Articles

Structural Diversity in Monomeric Cadmium Phenoxides

Donald J. Darensbourg,* Sharon A. Niezgoda, Joseph H. Reibenspies, and Jennifer D. Draper

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Received August 8, 1997[⊗]

Three monomeric Cd(II) phenoxide complexes have been prepared by reacting Cd[N(SiMe$_3$)$_2$]$_2$ with 2 equiv of 2,6-disubstituted phenols bearing sterically bulky *tert*-butyl or phenyl groups. The strongly coordinating solvents THF, tetrahydrothiophene (THT), and pyridine used for these reactions were incorporated into the metal's coordination sphere, leading to complexes with a general formulation of Cd(O-2,6-R$_2$C$_6$H$_3$)$_2$(solv)$_{2-3}$. The Cd complexes obtained have been characterized crystallographically and have been found to adopt differing solid-state geometries. The X-ray crystal structure of Cd(O-2,6-^{t}BuC$_6$H$_3$)$_2$(THF)$_2$, **1**, previously reported by Buhro, displayed unusual square-planar coordination of the metal center. Complex **2**, Cd(O^{t}BuC$_6$H$_3$)$_2$(THT)$_2$, has been found to take on the same square-planar geometry, even with the more strongly donating thioether ligand. Alternatively, complex **3**, Cd(O-2,6-Ph$_2$C$_6$H$_3$)$_2$(THF)$_2$, has been found to adopt distorted-tetrahedral geometry, quite similar to its zinc congener. The O(1)−Cd−O(2) angle between the phenoxide ligands in **3** is 150.1(2)°, and the angle between the ether ligands is 83.1(3)°. When the strongly basic solvent pyridine was used, a five-coordinate complex **4**, Cd(O-2,6-^{t}BuC$_6$H$_3$)$_2$(py)$_3$, was isolated. This complex **4** is best described as having trigonal bipyramidal geometry with the phenoxide ligands and one pyridine defining the equatorial plane and two axial pyridine ligands having an angle of 169.7(2)°. The angle between the phenoxide ligands in **4** is 156.1(2)°. These complexes **1**−**4** have also been characterized in noncoordinating solvent solutions by ^{1}H, ^{13}C, and ^{113}Cd NMR spectroscopy and have been found to contain labile donor ligands. Preliminary studies indicate that, in a noncoordinating solvent, a rapid equilibrium exists between species with and without coordinated donor solvent ligands.

We have recently demonstrated that monomeric Zn(II) phenoxides with bulky substituents in the 2,6-positions, exemplified by (2,6-diphenylphenoxide)$_2$Zn(THF)$_2$, are very active catalysts for the copolymerization and terpolymerization of epoxides and CO$_2$ to afford high-molecular-weight polycarbonates.[1] These complexes exhibit highly distorted tetrahedral geometries in the solid state, while the two ether ligands are quite labile in solution as shown by ^{1}H NMR.[2,3] In an effort to better understand the initiation step in this copolymerization process, it was of interest to examine Cd(II) analogs where the reaction could be monitored by ^{113}Cd NMR spectroscopy. Similar modeling studies of the reaction of Zn(II) carboxylates with epoxides utilizing Cd(II) carboxylates have been successful.[4] It was intriguing to note that although a variety of Cd thiophenol derivatives have been structurally characterized,[5] there is only one example of a mononuclear Cd(II) phenoxide complex which is well-defined. Buhro and co-workers have reported the solid-state structure of Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(THF)$_2$, **1**, to have a square-planar geometry at ambient temperature.[6,7] The structure of complex **1** is quite different from that found by Caulton[2] and ourselves for a variety of Zn(II) phenoxides which all display the distorted-tetrahedral geometry.[1,3] Hence, in addition to utilizing monomeric cadmium analogs for investigating certain mechanistic aspects of the zinc-catalyzed copolymerization process, it was of interest to understand the influences behind the differences observed in solid-state structures. This difference has added significance in that substitution of Zn(II) with Cd(II) as a sensitive spectroscopic probe has been used extensively to study enzymes.[8]

In this communication we report the structure of three new complexes which exhibit a variety of conformations: a square-planar Cd(II) phenoxide complex, Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(THT)$_2$, **2** (THT = tetrahydrothiophene); a complex which displays the expected distorted-tetrahedral geometry based on discussions of bonding theory,[9] Cd(O-2,6-Ph$_2$C$_6$H$_3$)$_2$(THF)$_2$, **3**; and a five-coordinate complex which displays distorted-square-pyramidal

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

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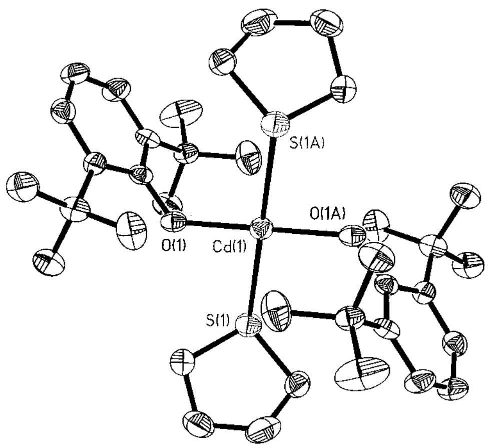

Figure 1. Thermal ellipsoid drawing of $Cd(O^tBu_2C_6H_3)_2(THT)_2$, **2** (50% probability). Additional selected bond lengths and angles: O(1)−C(6) = 1.343(10) Å, S(1)−Cd−O(1) = 77.7(2)°, O(1A)−Cd−S(1) = 102.3(2)°, Cd−O(1)−C(6) = 125.3(5)°, Cd−S(1)−[SC_2H_4 plane] = 125.6°.

geometry, $Cd(O\text{-}2,6\text{-}^tBu_2C_6H_3)_2(py)_3$, **4**. We also report the solution ^{113}Cd NMR spectra obtained for these complexes which contain an interesting mix of donor ligands.

All complexes were synthesized by reacting $Cd[N(SiMe_3)_2]_2$ with 2 equiv of 2,6-disubstituted phenol in a small volume of the appropriate solvent. The yellow reaction solutions were stirred at ambient temperature for at least 1 h and then allowed to stand undisturbed at −20 °C. Clear, colorless crystals of the products which were suitable for X-ray diffraction were obtained from these concentrated solutions within 2 days.[10] The complexes **1**−**4** were isolated by removal of the supernatant solution from the crystals and drying for a short time under vacuum to give pale yellow, microcrystalline powders. The complexes were characterized by ^{1}H and ^{13}C NMR in methylene chloride-d_2 or benzene-d_6 solutions and by elemental analyses.[11] They are very sensitive to moisture, hydrolyzing to phenol and $Cd(OH)_2$ rapidly in air and more slowly when stored under presumably inert conditions.

The unusual square-planar geometry noted in complex **1** was suggested to arise from a linear $Cd(O\text{-}2,6\text{-}^tBu_2C_6H_3)_2$ unit with weak THF interactions. Indeed, the somewhat longer than expected Cd−O(THF) seen in complex **1** is supportive of this view (*vide infra*). Hence, we initially reasoned that a stronger ether donor, e.g., the soft donor ligand THT, would promote formation of a distorted-tetrahedral geometry similar to that observed in the zinc analogs. Complex **2**, $Cd(O\text{-}2,6\text{-}^tBu_2C_6H_3)_2(THT)_2$, was synthesized in 72% yield and structurally characterized by single-crystal X-ray diffraction.[12] This complex, as well, exhibited the same crystallographically imposed geometry about the metal center as seen in **1** and illustrated in Figure 1. The Cd−O(phenoxide) bond length in **2** of 2.102(6) Å is slightly longer than that found in **1**, 2.058 Å. On the other hand, the Cd−S bond length for the thioether ligands at 2.768(2) Å is comparable to that observed for the Cd−O(THF) bond if the difference in covalent radii of oxygen and sulfur is taken into account. As expected, this Cd−S(THT) bond is longer than the Cd−thiolate bond observed in the distorted-tetrahedral thiophenol complex, $[Cd(S\text{-}2,4,6\text{-}^iPr_3C_6H_2)_2(1\text{-Me-imid})_2]$ which has an average Cd−S distance of 2.461 Å.[5a]

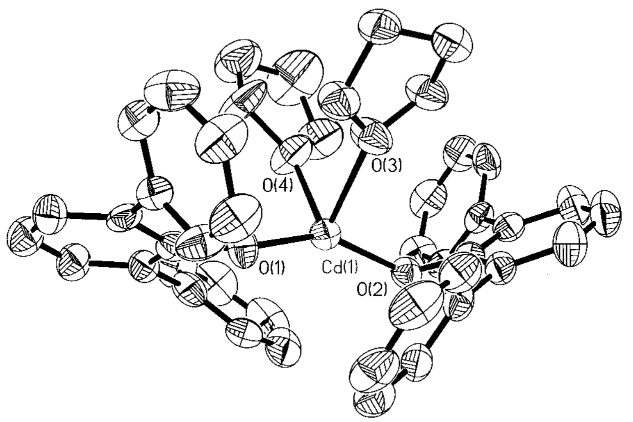

Figure 2. Thermal ellipsoid drawing of $Cd(OPh_2C_6H_3)_2(THF)_2$, **3** (50% probability). Additional selected bond lengths and angles: Cd−O(1) = 2.073(5) Å, Cd−O(2) = 2.074(5) Å, Cd−O(3) = 2.320(6) Å, Cd−O(4) = 2.293(6) Å, O(1)−C(1) = 1.307 Å, Cd−O(1)−C(1) = 130.1(5)°, Cd−O(3)−[OC_2H_4 plane] = 172.7(3)°, Cd−O(4)−[OC_2H_4 plane] = 169.4(4)°.

When the *tert*-butyl groups of the phenoxide ligand were replaced with smaller, electron-withdrawing phenyl rings, a complex which displayed distorted-tetrahedral geometry in the solid state was obtained. $Cd(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(THF)_2$, **3**, was isolated in only 52% yield due to its high solubility in THF.[13] The structure of **3** is displayed in Figure 2. The average Cd−O(phenoxide) bond length, 2.074(5) Å, is only slightly longer than those found in **1**, while the average Cd−O(THF) distance, 2.307(6) Å, is significantly shorter than that seen in **1**, 2.498(5) Å. The Cd−O(THF) distance in **3** is similar to that seen in the six-coordinate adduct complex, $[Tp^{Ph}]Cd(acetate)\cdot THF$, which was 2.388(8) Å.[4a] The distorted-tetrahedral geometry of **3** is defined by the O(1)−Cd−O(2) angle between the phenoxide ligands of 150.1(2)° and a O(THF)−Cd−O(THF) angle of 83.1(3)°. The zinc analog of **3**, $Zn(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(THF)_2$, displays a comparable geometry with O(1)−Zn−O(2) found to be 136.2(2)° and an angle of 90.5(2)° between the THF ligands.[3]

When the reaction of $Cd[N(SiMe_3)_2]_2$ and 2,6-di-*tert*-butylphenol was performed in the presence of pyridine as the donor solvent, complex **4** was isolated in 71% yield. As depicted in Figure 3, this cadmium derivative is five-coordinate, containing three pyridine bases in addition to the two phenoxide ligands.[14] The geometry about the cadmium center can be described as either a distorted square pyramid or trigonal bipyramid. In accordance with the related monomeric bis(aryloxide) derivative of calcium, $Ca(OAr)_2(THF)_3$, complex **4** is probably best depicted as a distorted trigonal bipyramid.[15] That is, if atoms N(1), O(1), O(2), and Cd(1) are used to define the trigonal plane (mean deviation from planarity = 0.0122 Å), the two axial pyridine bases provide a N(2)−Cd−N(3) angle of 169.7(2)°. The average Cd−O(phenoxide) bond distance is 2.192(5) Å,

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(10) Crystals of complex **4** suitable for X-ray diffraction were recrystallized from toluene solution.

(11) Analytical data for **1**−**4** reflect loss of donor ligands which occurs while drying under vacuum. Data for complex **3**: Anal. Calcd for $C_{44}H_{42}O_4$: C, 70.73; H, 5.67. Found: C, 68.79; H, 5.50. ^{1}H NMR (C_6D_6): δ 6.8−7.3 (br, 13H, 2,6-$Ph_2C_6H_3$), 3.59 (m, 4H, THF), 1.43 (m, 4H, THF). $^{13}C\{H\}$ NMR (C_6D_6): δ 168.1 (*ipso*-C_6O), 125−132 (2,6-Ph_2C_6), 67.9 (THF), 25.9 (THF).

(12) Crystal data for **2**: $C_{44}H_{42}CdO_4$, M_r = 747.18, triclinic, $P\bar{1}$, a = 8.868(2) Å, b = 11.066(2) Å, c = 19.554(4) Å, α =78.38(3)°, β = 83.29(3)°, γ = 73.51(3)°, T = 193(2) K, Z = 2, V = 1798.4(6) Å^3, 5322 reflections with $I > 2\sigma(I)$ used, R = 0.0586, and R_w = 0.1314.

(13) Crystal data for **3**: $C_{36}H_{58}CdO_2S_2$, M_r = 699.34, triclinic, $P\bar{1}$, a = 9.251(2) Å, b = 9.493(2) Å, c = 11.516(2) Å, α = 74.74(3)°, β = 81.92(3)°, γ = 64.95(3)°, T = 203(2) K, Z = 1, V = 883.4(3) Å^3, 2639 reflections with $I > 2\sigma(I)$ used, R = 0.0695, and R_w = 0.1780.

(14) Crystal data for **4**: $C_{48}H_{62}CdO_2N_4$, M_r = 839.42, monoclinic, $P2_1/n$, a = 19.249(5) Å, b = 15.152(2) Å, c = 18.085(3) Å, β = 117.46(2)°, T = 293(2) K, Z = 4, V = 4680(2) Å^3, 8223 reflections with $I > 2\sigma(I)$ used, R = 0.0744, and R_w = 0.1387.

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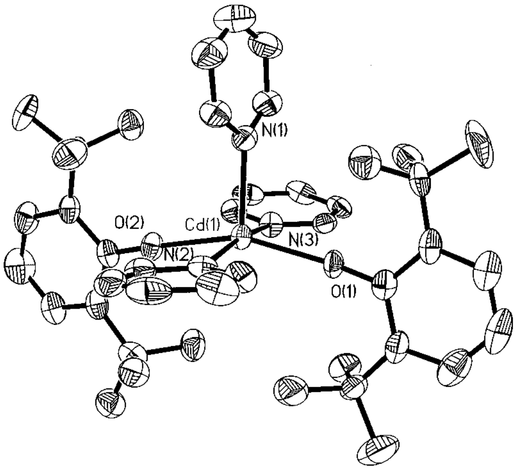

Figure 3. Thermal ellipsoid drawing of $Cd(O^tBu_2C_6H_3)_2(py)_3$, **4** (50% probability). Additional selected bond lengths and angles: Cd−O(1) = 2.193(5) Å, Cd−O(2) = 2.190(5) Å, Cd−N(1) = 2.342(7) Å, Cd−N(2) = 2.347(6) Å, Cd−N(3) = 2.372(6) Å, O(1)−C(1) = 1.314(9) Å, O(1)−Cd−N(1) = 102.(2)°, O(2)−Cd−N(1) = 101.3(2)°, Cd−O(1)−C(1) = 165.0(5)°.

and the angle, O(1)−Cd−O(2), between the phenoxide ligands is 156.1(2)°. ^{113}Cd NMR studies in solution suggest that complex **4** forms in a stepwise process, initially affording either a square-planar or distorted-tetrahedral bis(pyridine) derivative, which subsequently binds another pyridine base (*vide infra*.)

Finally, in addition to complexes **1**−**4**, we have synthesized a derivative (**5**) from the less bulky 2,4,6-trimethylphenol. Complex **5**, as is its zinc analog, is insoluble in most organic solvents which is indicative of aggregation in the solid state. Nevertheless, both of these derivatives are solubilized in the presence of pyridine, and a distorted-tetrahedral structure has been defined for the $Zn(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2(py)_2$ species.[3] Thus far, X-ray quality crystals of the cadmium derivative (**5**) have eluded our efforts. However, ^{113}Cd NMR suggests a solution structure for **5** which is similar to that for **4** in solution at ambient temperature.

Table 1. ^{113}Cd NMR Resonance Obtained from 0.05 M CD_2Cl_2 Solution of **1**−**5**^{a} at Ambient Temperature

	δ (ppm)
$Cd(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(THF)_2$, **1**	−2
$Cd(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(THT)_2$, **2**	149
$Cd(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(THF)_2$, **3**	73
$Cd(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2(py)_3$, **4**	109
$[Cd(O\text{-}2,4,6\text{-}Me_3C_6H_3)_2]_n$, **5**^{b}	113

^{a} All peaks relative to external 0.1 M $Cd(ClO_4)_2/D_2O$ reference. ^{b} A 0.05 M C_5D_5N solution was used for complex **5** due to insolubility in CD_2Cl_2.

Relevant to the solution structure of these newly prepared monomeric cadmium phenoxide derivatives, we have begun to examine these in CD_2Cl_2 solutions by ^{113}Cd NMR. The ^{113}Cd resonances obtained in methylene chloride-d_2 solutions at room temperature for complexes **1**−**5** are provided in Table 1. Both ^{1}H and ^{113}Cd NMR studies are consistent with all of these complexes having labile donor ligands, and hence these resonances represent average chemical shifts for rapidly exchanging species in equilibrium. In the case of the THT ligands (complex **2**), the equilibrium favors the four-coordinate species. In the presence of pyridine, there appear to be two predominant complexes present, a four-coordinate derivative from ambient temperature to −60 °C (giving rise to a signal close to 109 ppm) and a five-coordinate species (^{113}Cd resonance at 50 ppm) at temperatures below −60 °C.

In conclusion, it is apparent that there are significant differences in the solid-state structure of zinc and cadmium analogs, with the latter metal possessing a richer coordination chemistry. Hence, as has been previously noted, it is important to take notice of this divergence when substituting cadmium,[16] or other metals,[17] for zinc in catalytic (either enzymatic or nonenzymatic) processes.

Acknowledgment. Financial support of this research by the National Science Foundation (Grant 96-15866) is greatly appreciated. S.A.N. thanks the Department of Education for a GAANN fellowship. We are most grateful to Professor W. E. Buhro for helpful discussions.

Supporting Information Available: Ball-and-stick drawings and tables of anisotropic thermal parameters, bond lengths, and bond angles for complexes **2**−**4** (25 pages). Ordering information is given on any current masthead page.

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