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Trigonal-Planar Zinc(II) and Cadmium(II) Tris(phenoxide) Complexes

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Cadmium and zinc complexes in which the metal occupies a planar coordination site with only oxygen ligands are uncommon. In fact, there is only one report of a solid-state structure in which zinc occupies a site within a square-planar arrangement of oxygens,[1] while there have been few reports of cadmium in a square-planar coordination of oxygen ligands.[2] Furthermore, only a small number of monomeric or dimeric complexes containing these metals in trigonal-planar sites have been crystallographically characterized, and most of these have contained thiolate or selenolate ligands with sterically encumbering alkyl or aryl groups.[3,4] Trigonal-planar CdS_3 coordination has also been observed crystallographically for a series of group 12 thiobenzoate complexes, although these showed additional metal−ligand interactions.[5] The first reported crystal structure of a tris-aryloxide of Zn, $Na[Zn(2,6\text{-diphenylphenoxide})_3(H_2O)]$, contained a coordinated water molecule leading to a distorted tetrahedral conformation about the zinc center.[6] The structure of this zinc complex also had a sodium cation coordinated within the phenyl rings of the aryloxide ligands causing further distortion of the structure.

Generally, incorporation of alkali metals into solid-state structures of zinc alkoxides, coordinated to one or more of the oxygen atoms in alkoxide salts, is not unusual and is often unavoidable in metathesis reactions used to synthesize these complexes.[7] Early reports of “double alkoxides” of zinc, borrowing a term used for complexes which contain a single alkali metal associated with another metal alkoxide system,[8] have included complexes such as $K[Zn(OMe)_3]$, $K[Zn(\text{ethylate})_3]$, $Na[Zn(\text{isopropylate})_3]$,[9] and $Li[Zn(OMe)_3]$,[10] although these reports did not include structural data. On the other hand, the coordination of potassium cations into arene ligands in an η^6-mode has similarly been observed for a series of salts of lanthanide tetrakis(aryloxide) anions, leading to chain structures in the solid state.[11]

The synthesis and structural characterization of the monomeric three-coordinate triphenoxide complexes of Zn and Cd, $[K(THF)_6][M(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_3]$ {M = Zn (**1**), Cd (**2**)}, are simply an extension of studies carried out recently in our laboratories on the catalytic activity and structure of bis(phenoxide) complexes of these group 12 metals.[12,13] Monomeric zinc(II) phenoxides, exemplified by $Zn(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(THF)_2$, have been found to be excellent homogeneous catalysts for the copolymerization of CO_2 with epoxides to give high-molecular weight polycarbonate polymers. The use of phenoxide ligands which have sterically bulky substituents in the 2,6-positions has now allowed us to isolate monomeric tri-coordinate complexes. The zinc complex, **1**, has been examined for its catalytic activity in the copolymerization of epoxides with CO_2 to provide polycarbonates and in the homopolymerization of propylene oxide to yield polyethers.

Experimental Section

Methods and Materials. All complexes are fairly air- and moisture-sensitive and were handled using Schlenk and glovebox techniques under an argon atmosphere. Solvents were freshly distilled before use. Cyclohexene oxide was distilled over CaH_2 prior to use, whereas, 2,6-di-*tert*-butylphenol (purchased from Aldrich) was used as received. $Cd[N(SiMe_3)_2]_2$ and $Zn[N(SiMe_3)_2]_2$ were synthesized and distilled according to the literature procedure.[14] $K(O\text{-}2,6\text{-}{}^tBuC_6H_3)$ was synthesized and isolated from the reaction of KH with the phenol in THF. All isotopically labeled chemicals for NMR experiments were purchased from Cambridge Isotope Laboratories. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-200E superconducting high-resolution spectrometer. ^{113}Cd NMR spectra were recorded on a Varian XL-400E superconducting high-resolution spectrometer operating at 88 MHz using an external 0.1 M $Cd(ClO_4)_2/D_2O$ reference. Elemental analyses were carried out by Canadian Microanalytical Services, Ltd.

Synthesis of $K[M(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_3]$, M = Zn (1), Cd (2). A 5-mL THF solution of 2 equiv of 2,6-di-*tert*-butylphenol (0.267 g for Zn, 0.238 g for Cd) was cannulated into a 5-mL THF solution of $M[N(SiMe_3)_2]_2$ (0.25 g). After this solution stirred for approximately 5 min, a 5-mL THF solution of 1 equiv of $K(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)$ (0.122 g for Zn, 0.117 g for Cd) was added to it. The resulting solution was stirred for 1 day, after which the solution was concentrated to approximately 5 mL. An equal portion of hexanes, approximately, was added slowly to the THF solution. The flask was sealed and placed at −20 °C for 2−3 days while block crystals suitable for X-ray diffraction formed. Alternatively, the complexes were isolated as powders by concentrating the THF solution, precipitating the product with hexanes, and filtering onto a glass frit. The pale yellow or white powders were dried under vacuum and collected in 90% yield (0.323 g) for Zn and 51% yield (0.186 g) for Cd, based on the amount of potassium salt used. These complexes are soluble in THF and CH_3CN but not in

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Table 1. Crystallographic Data for **1** and **2**

	1	**2**
empirical formula	$C_{66}H_{111}O_9ZnK$	$C_{68}H_{115}O_{9.5}CdK$
fw	1153.02	1236.2
space group	$P2_1/c$	$P\bar{1}$
a, Å	11.547(2)	14.2168(14)
b, Å	23.023(4)	14.3540(17)
c, Å	25.802(6)	18.679(2)
α, deg		81.101(10)
β, deg	97.519(14)	67.763(9)
γ, deg		89.107(9)
V, Å^3	6800(2)	3481.9(7)
Z	4	2
d (calcd), g/cm^3	1.126	1.169
absorption coeff, mm^{-1}	0.472	0.424
λ, (Å)	0.710 73	0.710 73
T, K	193(2)	193(2)
R^a, %	7.27	6.60
$R_w{}^a$, %	17.12	16.21

[a] $R = \Sigma||F_o| - |F_c||/\Sigma F_o$. $R_w = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$.

benzene, dichloromethane, or chloroform. Anal. Calcd for $ZnO_3C_{42}H_{45}K$: C, 70.02; H, 8.81. Found: C, 69.55; H, 8.74. Calcd for $CdO_3C_{42}H_{45}K$: C, 65.73; H, 8.27. Found: C, 65.73; H, 8.30. ^{1}H NMR for **1** (CD_3CN): δ 1.31 [s, 36H, {-^{t}Bu}], 1.38 [s, 18H, {-^{t}Bu}], 6.27 [t, 2H, {4-H}], 6.47 [t, 1H, {4-H}], 6.90 [d, 4H, {3,5-H}], 7.02 [d, 2H, {3,5-H}]. ^{1}H NMR for **2** (CD_3CN): δ 1.40 [s, 18H, {-^{t}Bu}], 6.18 [t, 1H, {4-H}], 6.90 [d, 2H, {3,5-H}]. ^{113}Cd NMR for **2** (THF): δ 120 (THF), δ 111 ppm (CD_3CN).

High-Pressure Copolymerization of CO_2 with Cyclohexene Oxide. The reactor was heated at 80 °C under vacuum overnight prior to addition of reactants to remove all traces of water. A solid sample of the zinc complex, **1** (0.120 g), was put into the reactor in the glovebox. The cyclohexene oxide (10 mL) was added through the injection port and the reactor was then pressurized to 800 psi with CO_2. The reactor was then heated to 80 °C, raising the pressure to approximately 1000 psi, and held under these conditions for a period of 69 h. After this time, the reactor was opened and the slightly viscous, yellow-colored solution was removed. The solution was analyzed by infrared spectroscopy.

Homopolymerization of Propylene Oxide. A 0.120 g amount of complex **1** was placed in a dry 100-mL flask. Freshly distilled propylene oxide, 10 mL, was added to give a bright yellow solution. Within 1 h of stirring, some small chunks of solid could be seen in the solution. After 1 day of stirring, more solid could be observed on the walls of the flask and in the solution. The reaction was stirred at room temperature for 1 week.

X-ray Crystallographic Study of 1 and 2. Crystal data and details of the data collections are given in Table 1. A colorless block crystal of **1** and colorless plate crystal of **2** were mounted of a glass fiber with epoxy cement at room temperature and cooled to 193 K in a N_2 cold stream. Preliminary examination and data collection were performed on a Siemens P4 X-ray diffractometer (Mo Kα, $\lambda = 0.710\,73$ Å). Cell parameters were calculated from the least-squares fitting of the setting angles for 25 reflections, and ω scans for several intense reflections indicated acceptable crystal quality. Data were collected for $4.0° \le 2\theta \le 50.0°$. Three control reflections collected for every 97 reflections showed no significant trends. Background measurements by stationary-crystal and stationary-counter techniques were taken at the beginning and end of each scan for half of the total scan time. Lorentz and polarization corrections were applied to the total reflections for each complex, listed in Table 1. A semiempirical absorption correction was applied to all complexes. Totals of unique reflections for each complex (Table 1) with $|I| \ge 2.0\sigma_I$ were used in further calculations. Structures were solved by direct methods.[15a] Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded R, $R_w(F^2)$, and S values at convergence for all complexes, listed in Table 1. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. Neutral-atom scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*.[15b]

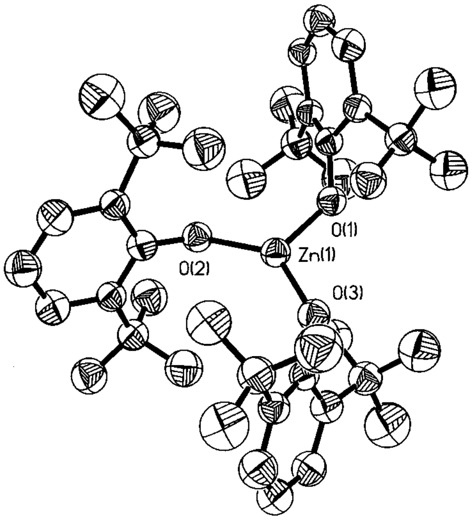

Figure 1. ORTEP representation of $[K(THF)_6][Zn(O\text{-}2,6\text{-}^tBu_2C_6H_3)_3]$, **1** (50% probability).

Results and Discussion

The zinc and cadmium complexes are readily synthesized through the reaction of the $M[N(SiMe_3)_2]_2$ complex with 2 equiv of 2,6-di-*tert*-butylphenol and 1 equiv of the potassium salt of the phenol, as shown in eq 1.

$$\begin{gathered} M[N(SiMe_3)_2]_2 + 2\ 2,6\text{-}^tBuC_6H_3OH + \\ K(O\text{-}2,6\text{-}^tBuC_6H_3) \xrightarrow[THF]{} \\ [K(THF)_6][M(O\text{-}2,6\text{-}^tBuC_6H_3)_3] + 2HN(SiMe_3)_2 \quad (1) \\ M = Zn\ (\mathbf{1}),\ Cd\ (\mathbf{2}) \end{gathered}$$

The amide complexes of Zn and Cd are used as starting material because the product amine is a weak base and good leaving group, thus the reaction to yield the bis(phenoxide) complexes occurs quickly, indicated in the cadmium solution by a yellow color change. The subsequent reaction of the bis(phenoxide) with the potassium salt is much slower, going to completion over a prolonged reaction time. The complexes were precipitated from the THF solution with hexanes and filtered from the mixture to isolate the white (Zn) or yellow (Cd) powders. The complexes **1** and **2** are somewhat soluble in coordinating organic solvents and are sensitive to moisture in solution but less sensitive as solids.

Crystals of **1** and **2** were grown from the original THF reaction mixture, as described in the Experimental Section. Large, colorless block and plate crystals of **1** and **2**, respectively, formed after 2−4 days of standing at −20 °C. The X-ray crystallographic structure determinations found that the metal atoms in each complex were identically coordinated in a trigonal-planar arrangement by the phenoxide ligands. The potassium counterions do not interact with the tris(phenoxide) anions but are octahedrally coordinated by THF molecules. The representations of **1** and **2** are displayed in Figures 1 and 2 as thermal ellipsoid drawings. The metal−oxygen bond distances and bond angles for both complexes are listed in Table 2.

Crystals of **1** were found to be poorly scattering as compared to those of complex **2**. The average Zn−O bond length observed

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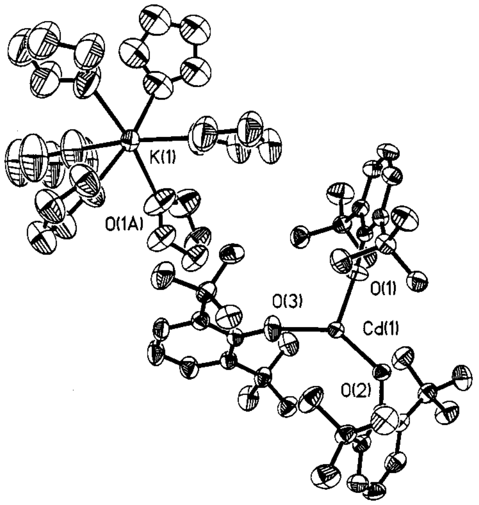

Figure 2. ORTEP representation of [K(THF)$_6$][Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_3$], **2** (50% probability).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1** and **2**

complex **1**		complex **2**	
Zn−O(1)	1.886(19) Å	Cd−O(1)	2.078(3) Å
Zn−O(2)	1.86(2) Å	Cd−O(2)	2.081(3) Å
Zn−O(3)	1.85(2) Å	Cd−O(3)	2.057(4) Å
O(1)−Zn−O(2)	118.1(9)°	O(1)−Cd−(2)	116.9(2)°
O(2)−Zn−O(3)	133.0(10)°	O(2)−Cd−O(3)	135.7(2)°
O(1)−Zn−O(3)	108.8(9)°	O(1)−Cd−O(3)	107.1(2)°

of 1.86 Å is close to that found in the bis(phenoxide) derivative, Zn(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(THF)$_2$,[13] which had an average Zn−O(phenoxide) distance of 1.876 Å. The sum of the three O−Zn−O bond angles equals 359.9°, and the Zn atom has been calculated to be only 0.04 Å out of the least-squares plane defined by the oxygen ligands of the three phenoxide ligands, thus a nearly-perfect planar arrangement was attained. The phenoxide ligands have adopted a fanlike arrangement, with the *ortho*-^{t}Bu- groups located above and below the ZnO$_3$ plane.

A good crystallographic data set was easily obtained for the Cd tris(phenoxide) complex and the structure of **2** is identical to that of **1**. However, an extra THF molecule is present in the asymmetric unit of **2**. There are two equivalent Cd−O bond lengths and one shorter by 0.02 Å, with the average Cd−O distance equal to 2.071 Å. Again, this is comparable to the Cd−O(phenoxide) bond lengths of 2.068(3) Å found in the square-planar bis(phenoxide) analogue, Cd(O-2,6-^{t}Bu$_2$C$_6$H$_3$)$_2$(THF)$_2$.[2] The Cd atom is located only 0.0602 Å above the O$_3$ plane defined by the phenoxide ligands. The sum of the O−Cd−O bond angles equals nearly 360°, supporting the assignment of planar coordination of the Cd atom. The phenoxide ligands are arranged similar to those in **1**.

In both solid-state structures, the potassium cation is held separate from the metal anion by THF coordination. The average K−O bond length is approximately 2.70 Å for both complexes. When the crystals are dried under vacuum, these THF molecules are removed, as determined from a ^{1}H NMR sample prepared from the dried crystals. Additional verification of this is found in the results of C, H analyses obtained from samples of dried crystals of both complexes which matched very well with the values calculated without inclusion of THF molecules (Experimental Section).

The solution ^{1}H NMR spectra for the cadmium complex **2** in CD$_3$CN displays only one set of signals for the phenoxide ligands. However, there are two sets of signals which differ by approximately 0.2 ppm observed for the phenoxides for the zinc complex, **1**. The integration of the peaks gives a 2:1 ratio for each type of chemical shift. The differences between the chemical shifts for the aromatic protons of the two sets (∼0.2 ppm) are slightly greater than the differences between the ^{t}Bu-peaks (∼0.1 ppm). Perhaps, in the case of the zinc complex, there is some interaction of the potassium cation with the aromatic rings or the oxygen atoms of two of the phenoxides ("double-alkoxide" formation), leading to a slight difference in their chemical shift. Since only one set of phenoxide signals appears in the ^{1}H NMR of **2**, potassium interaction with the cadmium complex would have to be either nonexistent or need to be in a somewhat symmetric fashion. The ^{113}Cd NMR resonance obtained from a THF solution of **2** was located further downfield than expected at 120 ppm.[16] Similarly, the ^{113}Cd NMR signal in CD$_3$CN **2** was observed at $\delta = 111$ ppm.

Polymerization Experiments. The Zn complex, **1**, was tested for its catalytic activity in the copolymerization of an cyclohexene oxide with CO$_2$ and in homopolymerization of epoxides. Since the complex is soluble in epoxides a homogeneous catalyst system could be possible. A copolymerization experiment with CO$_2$ and cyclohexene oxide conducted at the same pressure and temperature conditions as those used for the bis(phenoxide) catalysts yielded no CO$_2$-containing products, as determined from the IR spectrum of the reaction solution. The Zn complex was then tested for its ability to homopolymerize propylene oxide. The complex was dissolved in 10 mL of propylene oxide at a concentration of 0.016 M catalyst. The solution was stirred for 1 week at ambient temperature in a sealed flask. After the first hour of stirring, small pieces of material were observed floating in the solution. However, after 1 week, the solution had not solidified or even turned viscous, although slightly more of the insoluble material remained. Upon isolation of the products, only traces of polymeric material were identifiable in the ^{1}H NMR spectrum. One of the most active catalysts for the ring-opening homopolymerization of epoxides is another potassium salt (KO^{t}Bu). The polymerization occurs through an anionic mechanism in which the potassium cation acts to coordinate and ring-open the epoxide and is associated with the anionic oxygen of the growing polymer chain.[17] Hence, it is most probable that trace quantities of K(O-2,6-^{t}Bu$_2$C$_6$H$_3$) could be performing the catalysis.

Conclusions

The synthesis and structural characterization of trigonal planar tris(phenoxides) of zinc and cadmium have been achieved. This type of coordination is not usual for dipositive metal ions. The use of phenoxides with sterically bulky alkyl groups ortho- to the alcohol function protected the MO$_3$ core, and the unmindful use of THF as the crystallization solvent aided in the characterization of the desired tricoordinate product without having to employ noncoordinating cations or encapsulating the alkali metal. These complexes have not shown any activity in coupling

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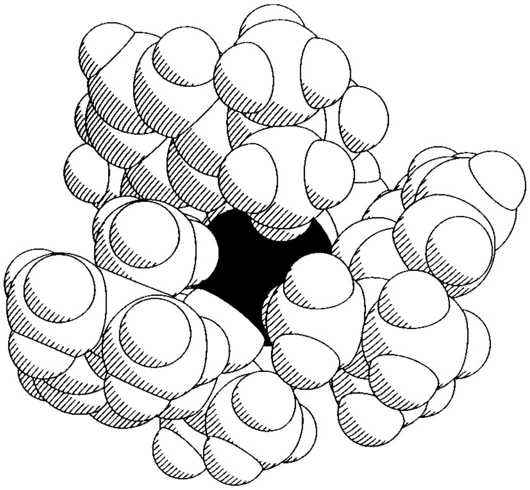

Figure 3. Space-filling model of the $Zn(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_3^-$ anion.

CO_2 with cyclohexene oxide, under the same conditions which are optimal for the Zn bis(phenoxides) catalysts. The lack of activity in the ring-opening polymerization of propylene oxide additionally leads us to believe that no CO_2/epoxide coupling will be observed with **1** as catalyst under any conditions. We have recently uncovered evidence pointing to the coordination and subsequent ring-opening of an epoxide as the initiation step in the copolymerization mechanism for sterically encumbered Zn bis(phenoxide) catalysts.[13] Because of the steric congestion about the zinc center (see space-filling model in Figure 3) coupled with the net negative charge of the complexes binding of the epoxide to complex **1** is highly unlikely as indicated by the lack of THF coordination. Thus, the absence of homo- or copolymerization activity exhibited by **1** is not surprising.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **1** and **2** are available free of charge via the Internet at http://pubs.acs.org.

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