding in I and a monomeric seven-coordinate species existing in solution[53] as seven oxygen atoms coordinated to Cd with one Cd–O bond formed from oxygen of methanol (weak electron donor). In the solid state, III is an infinite polymer chain utilizing amino group nitrogen atoms from an adjacent ligand to complete the coordination sphere. In solution this polymer is likely to be destroyed by the cleaving of the Cd–N bonds, retaining the PBP geometry and utilizing two oxygen atoms of the solvent to give seven-oxygen PBP coordination.

One would have expected II to dissolve directly into methanol solution without any dissociation, but the methanol solution ^{113}Cd NMR chemical shift clearly implies that some of the pyridine ligands have been replaced by solvent. In fact, pure II is insoluble in methanol.

Of relevance to the S_2 site of concanavalin A and the EF site of parvalbumin, calmodulin, and troponin C is the fact that it is not expected to find ions such as nitrate or sulfate in these sites, and the most likely reason for the shielded values of the ^{113}Cd resonance is that due to the utilization of carboxyl groups in combination with water molecules to give a coordination number greater than 6, possibly 7 as a PBP geometry, or even 8.[54]

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Supplementary Material Available: Figures showing the unit cell of II and a dimer of I and listings of positional parameters, isotropic thermal parameters, anisotropic librational parameters, bond distances and angles, and observed and calculated structure amplitudes (62 pages). Ordering information is given on any current masthead page.

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New Preparative Route to Bi-oxo-capped Trinuclear Molybdenum(IV) Clusters by Reduction of Molybdate(VI). Structure of $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot 16H_2O$

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It has been shown that the equilateral triangular, bi-oxo-capped type of trimolybdenum cluster compound can be obtained by reducing Na_2MoO_4 in acetic anhydride. Both $W(CO)_6$ and zinc dust have been used as reductants. A red solid was first isolated and shown to conform closely to the formula $Na[Mo_3O_2(O_2CCH_3)_9]$. In acid solution this is quickly hydrolyzed to replace the three equatorial acetate ions by H_2O molecules. In neutral water hydrolysis is slow, affording crystals of the compound $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot 16H_2O$, which was characterized by X-ray crystallography. The compound forms monoclinic crystals in space group *C2/m* with the following unit cell dimensions: $a = 18.825$ (5) Å, $b = 19.017$ (6) Å, $c = 10.871$ (3) Å, $\beta = 95.5$ (1)°, $V = 3873$ (1) Å^3, $Z = 4$. The molecule is bisected by a crystallographic mirror plane and has Mo–Mo distances of 2.796 (1) Å (twice) and 2.773 (1) Å. Mo–OH bonds are shorter (ca. 1.98 Å) than Mo–OH_2 distances (ca. 2.11 Å). There is an inverse relationship between an Mo–O (equatorial) distance and the adjacent Mo–Mo distances, which accounts for the lack of 3-fold symmetry in the Mo_3 cluster. ^1H NMR studies show that the hydrolytic cleavage of equatorial acetate ligands is acid catalyzed and is about 90% complete in about 1 h.

Introduction

Over the last few years it has been well established that the reactions of $Mo(CO)_6$ or $W(CO)_6$ with acetic acid or mixtures of acetic acid and acetic anhydride lead to the formation of trinuclear bicapped metal cluster compounds.[2-9] Other carboxylic acids may also be used, and the general formula for the species produced is $[M_3X_2(O_2CR)_6L_3]^{n\pm}$. In such a unit there is a central trigonal-bipyramidal $M_3(\mu_3\text{-}X)_2$ unit, with two RCO_2^- groups bridging across each M–M edge and one additional unidentate ligand, L (most often H_2O), attached to each metal atom. For tungsten[7] the only capping groups so far identified are oxygen atoms and the only formal oxidation state for the metal atoms is +4. The behavior of molybdenum has been more varied, with CCH_3 groups as well as O atoms in the capping positions and mean formal oxidation numbers of $+4^1/_2$ and $+4^2/_3$ as well as +4.0. With tungsten, however, it has also been possible to obtain a hemicapped (μ_3-O) species[10] for which no molybdenum analogue is yet known.

In exploring this chemistry further, one of our goals has been to find other ways in which the bicapped cluster compounds might be prepared. In this paper we report that they can be obtained from sodium molybdate by using either zinc dust or $W(CO)_6$ as a reductant. In addition, it was found that the initial product of these preparative reactions, $Na[Mo_3O_2(O_2CCH_3)_9]$, hydrolyzes in aqueous solution to deposit well-formed crystals of a compound that has been shown by X-ray crystallography to be $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot 16H_2O$. The hydrolysis reaction has been studied by NMR, and the structural consequence of the mixed ligand set, H_2O + 2 OH^-, in the final product are discussed.

Experimental Section

Preparations. The preparative procedures to be described below require the use of pure (freshly recrystallized) $Na_2MoO_4\cdot 2H_2O$. If material that has been on the shelf for long periods of time is used, an initial blue (rather than red) product may be obtained. If this is dissolved in water, the color changes to red. This red material can then be quantitatively adsorbed to a cation-exchange resin and eluted with 2 M CF_3SO_3H. The visible spectrum of the eluate corresponds in all respects to the one reported[8] for $[Mo_3O_2(CH_3COO)_6(H_2O)_3]^{2+}$. In addition, crystals of $[Mo_3O_2(CH_3COO)_6(H_2O)_3](CF_3SO_3)_2$ were grown by slow evaporation. Unit cell constants were identical with the ones reported elsewhere.[10] The blue compound is insoluble in dry nonprotic solvents. In Me_2SO that was dried over molecular sieves it forms initially a blue suspension that partly turns into a red solution over a period of ca. 3 h. This red solution shows NMR signals at 2.22 and 1.85 ppm (singlets, chemical shifts relative to Me_4Si). They can reasonably be assigned to bridging acetate ions in $[Mo_3O_2(CH_3COO)_6L_3]^{2+}$ (2.22 ppm), where $L_3 = (Me_2SO)_3$, $(H_2O)_3$, or a mixture of both, and to free acetate ion (1.85 ppm).

To purify $Na_2MoO_4\cdot 2H_2O$, about 7 g of commercially available product was dissolved in 30 mL of H_2O. A 30-mL portion of methanol was added to the filtered solution, and the precipitate was collected

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