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Solid-State and Solution ^{113}Cd NMR, Shielding Tensor Components, and Crystal and Molecular Structures of (Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] oxide)bis(nitrato-*O*,*O*′)cadmium(II) and (Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine)bis(nitrato-*O*,*O*′)cadmium(II)

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The ^{113}Cd NMR spectra have been observed for the title compounds, A and B, respectively, in methanol solution and in the solid state by magic-angle cross-polarization (MAS/CP) techniques. In solution A and B each give a single line at −96.3 and −95.2 ppm (deshielded relative to the 0.1 M $Cd(ClO_4)_2$ in D_2O standard), respectively, with half-widths at half peak heights of 7.1 and 1.5 ppm, respectively. In the solid state both compounds give a single line at −106 ppm with half-width at half peak height of 6 and 3 ppm, respectively. Essentially the same species is present both in the solution and in the solid state. The components of the chemical shift tensor were calculated from the spinning side bands for both A and B and were found to be −170, −175, +31 and −169, −170, +12 ppm in a well-defined orientation to the pseudo-fivefold molecular axis. The crystal structures of A and B are made up of discrete molecules separated by ordinary van der Waals distances. The B molecules contain fairly regular pentagonal-bipyramidal Cd^{2+} with one equatorial and two axial nitrogen donors from the ligand and four equatorial oxygen donors from asymmetric bidentate nitrate groups. The structure of A is made up of two different molecules, A and A′, both of which have very distorted pentagonal bipyramidal Cd^{2+} with two axial nitrogens and one equatorial oxygen from the ligand and four equatorial oxygen atoms from symmetrical bidentate nitrate groups. X-ray Data: A, a = 14.854 (8) Å, b = 16.672 (8) Å, c = 9.112 (3) Å, α = 103.09 (7)°, β = 93.13 (8)°, γ = 113.40 (8)°, triclinic, $P\bar{1}$, Z = 4, D_{measd} = 1.65 g/cm^3, D_{calcd} = 1.66 g/cm^3, NO = 9911, NV = 636, final R with full matrix least squares 0.051 including anisotropic temperature factors for all non-hydrogen atoms, μ = 11.4 cm^{-1}, maximum and minimum transmission factors 0.717 and 0.611; B, a = 9.145 (3) Å, b = 14.328 (4) Å, c = 15.552 (7) Å, β = 100.64 (3)°, monoclinic, $P2_1/c$, Z = 4, D_{measd} 1.65 (2) g/cm^3, D_{calcd} = 1.65 g/cm^3, NO = 5312, NV = 322, final R with full matrix least squares 0.034 including anisotropic temperature factors for all non-hydrogen atoms, μ = 11.4 cm^{-1}, maximum and minimum transmission factors 0.770 and 0.689.

Introduction

^{113}Cd NMR has been observed in a wide variety of chemical and biological compounds ranging from simple inorganic salts and organometallics to Cd substituted in proteins and enzymes that naturally contain Ca and Zn.[1-4] The chemical shift range of ~+800 ppm (deshielded) represented by, e.g., a tetrahedral four-sulfur environment in horse liver alcohol dehydrogenase[5] and ~−100 ppm (shielded relative to a 0.1 M solution of $Cd(ClO_4)_2$ in D_2O) represented by Cd in one of the Ca sites of parvalbumin[6] with six oxygen atoms more or less in an octahedral[7] arrangement makes this nucleus an attractive probe of metal sites in a wide variety of compounds. The recent advances in solid-state NMR[8,9] with magic-angle spinning (MAS) and cross-polarization (CP) techniques make it attractive to synthesize specific compounds to measure their solid-state MAS/CP ^{113}Cd NMR spectra, to determine their crystal structures, and to observe the solution ^{113}Cd NMR spectra as well. Such experiments should establish relationships between coordination number, ligands, and ^{113}Cd NMR chemical shifts, if they exist.[4,10-24] Of particular interest here is the large shielded chemical shifts of approximately 100 ppm observed for the proteins parvalbumin,[6] troponin C,[25] calmodulin,[26] and concanavalin A.[27] Such large shielded values are rare in model systems with the notable exceptions of $CdSO_4{\cdot}2H_2O$[28] and $Cd(NO_3)_2{\cdot}2H_2O$.[28] However, there are good indications that with higher coordination numbers (greater than 6) and in the presence of only oxygen donor ligands sizable shielded values can be obtained.[12,13,16,18,20] The ligands in A and B of the title should promote the formation of higher coordination numbers, particularly in the presence of nitrate ions, with Cd^{2+}. In addition, A and B differ in the presence of one of the donor atoms (O for N), which gives the opportunity to study the effect on the chemical shift of such a change, assuming all other factors remain equal. Preliminary ^{113}Cd solution NMR indicated substantial shielded chemical shifts and encouraged us to proceed with further ^{113}Cd studies in the solution and solid state and the X-ray structure determinations of A and B.

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Experimental Section

A methanol solution containing 0.026 g (1 mmol) of the appropriate ligand (courtesy of Professor T. H. Sorrell, Department of Chemistry, The University of North Carolina at Chapel Hill) was added to a methanolic solution containing 0.31 g (1 mmol) of $Cd(NO_3)_2{\cdot}2H_2O$ (Fisher) with stirring and gentle warming (60 °C). The resultant solution (~50 mL) was heated 10–20 min and set aside to evaporate slowly at ambient temperature. Crystals appeared after 2–3 days. The crystals were removed by vacuum filtration, air-dried, and either stored in sealed bottles for the NMR experiments or mounted in capillaries for X-ray intensity data collection. The NMR instrumentation and techniques have been described elsewhere.[4] The principal components of the ^{113}Cd shielding tensor were determined by simplex optimization of computed spinning sideband intensities to the experimental values.[29,30] Good fits were obtained for both cases. The optimization procedure involved a two-parameter fit that resulted in best estimates for the anisotropy (δ) and the asymmetry parameter (η). These two parameters along with the rotor spinning speed and the spectrometer frequency determine the relative sideband intensities in the MAS spectra. From these optimized parameters were obtained the best estimates of the principal values of the cadmium shielding tensor. The computer program to carry out this calculation was obtained from Marchetti.[31]

Data Collection, Structure Solution, and Refinement Parameters. Diffractometer: Enraf-Nonius CAD4 interfaced to PDP-11/60. Computers used in the solution and refinement: PDP-11/60, VAX-11/780. Computer programs used: SDP[32] and SHELX-76[33] with some local modifications. Wavelength = 0.71073 Å. Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] oxide)bis(nitrato-*O,O'*)cadmium(II) (A): fw = 498.8, formula $C_{14}H_{22}N_6O_7Cd$, $F(000)$ = 999.98. (Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine]bis(nitrato-*O,O'*)cadmium(II) (B): fw = 497.8, formula $C_{14}H_{23}N_7O_6Cd$, $F(000)$ = 995.98. Crystal size: A, 0.46 × 0.58 × 0.36 mm; B, 0.46 × 0.26 × 0.54 mm. Crystals were mounted on the diffractometer and aligned by standard techniques. Intensities were measured by standard θ–2θ scan techniques. Cell constants: A, a = 14.854 (8) Å, b = 16.672 (8) Å, c = 9.112 (3) Å, α = 103.09 (7)°, β = 93.13 (8)°, γ = 113.40 (8)°, volume 1990 (4) Å^3, triclinic, $P1$, Z = 4, D_{measd} = 1.65 (2) g/cm^3 by flotation in bromoform/carbon tetrachloride mixtures, D_{calcd} = 1.66 g/cm^3, 25 reflections with θ range 10–20° used to determine unit cell parameters for both A and B; B, a = 9.145 (3) Å, b = 14.328 (4) Å, c = 15.552 (7) Å, β = 100.64 (3)°, volume 1999 (2) Å^3, monoclinic, $P2_1/c$, Z = 4, D_{measd} = 1.65 (2) g/cm^3 by flotation in bromoform/carbon tetrachloride mixtures, D_{calcd} = 1.65 g/cm^3. Systematic absences: A, none; B, $l = 2n + 1$ for $h0l$, $k = 2n + 1$ for $0k0$. For both A and B data were measured to $2\theta = 60° = 0.704[(\sin\theta)/\lambda]$ with graphite monochromator; θ = 6.1°. Range of hkl values: A, h = 0–20, k = −23 to +23, l = −12 to +12; B, h = 0–12, k = 0–20, l = −21 to +21. Number of reflections measured: A, 11573; B, 5817. Standard reflections for A 3,−2,7; 5,4,−5; −11,6,−5. Standard reflections for B: 357; 6,2,−10; −7,−5,5. Variation of these reflections was less than 1.5% I, and corrections were made. Reflections were considered non-zero if F_o^2 was greater than σF^2. $\sigma(F_o^2) = [\sigma(I_{raw}^2) + (PI_{raw})^2]^{1/2}/Lp$ with P = 0.03. Number of unique reflections used to solve and refine the structure: A, 9911; B, 5312. Faces: A, (010), (−1,0,1), (1,0,−1), (100), (−1,0,0), (0,−1,1), (0,1,−1), (0,−1,0); B, (−1,0,0), (100), (011), (0,−1,−1), (0,−1,1), (0,1,−1), (101), (−1,0,−1), (1,0,−1), (−1,0,1). Absorption corrections were made by analytical means with the SDP program. Maximum and minimum transmission factors: A, 0.717 and 0.611 with μ = 11.4 cm^{-1}; B, 0.770 and 0.689 with μ = 11.4 cm^{-1}. The structures were solved by standard heavy-atom methods, and the initial refinement was made with the SDP package on the PDP 11/60 computer. Final refinement was made with our version of SHELX-76 on the VAX-11/780 with scattering factors and real and imaginary dispersion corrections from ref 44. Function minimized in least-squares: $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/(\sigma F_o)^2$. Final R, weighted R, and S: A, 0.051, 0.036, and 1.13; B, 0.034, 0.025, and 0.77. H atom positions were located from difference maps and coordinates refined but temperature factors held fixed at U = 0.07 Å^2 for both A and B. Total number of parameters: A, 636, but the refinement carried out with blocked-matrix least squares utilizing 364 × 364 overlapping blocks; B, 322, full-matrix refinement without blocking. Shifts for final cycle for A: block 1 maximum shift 0.005σ, average shift 0.001σ; block 2, maximum shift 0.0256σ, average shift 0.002σ. Shifts for final cycle for B: maximum shift 0.020σ, average shift 0.005σ. Maximum and minimum in final difference map: A, +0.49 and −1.0 e/Å^3; B, +0.39 and −0.69 e/Å^3.

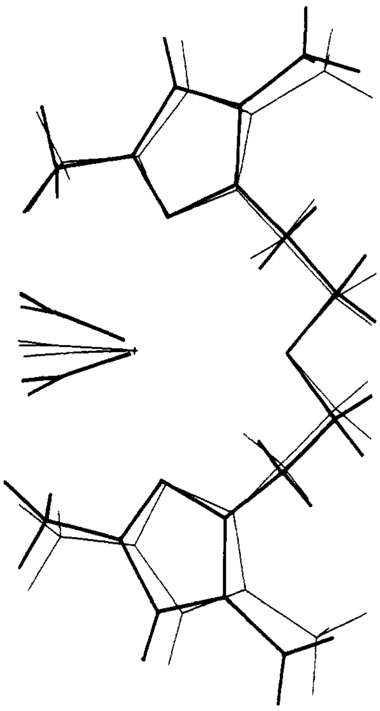

Figure 1. Differences between the two molecules (A and A′) in the crystal structure of A. In this drawing with FRODO,[43] the Cd atoms from A (light lines) and A′ (dark lines), the corresponding oxygen atoms [O(11) and O(21)], and the corresponding ring nitrogen atoms to the right of center [N(11) and N(21)] are superposed in pairs. The differences in the conformation of the nitrate groups between A and A′ are readily seen.

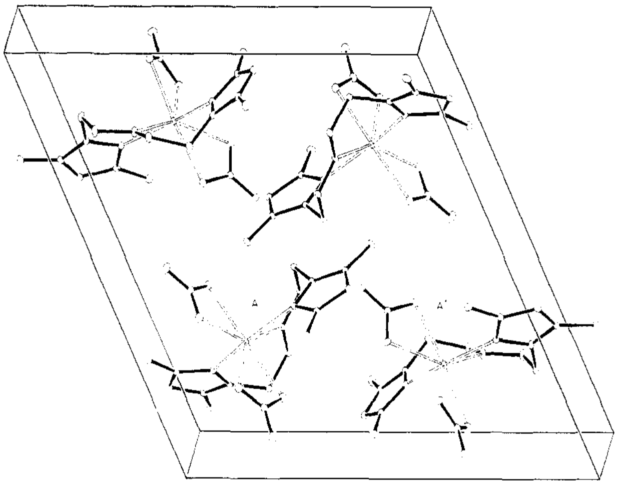

Figure 2. ORTEP packing diagram of the crystal structure of A. The two independent molecules are denoted by A and A′, consistent with Figure 1. The origin of the coordinate system is in the inside lower left hand corner with x horizontal, y approximately vertical, and z up toward the observer.

Details of Nonroutine Structure Solution and Refinement (A). Our version of SHELX-76 is limited to a matrix of 364 × 364, and therefore

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Table I. Fractional Atomic Coordinates with Esd's in Parentheses and Equivalent Isotropic Temperature Factors

	x/a	y/b	z/c	B, Å^2		x/a	y/b	z/c	B, Å^2
(a) (Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] oxide)bis(nitrato-*O,O'*)cadmium(II)									
Cd(1)	−0.2294 (0)	−0.2468 (0)	−0.3127 (0)	3.46	Cd(2)	0.2727 (0)	−0.2507 (0)	0.1750 (0)	3.58
N(11)	−0.3915 (2)	−0.3416 (2)	−0.4093 (3)	3.26	N(21)	0.4008 (2)	−0.1828 (2)	0.3693 (3)	3.79
C(11)	−0.4506 (3)	−0.3433 (3)	−0.5289 (4)	3.41	C(21)	0.4907 (3)	−0.1155 (3)	0.3753 (5)	3.92
C(12)	−0.4096 (4)	−0.2978 (3)	−0.6474 (5)	4.91	C(22)	0.5174 (4)	−0.0806 (3)	0.2400 (6)	5.09
C(13)	−0.5504 (3)	−0.3950 (3)	−0.5223 (4)	3.81	C(23)	0.5458 (3)	−0.0911 (3)	0.5194 (5)	4.71
C(14)	−0.5506 (3)	−0.4237 (3)	−0.3917 (4)	3.57	C(24)	0.4884 (3)	−0.1445 (3)	0.6027 (5)	4.42
C(15)	−0.6341 (3)	−0.4777 (3)	−0.3222 (6)	4.87	C(25)	0.5117 (4)	−0.1475 (4)	0.7613 (6)	6.08
N(12)	−0.4545 (2)	−0.3912 (2)	−0.3265 (3)	3.21	N(22)	0.4009 (2)	−0.1988 (2)	0.5104 (4)	4.01
C(16)	−0.4152 (3)	−0.4101 (3)	−0.1942 (4)	3.56	C(26)	0.3149 (4)	−0.2689 (4)	0.5429 (5)	4.90
C(17)	−0.3904 (3)	−0.3352 (3)	−0.0510 (4)	3.82	C(27)	0.2275 (3)	−0.2459 (4)	0.5575 (5)	5.36
O(1)	−0.3133 (2)	−0.2541 (2)	−0.0706 (3)	3.81	O(2)	0.1862 (2)	−0.2499 (2)	0.4084 (3)	5.16
C(18)	−0.2887 (3)	−0.1789 (3)	0.0610 (5)	4.56	C(28)	0.0912 (4)	−0.2480 (4)	0.4118 (5)	6.27
C(19)	−0.2079 (3)	−0.0977 (3)	0.0315 (5)	4.28	C(29)	0.0611 (4)	−0.2309 (4)	0.2691 (6)	5.73
N(13)	−0.1159 (2)	−0.1085 (2)	0.0191 (3)	3.42	N(23)	0.0364 (2)	−0.3033 (2)	0.1315 (4)	4.19
C(110)	−0.0352 (3)	−0.0742 (3)	0.1243 (4)	4.02	C(210)	−0.0525 (3)	−0.3578 (3)	0.0444 (5)	4.73
C(111)	−0.0283 (4)	−0.0248 (4)	0.2863 (5)	5.94	C(211)	−0.1467 (4)	−0.3540 (4)	0.0823 (8)	6.55
C(112)	0.0356 (3)	−0.0973 (3)	0.0581 (5)	4.11	C(212)	−0.0350 (3)	−0.4113 (3)	−0.0768 (6)	5.09
C(113)	−0.0100 (3)	−0.1487 (3)	−0.0911 (4)	3.61	C(213)	0.0664 (3)	−0.3873 (3)	−0.0595 (5)	4.30
C(114)	0.0334 (4)	−0.1914 (3)	−0.2116 (6)	5.15	C(214)	0.1247 (4)	−0.4236 (3)	−0.1610 (6)	5.41
N(14)	−0.1031 (2)	−0.1553 (2)	−0.1159 (3)	3.39	N(24)	0.1115 (2)	−0.3205 (2)	0.0680 (4)	3.95
N(1)	−0.2173 (3)	−0.1040 (3)	−0.4420 (5)	6.50	N(3)	0.2906 (2)	−0.1198 (3)	0.0076 (4)	4.66
O(11)	−0.1785 (2)	−0.1570 (2)	−0.4926 (4)	6.44	O(31)	0.3018 (2)	−0.1904 (2)	−0.0483 (3)	5.35
O(12)	−0.2617 (2)	−0.1162 (2)	−0.3286 (4)	6.11	O(32)	0.2768 (2)	−0.1060 (2)	0.1460 (3)	5.45
O(13)	−0.2113 (3)	−0.0426 (3)	−0.4964 (5)	10.06	O(33)	0.2941 (3)	−0.0669 (2)	−0.0658 (4)	7.02
N(2)	−0.1580 (3)	−0.3800 (3)	−0.4271 (5)	5.69	N(4)	0.3461 (3)	−0.3868 (2)	0.0934 (4)	3.96
O(21)	−0.1567 (2)	−0.3220 (2)	−0.4961 (4)	6.12	O(41)	0.2783 (2)	−0.3957 (2)	0.1752 (3)	5.05
O(22)	−0.1961 (2)	−0.3775 (2)	−0.3047 (4)	5.64	O(42)	0.3753 (2)	−0.3192 (2)	0.0396 (3)	4.95
O(23)	−0.1252 (3)	−0.4348 (3)	−0.4731 (4)	9.43	O(43)	0.3817 (2)	−0.4423 (2)	0.0650 (3)	5.26
(b) (Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine)bis(nitrato-*O,O'*)cadmium(II)									
Cd	0.1915 (0)	0.7170 (0)	0.3640 (0)	2.86	C(10)	0.3974 (4)	1.0011 (2)	0.3690 (2)	4.63
N(1)	0.0540 (2)	0.5887 (2)	0.3888 (1)	3.20	C(11)	0.4001 (6)	1.0981 (3)	0.4044 (4)	7.00
C(1)	0.0647 (3)	0.5020 (2)	0.3592 (2)	3.29	C(12)	0.4898 (4)	0.9574 (3)	0.3227 (2)	4.93
C(2)	0.2056 (4)	0.4675 (3)	0.3342 (3)	4.54	C(13)	0.4364 (3)	0.8670 (2)	0.3072 (2)	3.88
C(3)	−0.0673 (3)	0.4538 (2)	0.3572 (2)	3.68	C(14)	0.4933 (4)	0.7907 (3)	0.2579 (2)	4.97
C(4)	−0.1627 (3)	0.5140 (2)	0.3876 (2)	3.26	N(4)	0.3158 (2)	0.8544 (2)	0.3437 (1)	3.44
C(5)	−0.3173 (4)	0.4991 (2)	0.4031 (3)	4.39	N(6)	0.4432 (3)	0.6908 (2)	0.4981 (2)	3.39
N(2)	−0.0887 (2)	0.5954 (2)	0.4051 (1)	3.17	O(61)	0.4232 (2)	0.6575 (2)	0.4211 (1)	4.32
C(6)	−0.1358 (4)	0.6763 (2)	0.4498 (2)	3.84	O(62)	0.3351 (2)	0.7317 (2)	0.5214 (1)	4.20
C(7)	−0.1274 (3)	0.7681 (2)	0.4033 (2)	3.55	O(63)	0.5631 (2)	0.6819 (2)	0.5467 (1)	5.21
N(5)	0.0250 (2)	0.8071 (2)	0.4217 (1)	2.76	N(7)	0.0743 (4)	0.6773 (2)	0.1820 (2)	4.54
C(8)	0.0287 (3)	0.9057 (2)	0.3944 (2)	3.68	O(71)	0.1986 (3)	0.6530 (2)	0.2234 (2)	5.75
C(9)	0.1764 (4)	0.9507 (2)	0.4326 (2)	4.13	O(72)	−0.0002 (3)	0.7312 (2)	0.2198 (2)	6.20
N(3)	0.2927 (3)	0.9383 (2)	0.3806 (2)	3.67	O(73)	0.0274 (3)	0.6487 (2)	0.1074 (1)	6.86

the refinement was carried out in these size blocks. Block 1 contained Cd(1), Cd(2), ligand 2, and three of four nitrate groups, which varied from cycle to cycle. Block 2 contained Cd(1), Cd(2), ligand 1, and three of four nitrate groups, which varied from cycle to cycle. As is the case with any crystal structure with two molecules in the asymmetric unit, it was of some concern as to why there were two molecules in the asymmetric unit of A. That is, why is the correct space group not monoclinic and isomorphous with B instead of being triclinic? An analysis shows that the two molecules are not exactly the same and they differ in the orientation of the nitrate groups bound to the metal atom. This difference can be most readily seen by reference to Figure 1, in which the two molecules in the asymmetric unit are essentially superposed.

The structure factor tables have been deposited as supplementary material along with the hydrogen atom position tables and the anisotropic temperature factor tables. The atomic positional and isotropic equivalent thermal parameters are shown in Table I. The interatomic distances and angles are found in Table II. The relevant least-squares planes are to be found in Table III. All the tables were generated by local programs from the output of SHELX. The ORTEP[34] drawings of individual molecules of A and B and the packing drawings of A and B are seen in Figures 2–5.

Results

Description of Structures. The crystal structure of A may be described as made up of uncharged molecules of A and A′ (Figure 2) separated by ordinary van der Waals distances, in which A and A′ differ in the orientation of the nitrate ligands (Figure 1). The molecular structure of A is indicated in Figure 3, and the geometry about the central metal may be described as a very distorted pentagonal bipyramidal with five oxygen donor groups (four from two nitrate groups and one from the organic ligand) making up the equatorial plane. It is to be noted that the dihedral angle between nitrate groups in A is 6.86 (9)° and this same angle in

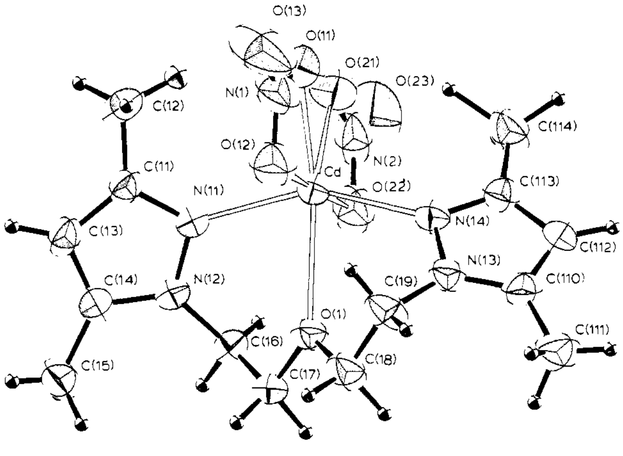

Figure 3. ORTEP drawing of the molecule A in the crystal structure of A containing the molecules A and A′. The non-hydrogen atom ellipses are drawn at the 50% probability level and the hydrogen atoms with a small arbitrary radius of 0.1 Å. The distorted pentagonal bipyramidal geometry about Cd is made up of O(11), O(12), O(21), O(22), and O(1) in the equatorial plane and N(11) and N(14) as the axial ligands.

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[34] Johnson, C. K. "ORTEPII"; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table II. Interatomic Distances and Angles with Esd's in Parentheses

(a) (Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] oxide)bis(nitrato-*O*,*O*′)cadmium(II)

Distances (Å)

Cd(1)–N(11)	2.277 (2)	Cd(2)–N(21)	2.247 (2)	N(12)–C(16)	1.461 (4)	N(22)–C(26)	1.448 (5)
Cd(1)–O(1)	2.595 (2)	Cd(2)–O(2)	2.544 (2)	C(16)–C(17)	1.497 (5)	C(26)–C(27)	1.497 (4)
Cd(1)–N(14)	2.277 (2)	Cd(2)–N(24)	2.249 (2)	C(17)–O(1)	1.440 (4)	C(27)–O(2)	1.436 (5)
Cd(1)–O(11)	2.418 (3)	Cd(2)–O(31)	2.453 (3)	O(1)–C(18)	1.432 (5)	O(2)–C(28)	1.426 (3)
Cd(1)–O(12)	2.441 (2)	Cd(2)–O(32)	2.462 (2)	C(18)–C(19)	1.502 (5)	C(28)–C(29)	1.476 (7)
Cd(1)–O(21)	2.420 (3)	Cd(2)–O(41)	2.452 (2)	C(19)–N(13)	1.455 (3)	C(29)–N(23)	1.441 (6)
Cd(1)–O(22)	2.434 (2)	Cd(2)–O(42)	2.470 (2)	N(13)–C(110)	1.328 (4)	N(23)–C(210)	1.344 (4)
N(11)–C(11)	1.349 (4)	N(21)–C(21)	1.349 (4)	N(13)–N(14)	1.366 (3)	N(23)–N(24)	1.382 (3)
N(11)–N(12)	1.369 (3)	N(21)–N(22)	1.371 (4)	C(110)–C(111)	1.495 (6)	C(210)–C(211)	1.481 (4)
C(11)–C(12)	1.479 (5)	C(21)–C(22)	1.487 (6)	C(110)–C(112)	1.380 (4)	C(210)–C(212)	1.361 (6)
C(11)–C(13)	1.401 (4)	C(21)–C(23)	1.391 (6)	C(112)–C(113)	1.397 (5)	C(212)–C(213)	1.386 (3)
C(13)–C(14)	1.379 (5)	C(23)–C(24)	1.367 (5)	C(113)–C(114)	1.489 (5)	C(213)–C(214)	1.491 (5)
C(14)–C(15)	1.486 (5)	C(24)–C(25)	1.484 (7)	C(113)–N(14)	1.345 (3)	C(213)–N(24)	1.332 (5)
C(14)–N(12)	1.353 (3)	C(24)–N(22)	1.348 (4)				
N(1)–O(11)	1.255 (4)	N(2)–O(21)	1.262 (4)	N(3)–O(31)	1.251 (4)	N(4)–O(41)	1.267 (4)
N(1)–O(12)	1.268 (5)	N(2)–O(22)	1.278 (5)	N(3)–O(32)	1.273 (4)	N(4)–O(42)	1.259 (3)
N(1)–O(13)	1.210 (5)	N(2)–O(23)	1.204 (4)	N(3)–O(33)	1.209 (4)	N(4)–O(43)	1.224 (3)

Angles (deg)

N(11)–Cd(1)–O(1)	76.8 (1)	N(21)–Cd(2)–O(2)	77.3 (1)	N(11)–N(12)–C(16)	120.5 (2)	N(21)–N(22)–C(26)	120.4 (2)
N(11)–Cd(1)–N(14)	152.5 (1)	N(21)–Cd(2)–N(24)	155.4 (1)	C(14)–N(12)–C(16)	127.9 (2)	C(24)–N(22)–C(26)	128.2 (3)
N(11)–Cd(1)–O(11)	103.7 (1)	N(21)–Cd(2)–O(31)	114.8 (1)	N(12)–C(16)–C(17)	112.5 (2)	N(22)–C(26)–C(27)	114.0 (3)
N(11)–Cd(1)–O(12)	90.4 (1)	N(21)–Cd(2)–O(32)	93.6 (1)	C(16)–C(17)–O(1)	108.5 (2)	C(26)–C(27)–O(2)	108.4 (3)
N(11)–Cd(1)–O(21)	97.1 (1)	N(21)–Cd(2)–O(41)	88.2 (1)	Cd(1)–O(1)–C(17)	124.0 (2)	Cd(2)–O(2)–C(27)	125.5 (2)
N(11)–Cd(1)–O(22)	89.6 (1)	N(21)–Cd(2)–O(42)	86.3 (1)	Cd(1)–O(1)–C(18)	124.8 (2)	Cd(2)–O(2)–C(28)	124.5 (2)
O(1)–Cd(1)–N(14)	75.7 (1)	O(2)–Cd(2)–N(24)	78.1 (1)	C(17)–O(1)–C(18)	111.2 (2)	C(27)–O(2)–C(28)	109.9 (2)
O(1)–Cd(1)–O(11)	142.2 (1)	O(2)–Cd(2)–O(31)	143.7 (1)	O(1)–C(18)–C(19)	107.7 (3)	O(2)–C(28)–C(29)	108.7 (3)
O(1)–Cd(1)–O(12)	89.8 (1)	O(2)–Cd(2)–O(32)	95.2 (1)	C(18)–C(19)–N(13)	112.3 (3)	C(28)–C(29)–N(23)	116.4 (3)
O(1)–Cd(1)–O(21)	144.5 (1)	O(2)–Cd(2)–O(41)	92.0 (1)	C(19)–N(13)–C(110)	128.1 (2)	C(29)–N(23)–C(210)	129.4 (3)
O(1)–Cd(1)–O(22)	91.9 (1)	O(2)–Cd(2)–O(42)	141.2 (1)	C(19)–N(13)–N(14)	120.2 (2)	C(29)–N(23)–N(24)	119.5 (2)
N(14)–Cd(1)–O(11)	97.9 (1)	N(24)–Cd(2)–O(31)	86.1 (1)	C(110)–N(13)–N(14)	111.7 (2)	C(210)–N(23)–N(24)	111.0 (2)
N(14)–Cd(1)–O(12)	89.4 (1)	N(24)–Cd(2)–O(32)	89.4 (1)	N(13)–C(110)–C(111)	124.4 (3)	N(23)–C(210)–C(211)	123.2 (3)
N(14)–Cd(1)–O(21)	105.3 (1)	N(24)–Cd(2)–O(41)	91.8 (1)	N(13)–C(110)–C(112)	107.6 (3)	N(23)–C(210)–C(212)	106.3 (3)
N(14)–Cd(1)–O(22)	91.4 (1)	N(24)–Cd(2)–O(42)	112.9 (1)	C(111)–C(110)–C(112)	128.0 (3)	C(211)–C(210)–C(212)	130.4 (3)
O(11)–Cd(1)–O(12)	52.6 (1)	O(31)–Cd(2)–O(32)	51.8 (1)	C(110)–C(112)–C(113)	105.4 (3)	C(210)–C(212)–C(213)	107.7 (3)
O(11)–Cd(1)–O(21)	73.3 (1)	O(31)–Cd(2)–O(41)	121.3 (1)	C(112)–C(113)–C(114)	127.6 (3)	C(212)–C(213)–C(214)	129.5 (3)
O(11)–Cd(1)–O(22)	125.8 (1)	O(31)–Cd(2)–O(42)	75.1 (1)	C(112)–C(113)–N(14)	110.2 (3)	C(212)–C(213)–N(24)	109.6 (3)
O(12)–Cd(1)–O(21)	125.5 (1)	O(32)–Cd(2)–O(41)	172.9 (1)	C(114)–C(113)–N(14)	122.2 (3)	C(214)–C(213)–N(24)	120.9 (3)
O(12)–Cd(1)–O(22)	178.3 (1)	O(32)–Cd(2)–O(42)	121.0 (1)	Cd(1)–N(14)–N(13)	123.7 (2)	Cd(2)–N(24)–N(23)	124.5 (2)
O(21)–Cd(1)–O(22)	52.8 (1)	O(41)–Cd(2)–O(42)	52.1 (1)	Cd(1)–N(14)–C(113)	130.0 (2)	Cd(2)–N(24)–C(213)	130.0 (2)
Cd(1)–N(11)–C(11)	129.6 (2)	Cd(2)–N(21)–C(21)	127.9 (2)	N(13)–N(14)–C(113)	105.2 (2)	N(23)–N(24)–C(213)	105.4 (2)
Cd(1)–N(11)–N(12)	122.6 (2)	Cd(2)–N(21)–N(22)	126.2 (2)	O(11)–N(1)–O(12)	117.1 (3)	O(31)–N(3)–O(32)	116.6 (3)
C(11)–N(11)–N(12)	105.5 (2)	C(21)–N(21)–N(22)	105.8 (2)	O(11)–N(1)–O(13)	121.9 (3)	O(31)–N(3)–O(33)	121.5 (3)
N(11)–C(11)–C(12)	122.0 (3)	N(21)–C(21)–C(22)	120.7 (3)	O(12)–N(1)–O(13)	121.0 (3)	O(32)–N(3)–O(33)	121.9 (3)
N(11)–C(11)–C(13)	110.0 (3)	N(21)–C(21)–C(23)	108.8 (3)	Cd(1)–O(11)–N(1)	95.9 (2)	Cd(2)–O(31)–N(3)	96.3 (2)
C(12)–C(11)–C(13)	128.0 (3)	C(22)–C(21)–C(23)	130.5 (3)	Cd(1)–O(12)–N(1)	94.4 (2)	Cd(2)–O(32)–N(3)	95.2 (2)
C(11)–C(13)–C(14)	106.3 (3)	C(21)–C(23)–C(24)	107.9 (3)	O(21)–N(2)–O(22)	116.3 (3)	O(41)–N(4)–O(42)	117.8 (3)
C(13)–C(14)–C(15)	131.0 (3)	C(23)–C(24)–C(25)	130.0 (3)	O(21)–N(2)–O(23)	122.3 (3)	O(41)–N(4)–O(43)	121.7 (3)
C(13)–C(14)–N(12)	106.9 (3)	C(23)–C(24)–N(22)	106.1 (3)	O(22)–N(2)–O(23)	121.4 (3)	O(42)–N(4)–O(43)	120.4 (3)
C(15)–C(14)–N(12)	122.2 (3)	C(25)–C(24)–N(22)	123.9 (3)	Cd(1)–O(21)–N(2)	96.0 (2)	Cd(2)–O(41)–N(4)	95.2 (2)
N(11)–N(12)–C(14)	111.4 (2)	N(21)–N(22)–C(24)	111.4 (2)	Cd(1)–O(22)–N(2)	94.9 (2)	Cd(2)–O(42)–N(4)	94.6 (2)

(b) (Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine)bis(nitrato-*O*,*O*′)cadmium(II)

Distances (Å)

Cd–N(1)	2.299 (2)	Cd–N(5)	2.300 (2)	Cd–O(62)	2.560 (2)	Cd–O(72)	2.584 (3)
Cd–N(4)	2.324 (3)	Cd–O(61)	2.304 (2)	Cd–O(71)	2.379 (3)		
N(1)–C(1)	1.334 (4)	C(4)–N(2)	1.351 (4)	C(9)–N(3)	1.460 (4)	C(10)–C(12)	1.359 (5)
C(1)–C(2)	1.497 (4)	C(6)–C(7)	1.509 (4)	N(3)–N(4)	1.365 (4)	C(13)–C(14)	1.483 (5)
C(3)–C(4)	1.371 (4)	N(5)–C(8)	1.477 (4)				
N(6)–O(61)	1.268 (4)	N(6)–O(62)	1.258 (3)	N(6)–O(63)	1.217 (3)		
N(7)–O(71)	1.248 (4)	N(7)–O(72)	1.246 (4)	N(7)–O(73)	1.229 (4)		
N(1)–N(2)	1.378 (2)	N(2)–C(6)	1.456 (4)	N(3)–C(10)	1.350 (4)	C(12)–C(13)	1.389 (5)
C(1)–C(3)	1.386 (3)	C(7)–N(5)	1.480 (3)	C(10)–C(11)	1.493 (5)	C(13)–N(4)	1.342 (3)
C(4)–C(5)	1.493 (4)	C(8)–C(9)	1.515 (4)				

Angles (deg)

N(1)–Cd–N(5)	87.8 (1)	N(5)–Cd–O(71)	134.9 (1)	O(62)–Cd–O(71)	144.2 (1)	C(1)–C(3)–C(4)	106.6 (2)
N(1)–Cd–N(4)	175.1 (1)	N(5)–Cd–O(72)	84.3 (1)	O(62)–Cd–O(72)	165.2 (1)	C(3)–C(4)–C(5)	130.3 (3)
N(1)–Cd–O(61)	97.6 (1)	N(4)–Cd–O(61)	85.8 (1)	O(71)–Cd–O(72)	50.6 (1)	C(3)–C(4)–N(2)	106.6 (2)
N(1)–Cd–O(62)	96.1 (1)	N(4)–Cd–O(62)	83.2 (1)	Cd–N(1)–C(1)	127.6 (2)	C(5)–C(4)–N(2)	123.1 (2)
N(1)–Cd–O(71)	87.4 (1)	N(4)–Cd–O(71)	96.0 (1)	Cd–N(1)–N(2)	122.7 (1)	N(1)–N(2)–C(4)	111.1 (2)
N(1)–Cd–O(72)	84.5 (1)	N(4)–Cd–O(72)	95.0 (1)	C(1)–N(1)–N(2)	105.1 (2)	N(1)–N(2)–C(6)	121.1 (2)
N(5)–Cd–N(4)	87.3 (1)	O(61)–Cd–O(62)	52.4 (1)	N(1)–C(1)–C(2)	121.2 (3)	C(4)–N(2)–C(6)	127.0 (2)
N(5)–Cd–O(61)	133.3 (1)	O(61)–Cd–O(71)	91.8 (1)	N(1)–C(1)–C(3)	110.6 (2)	N(2)–C(6)–C(7)	114.8 (2)
N(5)–Cd–O(62)	80.9 (1)	O(61)–Cd–O(72)	142.3 (1)	C(2)–C(1)–C(3)	128.1 (2)	C(6)–C(7)–N(5)	111.5 (2)

Table II (Continued)

Cd-N(5)-C(7)	112.4 (2)	C(10)-N(3)-N(4)	111.3 (2)	C(14)-C(13)-N(4)	120.9 (2)	Cd-O(61)-N(6)	100.7 (2)
Cd-N(5)-C(8)	111.9 (2)	N(3)-C(10)-C(11)	122.4 (3)	Cd-N(4)-N(3)	124.9 (2)	Cd-O(62)-N(6)	88.8 (2)
C(7)-N(5)-C(8)	112.1 (2)	N(3)-C(10)-C(12)	106.8 (3)	Cd-N(4)-C(13)	129.2 (2)	O(71)-N(7)-O(72)	117.1 (3)
N(5)-C(8)-C(9)	111.1 (2)	C(11)-C(10)-C(12)	130.8 (3)	N(3)-N(4)-C(13)	105.2 (2)	O(71)-N(7)-O(73)	121.2 (3)
C(8)-C(9)-N(3)	114.8 (2)	C(10)-C(12)-C(13)	106.7 (3)	O(61)-N(6)-O(62)	117.5 (2)	O(72)-N(7)-O(73)	121.6 (3)
C(9)-N(3)-C(10)	126.8 (3)	C(12)-C(13)-C(14)	129.1 (3)	O(61)-N(6)-O(63)	120.1 (2)	Cd-O(71)-N(7)	100.9 (2)
C(9)-N(3)-N(4)	121.6 (2)	C(12)-C(13)-N(4)	110.0 (2)	O(62)-N(6)-O(63)	122.4 (3)	Cd-O(72)-N(7)	91.0 (2)

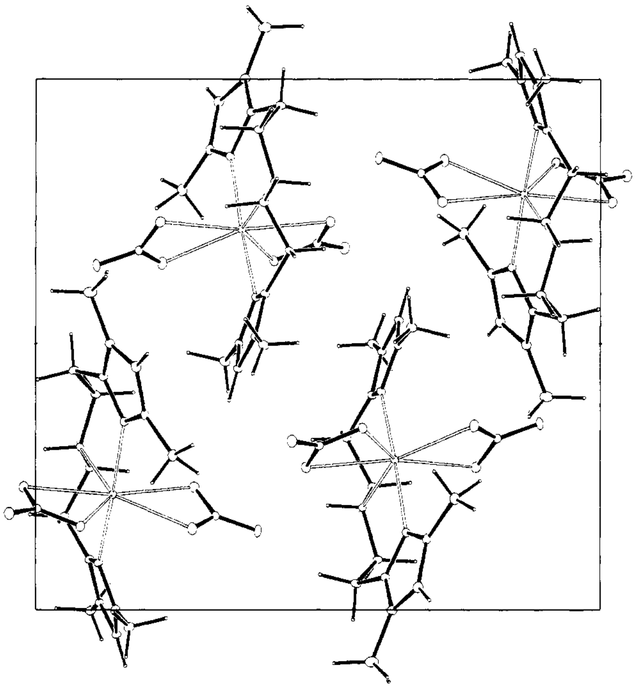

Figure 4. ORTEP drawing of the molecular packing in the structure of B. Due to overlap of molecules this is only the contents of the unit cell viewed down from $c/2$ with a horizontal and b vertical. The origin is at the lower left hand corner of the figure.

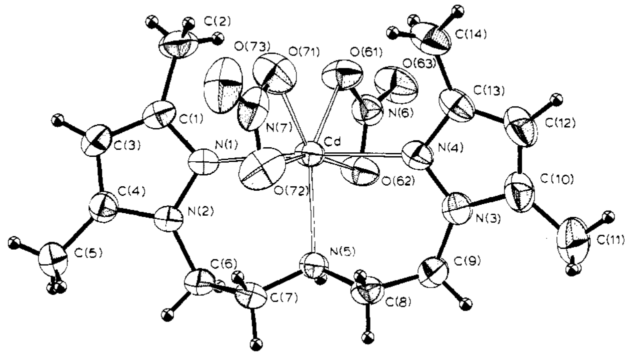

Figure 5. ORTEP drawning of an isolated molecule of B. The ellipses and circles are drawn as indicated for Figure 3. The pentagonal bipyramid about Cd is defined by O(71), O(72), O(61), O(62), and N(5) in the equatorial plane and N(1) and N(4) as the axial ligands.

A′ is 36.8 (7)°. In addition, the least-squares plane of the five oxygen equatorial donor ligands in A shows displacements of the nitrate oxygen atoms ±0.09 and ±0.05 Å from this plane. The analogous displacements for A′ are ±0.4 and ±0.2 Å. Clearly, A and A′ are conformationally different molecules. The axial ligands are nitrogen atoms from the organic ligand and are distorted from linearity with a N(11)-Cd-N(14) angle of 152.5 (1)°. This distortion is due mostly to the constraints placed on the system by a much longer Cd-O(ligand) distance of 2.595 (1) Å compared to the analogous Cd-N(ligand) distance of 2.300 (1) Å (vide infra) as well as the different geometry of the ligand imposed by the oxygen in the framework. Furthermore, in B (vide infra), the nitrate groups are essentially bidentate with equal Cd-O(nitrate) distances of 2.444 Å (average). The remaining distances and angles are normal and do not merit further comment.

The crystal structure of B may be described as made up of uncharged B molecules separated by ordinary van der Waals distances (Figure 4). The molecular structure of B is indicated in Figure 5, and the geometry about the central metal atom may be described as pentagonal bipyramidal with three nitrogen donor atoms from the organic ligand bound to the metal in a T-shaped fashion, analogous to the case for the copper complex[35] (see Table III). N(1) and N(4) make up the axial locations and N(5) one of the equatorial positions of the pentagonal bipyramid. The remaining four equatorial positions are made up from oxygen atoms of two bidentate nitrate groups. In contrast to the Cu structure, in which the T shape of the ligand causes the donor atoms to be arranged so that axial sites are available for further coordination by anions or solvent, the present structure leaves equatorial sites available for further coordination. The binding of nitrate groups to Cd, as either monodentate[4,17,36] or bidentate ligands,[37-40] is a common feature of Cd coordination chemistry, even in aqueous solution. It is interesting to note that, although the coordinating oxygen atoms of the nitrate groups in B lie in a well-defined plane, the binding of the metal to a nitrate group is asymmetric with Cd-O distances of 2.34 (average) and 2.57 Å (average). Although the second metal-oxygen interaction is clearly much weaker than the first, it is still part of the coordination sphere and it is of some importance to the ^{113}Cd NMR. A monodentate Cd-O(NO$_3$) linkage would be expected to be ~2.3 Å and a truly bidentate linkage ~2.4 Å. A normal Cd-O single bond should be ~2.2 Å. It is interesting to note that the shortest Ni-O(nitrate) distance goes with the oxygen not bound to the metal. The distances and angles in the organic ligand are normal and exhibit no unusual features.

^{113}Cd NMR Data. The ^{113}Cd NMR spectra of A in methanol solution (0.22 g in 2.4 mL of MeOH, 2.6 mL of MeOD) gives a single line at room temperature at −96.3 ppm (shielded relative to the 0.1 M Cd(ClO$_4$)$_2$ in D$_2$O standard) with a half-width at half peak height of 7.13 ppm. The ^{113}Cd NMR spectrum of B in methanol solution (0.21 g in 2.4 mL of MeOH, 2.6 mL of MeOD) gives a single line at room temperature at −95.2 ppm (shielded relative to the 0.1 M Cd(ClO$_4$)$_2$ in D$_2$O standard) with a half-width at half peak height of 1.5 ppm. Initially, this similarity of peak positions was cause for some concern since the comparable spectrum of Cd(NO$_3$)$_2$ is at −94.3 ppm and it is possible that the complexes dissociate in methanol solution. However, the magic-angle spinning/cross-polarization (MAS/CP) solid-state ^{113}Cd NMR spectrum shows a single resonance at −106 ppm for both A and B with a peak width at half peak height of 6 ppm for A and 3 ppm for B. This result coupled with ^{113}Cd NMR spectra of the solutions above with added Cd(NO$_3$)$_2$ indicates that the molecular species of A and B remain essentially intact in going from the solid state to solution. In addition, we have utilized the spinning sidebands observed in the MAS/CP ^{113}Cd solid-state spectra of A and B to determine the elements of the chemical shift tensors of A and B. These are as follows:

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Table III. Least-Squares Planes[a]

Central Metal Atom

Structure A, Molecule A

A = 10.1254, *B* = 2.4335, *C* = 3.5675, *D* = −4.0451

atoms in calcd plane	dev, Å	atoms out of plane	dev, Å
O(1)	0.003 (9)	Cd(1)	0.006 (8)
O(11)	0.099 (9)	N(1)	0.015 (9)
O(12)	−0.060 (9)	N(2)	−0.003 (9)
O(21)	−0.094 (9)		
O(22)	0.054 (8)		
Structure A, Molecule A′			
A = 10.1689, *B* = 2.0785, *C* = 3.7365, *D* = 2.8991			
O(2)	0.001 (8)	Cd(2)	0.006 (9)
O(31)	−0.406 (9)	N(3)	−0.165 (9)
O(32)	0.241 (9)	N(4)	0.165 (9)
O(41)	−0.237 (9)		
O(42)	0.402 (9)		
Structure B			
A = 4.5406, *B* = 11.9262, *C* = −5.1793, *D* = 7.5599			
N(5)	−0.004 (9)	Cd	−0.024 (4)
O(61)	0.023 (9)	N(1)	−2.307 (6)
O(62)	−0.012 (9)	N(4)	2.284 (6)
O(71)	−0.027 (9)		
O(72)	0.021 (9)		

Nitrate Groups, Structure A

Nitrate 1

A = 9.3647, *B* = 2.8251, *C* = 4.0517, *D* = −4.1131

atoms in calcd plane	dev, Å	atoms in calcd plane	dev, Å
N(1)	−0.007 (6)	O(12)	0.002 (7)
O(11)	0.002 (7)	O(13)	0.002 (6)
Nitrate 2			
A = 9.998, *B* = 3.4169, *C* = 3.0488, *D* = −4.1796			
N(2)	−0.001 (6)	O(22)	0.002 (6)
O(21)	0.002 (7)	O(23)	0.002 (6)
angle between nitrate groups 1 and 2 6.86 (9)°			
Nitrate 3			
A = 12.6117, *B* = 0.9600, *C* = 12045, *D* = 3.5638			
N(3)	−0.004 (7)	O(32)	0.001 (7)
O(31)	0.001 (6)	O(33)	0.002 (7)
Nitrate 4			
A = 7.2352, *B* = 1.6380, *C* = 6.0993, *D* = 2.4354			
N(4)	0.005 (8)	O(42)	−0.002 (8)
O(41)	−0.002 (8)	O(43)	−0.002 (7)
angle between nitrate groups 3 and 4 36.8 (7)°			
Nitrate Groups, Structure B			
A = 3.3982, *B* = 12.4018, *C* = −6.1866, *D* = 6.9887			
N(6)	0.003 (7)	O(62)	−0.001 (7)
O(61)	−0.001 (8)	O(63)	−0.001 (8)
A = 4.5411, *B* = 11.2255, *C* = −7.1229, *D* = 6.6417			
N(7)	0.002 (8)	O(72)	−0.001 (5)
O(71)	−0.001 (7)	O(73)	−0.001 (6)
angle between the nitrate planes 8.8 (1)°			

[a] The equation of the planes is of the form $Ax + By + Cz = D$ in an orthogonalized coordinate system in which *A*, *B*, *C*, and *D* are in angstroms.

A, −170, −175, and +31 ppm; +31; B, −169, −170, and +12 ppm. The larger peak width of A (6 ppm) compared to that of B (3 ppm) is expected because of two crystallographically independent Cd atoms in A, but these atoms are sufficiently similar so that the peak is not resolved into a doublet. The line broadening, however, need not come only from the two crystallographically and somewhat structurally different Cd atoms in the unit cell but could also arise from or at least have a component from the fact that the MAS may not completely remove the coupling (dipolar and scalar) between Cd and the nitrogen nuclei.[41,42] The observed and simulated ^{113}Cd NMR spectra with spinning sidebands have been deposited as supplementary material.

Discussion

There are now several seven-coordinate pentagonal bipyramidal geometry structures that have been reported in the literature for cadmium.[18,20,38–40] However, it is somewhat surprising to find that geometry with these particular ligands. In addition, the chelated nitrate groups making up part of the coordination sphere of Cd are not surprising. Again, numerous examples of this have been found by us and others (vide supra). However, the large difference in the Cd–N and Cd–O distances in the equatorial plane from structure B to structure A involving the organic ligand of 2.300 (2) and 2.595 (2) Å is surprising. In addition, the difference in mode of interaction of the nitrate groups with the metal in structure A and structure B is surprising. In A the Cd–O(nitrate) distances are all the same at 2.444 Å (average), whereas in B each nitrate has two distinctively different Cd–O distances of 2.341 (average) and 2.572 Å (average). Furthermore, in spite of these differences there seems to be relatively little difference in the ^{113}Cd NMR spectra between A and B, in solution or in the solid-state MAS isotropic values. This result is disturbing in the sense that it is generally accepted that this nucleus is very sensitive to environmental changes. The implication is that in the presence of groups that have a very profound effect upon the chemical shift, such as nitrate ions, minor changes or perhaps even major changes in the environment will give rise to very small or no change in the isotropic chemical shift. The importance of this to ^{113}Cd NMR as a structural probe is paramount. When Cd is substituted for Ca in proteins and the ^{113}Cd NMR spectrum is used as a structural probe via the isotropic chemical shift in the presence of strongly chemical shifting ligands, the results may be very misleading. This may well be the case for proteins such as parvalbumin, calmodulin, troponin C, and concanavalin A. This may also be important for the isotropic chemical shift involving sulfur ligands that have a pronounced chemical shift in the opposite direction, i.e., more deshielded (as much as 800 ppm), and may affect the interpretation of ^{113}Cd NMR spectra of proteins such as metallothioneins, liver alcohol dehydrogenase, and others.

It is interesting to examine the tensor components of the ^{113}Cd chemical shift. From the results of Ellis and co-workers[28,41] and the structure results in hand, one would expect that if one of the components of the chemical shielding tensor were perpendicular to the pseudoequatorial plane of the pentagonal bipyramid, it would be very large and negative, ~-300 ppm, and the other two would be small and positive. The results for A and B of −170, −175, +31 and −169, −170, +12 ppm, respectively, indicate that the positive elements lie close to the equatorial plane and the other two make some angle with the pseudo-fivefold axis of the pentagonal bipyramid. Since both the negative components of both A and B are approximately equal at ~-170 ppm, one would assume they make equal angles with the pseudo-fivefold axis. That is, if we call the positive tensor components in A and B $\sigma_{33} = +31$ and +12 ppm, respectively, the component should lie in the equatorial plane normal to the N, O, N or N, N, N plane of the T-shaped ligand donors. This difference reflects the difference in the donor abilities of these three atoms, and one would expect the ether oxygen to be a softer donor and consequently σ_{33} should be more deshielded for the N, O, N system than for the N, N, N system. On the other hand, σ_{22} and σ_{11} are essentially equal to each other and equal in A and B at ~-170 ppm. These components must make the same angle with the normal to the pseudo-fivefold axis to have the same value, i.e., $\sim45°$. The geometry of A and B from X-ray crystallography and the mag-

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nitude of tensor components of the shielding tensor from the spinning sidebands give the approximate orientation of the ^{113}Cd shielding tensor without single-crystal NMR data.

It is clear from these two examples that the isotropic chemical shifts in the liquid and the solid state are misleading as to environmental differences but the components of the chemical shift do reflect subtle differences, specifically, the differences between σ_{33} of +31 ppm for A and +12 ppm for B. Therefore, at this time the best structural probe seems to be the combination of solid-state MAS/CP ^{113}Cd NMR data utilizing the spinning sidebands. X-ray crystallography will point the way toward the correct interpretations along with single-crystal ^{113}Cd NMR.

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Supplementary Material Available: Observed and simulated MAS/CP ^{113}Cd NMR spectra and Tables SI and SII, listing thermal parameters and hydrogen positions (13 pages); tables of calculated and observed structure factors (106 pages). Ordering information is given on any current masthead page.

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Activated Ligand Substitution in Bridged Complexes. 2.[1] Base Hydrolysis of the (μ-Amido)decaamminedicobalt(5+) Ion. Synthesis and Structure of the (μ-Amido)chloroenneaamminedicobalt(4+) Ion

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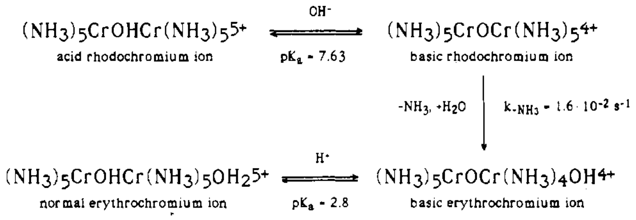
Deprotonation of the (μ-amido)decaamminedicobalt(III) ion (**1**) at one of the ammine ligands ($K_b = 89 \pm 19$ M^{-1}, p$K_a = 11.7 \pm 0.1$, 25 °C, $I = 0.1$ (KClO$_4$/NH$_4$ClO$_4$)) is followed by rapid ammonia loss ($k_{-\mathrm{NH_3}} = (4.6 \pm 1.0) \times 10^{-2}$ s^{-1}). The thus formed intermediate reacts either with water ($k_{\mathrm{H_2O}}$) to form $(NH_3)_5CoNH_2Co(OH)(NH_3)_4^{4+}$ (**2**) or with ammonia ($k_{\mathrm{NH_3}}$) to re-form the (deprotonated) reactant ($R = k_{\mathrm{NH_3}}/k_{\mathrm{H_2O}} = 0.135 \pm 0.011$ M^{-1}). The substitution of the first ammonia is followed by a series of further ammonia substitution and amido bridge cleavage steps. The first two reactions of **1** were retarded in aqueous ammonia. Product analyses under different conditions have established the absence of $(NH_3)_5CoOH^{2+}$ as a primary cleavage product of **1**. Thus, loss of the first ammonia is not accompanied by cleavage of **1** in a parallel pathway. Two of the observed reaction products, $(NH_3)_4Co(OH)_2^+$ and $Co(NH_3)_6^{3+}$, must arise in a later phase of the reaction, e.g. by cleavage of **2**. Kinetic studies have established conditions for the efficient synthesis of the "μ-amido–chloro–erythrocobalt" complex *cis*-$[(NH_3)_5CoNH_2CoCl(NH_3)_4]Cl_4 \cdot H_2O$. This compound crystallizes in the orthorhombic space group *Pcmn* with $a = 10.079$ (5) Å, $b = 12.382$ (8) Å, $c = 14.57$ (4) Å, and $Z = 4$. The molecules occupy special positions, and the two Co atoms and the Cl, N1, N2, N6, and N7 atoms as well as the oxygen atom of the water of crystallization lie on a mirror plane. The Co–N bond trans to Cl is slightly shortened (1.947 (9) Å); all others fall within the normal range (1.97–1.98 Å). The N1–Co2–Cl angle is distorted (97.2°). From the angle at the bridge, Co1–N1–Co2 = 140°, the cation appears strained, even in the most favorable, "staggered", conformation of the two octehedra that is adopted in the lattice. In acidic solution, *cis*-$(NH_3)_5CoNH_2CoCl(NH_3)_4^{4+}$ (**3**) first loses chloride ($k_{\mathrm{fast}} = (6 \pm 2) \times 10^{-5}$ s^{-1}, 25 °C, $I = 0.1$ (HClO$_4$)) and then cleaves into monomers ($k_{\mathrm{slow}} = (1.4 \pm 0.9) \times 10^{-6}$ s^{-1}).

Introduction

A little more than a century ago, Jørgensen prepared the rhodo- and erythrochromium complexes.[3] Since then, their structure and optical and magnetic properties as well as the unusual, fast formation of the erythrochromium ion by release of ammonia from the basic rhodochromium ion (Scheme I) have attracted continued interest.[4–9] In their classical paper (which established many of the important features of Scheme I), Schwarzenbach and Magyar[10] attributed the high reactivity of the basic rhodochromium ion to the trans labilizing effect of the μ-oxo ligand.

Scheme I



The cobalt(III) analogue of the acid rhodochromium ion, the so-called monool $(NH_3)_5CoOHCo(NH_3)_5^{5+}$, has been prepared by Siebert and Feuerhake.[11] The monool is unstable in aqueous solution at pH ≤4: 2 mol of aquapentaamminecobalt(III) is formed by acid-catalyzed and spontaneous bridge cleavage.[12–14] At pH >4 the monool decomposes rapidly, forming a dark brown solid.[12]

The (isoelectronic) μ-amido analogue of the monool, $(NH_3)_5CoNH_2Co(NH_3)_5^{5+}$ (**1**), has already been prepared by Werner.[15] This ion as well as the recently[1] prepared (±)-*cis*,*cis*-$(en)_2(NH_3)CoNH_2Co(NH_3)(en)_2^{5+}$ ion is stable in acid.

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