

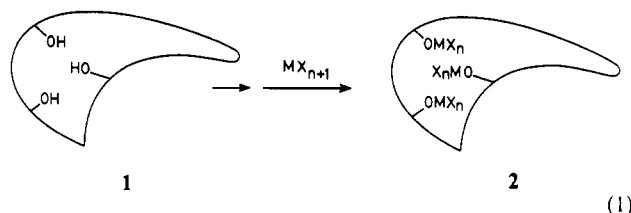
Multidentate Lewis Acids. Synthesis, Structure, and Reactions of Complexes of Bidentate Zirconium Trichloride Alkoxides

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The 1:2 tetrahydrofuran adduct **5** of zirconium trichloride isopropoxide adopts a *mer* octahedral geometry in solution. Partial redistribution occurs to give the 1:2 tetrahydrofuran adduct **3** of $ZrCl_4$. A bidentate zirconium trichloride alkoxide **8** could be prepared by treating the bis(trimethylsilyl) ether **7** of racemic *trans*-1,2-cyclohexanediol with 2 equiv of the 1:2 tetrahydrofuran adduct **3** of $ZrCl_4$. An X-ray crystallographic study of the tetrahydrofuran adduct of bidentate Lewis acid **8** showed that the electrophilic sites are *trans*-diaxially oriented and independently bind two molecules of tetrahydrofuran to give *mer* octahedral complexes. In solution, the adduct decomposes by a redistribution that produces the 1:2 tetrahydrofuran adduct **3** of $ZrCl_4$. The adduct crystallizes in the monoclinic space group $P2_1/c$ with $a = 16.111(9) \text{ \AA}$, $b = 10.868(6) \text{ \AA}$, $c = 25.178(13) \text{ \AA}$, $\beta = 121.32(4)^\circ$, $V = 3766.1 \text{ \AA}^3$, and $Z = 4$. Refinement of 3699 reflections yielded $R = 0.042$ and $R_w = 0.042$.

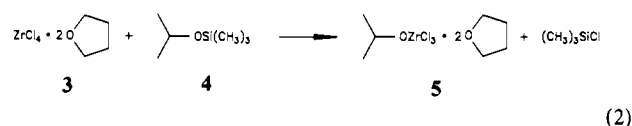
Host molecules with carefully oriented sites of Lewis acidity promise to be useful for the recognition, binding, transport, and chemical activation of complementary basic guests.¹ This potential has inspired the synthesis of a diverse and fascinating series of compounds of boron, mercury, silicon, and tin that make two or more sites of Lewis acidity available for the cooperative binding of basic substrates. Without exception, juxtaposition of the electrophilic atoms has been achieved by attaching them directly to carbon atoms in an organic framework. This strategy has several undesirable consequences. It creates multidentate Lewis acids that are typically difficult to prepare and modify, and it makes them substantially less Lewis acidic than purely inorganic analogues. These shortcomings prompted us to test an alternative route to multidentate Lewis acids. Addition of an inorganic halide MX_{n+1} to a suitable derivative of alcohol **1** should provide multidentate halide alkoxide **2** (eq 1). Related multidentate Lewis



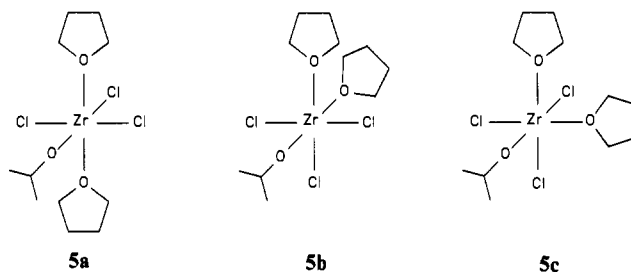
acids should be formed when frameworks with other reactive groups are treated with suitable inorganic salts. This approach is attractively simple and versatile, since it allows various electrophilic atoms to be attached to a wide variety of frameworks in a single step. However, the reactive groups of the framework must be cleverly oriented so that they are too far apart to be bridged by a single electrophilic atom, yet close enough together to create sites of Lewis acidity that can bind substrates cooperatively. In this paper, we describe our efforts to prepare bidentate zirconium chloride alkoxides in which this delicate balance is achieved.

Treatment of the 1:2 tetrahydrofuran adduct **3** of $ZrCl_4$ with an equimolar amount of isopropyl trimethylsilyl ether (**4**)³ in dichloromethane cleanly produced the 1:2 tetrahydrofuran adduct

5 of zirconium trichloride isopropoxide,^{4,5} which could be isolated in 96% yield by evaporation of the solvent (eq 2). Since the



average Zr–Cl bond dissociation energy in $ZrCl_4$ is 117 kcal/mol and the Si–Cl bond dissociation energy in $(CH_3)_3SiCl$ is 97 kcal/mol,⁶ the success of this reaction indicates that the alkoxide Zr–O bond in product **5** is significantly stronger than the Si–O bond in ether **4**. An elemental analysis established that zirconium trichloride isopropoxide, like $ZrCl_4$ itself,^{2a} binds 2 equiv of tetrahydrofuran. This stoichiometry suggested that adduct **5** is a monomeric octahedral complex with either *mer* (**5a** or **5b**) or *fac* (**5c**) geometries.⁷ A ¹H NMR spectrum of a 0.03 M solution



of adduct **5** in $CDCl_3$ at 25 °C showed a doublet at δ 1.39 (6 H) and a septet at δ 4.66 (1 H) characteristic of the isopropoxy group. In addition, signals at δ 2.05 (8 H) and δ 4.37 (8 H) attributable to bound tetrahydrofuran were shifted downfield by 0.22 and 0.66 ppm, respectively, from free tetrahydrofuran. At –50 °C, the low-field region of the spectrum became more complex and revealed two major signals of equal intensity at δ 4.31 and 4.43. A ¹H NMR spectrum recorded in CD_2Cl_2 at –80 °C contained two similar peaks in the same 1:1 ratio. The insensitivity of this ratio to solvent polarity suggests that a single adduct with non-equivalent molecules of tetrahydrofuran is favored. We therefore conclude that the major adduct in solution is *mer* isomer **5b**. This orientation is presumably favored because it places chlorine and the strongest π -donor, the alkoxy group,⁸ *trans* to the more weakly

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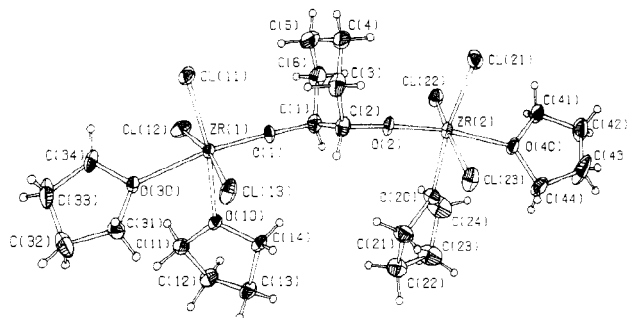
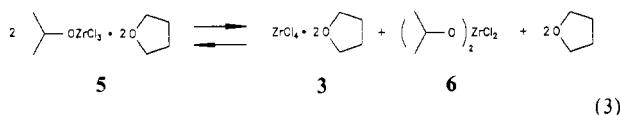


Figure 1. ORTEP drawing of the structure of the 1:4 tetrahydrofuran adduct of bidentate zirconium trichloride alkoxide **8**. The ellipsoids correspond to 50% probability. Hydrogen atoms are represented by spheres of arbitrary size.

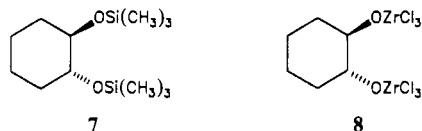
π -donating tetrahydrofuran ligands and thereby maximizes oxygen-*p*-zirconium-*d* π -bonding and chlorine-*p*-zirconium-*d* π -bonding.⁹

In the low-temperature NMR studies of tetrahydrofuran adduct **5**, we also observed signals characteristic of free tetrahydrofuran and the *cis* and *trans* isomers of the 1:2 adduct **3** of $ZrCl_4$ with tetrahydrofuran.^{2a} These products and uncomplexed zirconium dichloride diisopropoxide (**6**) presumably arise reversibly from the partial redistribution of adduct **5** (eq 3).⁵ Integration of the



¹H NMR spectrum of a nominally 0.05 M solution of adduct **5** in CD_2Cl_2 revealed 35% redistribution at -80°C . As expected, the redistribution was less extensive at higher concentrations.

The tendency of the 1:2 tetrahydrofuran adduct **5** of zirconium trichloride isopropoxide to undergo redistribution in solution was disquieting. Nevertheless, its simple preparation encouraged us to try to make a bidentate analogue by treating the bis(trimethylsilyl) ether **7**¹⁰ of racemic *trans*-1,2-cyclohexanediol with



2 equiv of the 1:2 tetrahydrofuran adduct **3** of $ZrCl_4$. Crystallization of the product from dichloromethane/pentane provided a 1:4 tetrahydrofuran complex of bidentate zirconium trichloride alkoxide **8** in 57% yield. The successful synthesis of an adduct of compound **8** demonstrated the soundness of our basic strategy for attaching strongly electrophilic sites to a preexisting organic framework.

An X-ray crystallographic study allowed us to determine how bidentate Lewis acid **8** binds tetrahydrofuran. The structure of the adduct is shown in Figure 1, crystallographic data are summarized in Table I, selected interatomic distances and bond angles are listed in Table II, and atomic coordinates and isotropic temperature factors are provided in Table III. The structure confirms that we prepared bidentate Lewis acid **8** but shows that the two electrophilic sites are *trans* diaxially oriented on the organic cyclohexyl framework. This preference minimizes dipolar repulsion but unfortunately places the sites of Lewis acidity where they cannot possibly bind tetrahydrofuran cooperatively. As a result, each site acts independently and binds two molecules of tetrahydrofuran to give *mer* octahedral complexes.¹¹ This observation

Table I. Crystallographic Data for the 1:4 Tetrahydrofuran Adduct of Bidentate Zirconium Trichloride Alkoxide **8**

formula	$C_{22}H_{42}Cl_6O_6Zr_2$	Z	4
fw	882.7	$d(\text{calcd}), \text{g cm}^{-3}$	1.557
syst. space group	monoclinic, $P2_1/c$	T, K	220
a, Å	16.111 (9)	μ, cm^{-1}	11.5
b, Å	10.868 (6)	radiation ($\lambda, \text{Å}$)	Mo K α
c, Å	25.178 (13)		(0.71069)
β , deg	121.32 (4)	R	0.042
$V, \text{Å}^3$	3766.1	R_w	0.042

Table II. Selected Interatomic Distances and Bond Angles in the 1:4 Tetrahydrofuran Adduct of Bidentate Zirconium Trichloride Alkoxide **8**

Distances (Å)			
Zr(1)-Cl(11)	2.412 (2)	Zr(2)-Cl(21)	2.415 (2)
Zr(1)-Cl(12)	2.460 (2)	Zr(2)-Cl(22)	2.452 (2)
Zr(1)-Cl(13)	2.453 (2)	Zr(2)-Cl(23)	2.466 (2)
Zr(1)-O(1)	1.870 (5)	Zr(2)-O(2)	1.867 (5)
Zr(1)-O(10)	2.234 (4)	Zr(2)-O(20)	2.236 (4)
Zr(1)-O(30)	2.275 (5)	Zr(2)-O(40)	2.291 (5)
Bond Angles (deg)			
O(1)-Zr(1)-Cl(11)	99.73 (16)	O(2)-Zr(2)-Cl(21)	98.73 (16)
O(1)-Zr(1)-Cl(12)	94.28 (16)	O(2)-Zr(2)-Cl(22)	96.00 (16)
O(1)-Zr(1)-Cl(13)	93.77 (16)	O(2)-Zr(2)-Cl(23)	93.51 (16)
O(1)-Zr(1)-O(1)	90.06 (19)	O(2)-Zr(2)-O(20)	90.87 (19)
O(1)-Zr(1)-O(30)	170.03 (19)	O(2)-Zr(2)-O(40)	171.43 (19)
Cl(11)-Zr(1)-Cl(12)	92.54 (7)	Cl(21)-Zr(2)-Cl(22)	92.72 (7)
Cl(11)-Zr(1)-Cl(13)	95.54 (7)	Cl(21)-Zr(2)-Cl(23)	94.33 (8)
Cl(11)-Zr(1)-O(10)	169.82 (12)	Cl(21)-Zr(2)-O(20)	170.37 (13)
Cl(11)-Zr(1)-O(30)	90.23 (12)	Cl(21)-Zr(2)-O(40)	89.74 (13)
Cl(12)-Zr(1)-Cl(13)	167.47 (8)	Cl(22)-Zr(2)-Cl(23)	167.16 (8)
Cl(12)-Zr(1)-O(10)	83.91 (12)	Cl(22)-Zr(2)-O(20)	85.54 (13)
Cl(12)-Zr(1)-O(30)	84.87 (12)	Cl(22)-Zr(2)-O(40)	84.77 (13)
Cl(13)-Zr(1)-O(10)	86.50 (12)	Cl(23)-Zr(2)-O(20)	85.72 (13)
Cl(13)-Zr(1)-O(30)	85.53 (12)	Cl(23)-Zr(2)-O(40)	84.55 (13)
O(10)-Zr(1)-O(30)	79.98 (16)	O(20)-Zr(2)-O(40)	80.67 (17)
Zr(1)-O(1)-C(1)	176.0 (5)	Zr(2)-O(2)-C(2)	171.6 (4)
Zr(1)-O(10)-C(14)	126.3 (4)	Zr(2)-O(20)-C(24)	122.4 (4)
Zr(1)-O(30)-C(31)	121.5 (4)	Zr(2)-O(40)-C(41)	128.1 (5)
Zr(1)-O(10)-C(14)	126.7 (4)	Zr(2)-O(40)-C(41)	123.0 (4)
Zr(1)-O(30)-C(34)	123.2 (4)	Zr(2)-O(40)-C(44)	128.9 (4)
C(14)-O(10)-C(11)	110.8 (5)	C(24)-O(20)-C(21)	108.6 (6)
C(34)-O(30)-C(31)	109.4 (5)	C(44)-O(40)-C(41)	107.9 (6)

supports our conclusion that the simpler 1:2 tetrahydrofuran adduct **5** of zirconium trichloride isopropoxide favors the same *mer* geometry. Of special interest are the large alkoxide Zr-O-C angles (176.0 and 171.6°), which reflect significant oxygen-*p*-zirconium-*d* π -bonding.^{8,12} For the same reason, the alkoxide Zr-O bonds are short (1.870 and 1.867 Å).¹³ As expected, the shortest Zr-Cl bonds are those *trans* to tetrahydrofuran, and the longest Zr-O bonds to tetrahydrofuran are those *trans* to the strongest π -donor, the alkoxy group. In each molecule of tetrahydrofuran, the sum of the angles around oxygen is very close to 360°, so the hybridization of the bound oxygens can be considered to be sp^2 . This preference indicates that tetrahydrofuran acts as a π -donor and might therefore be unwilling to bridge two zirconium trichloride alkoxides even if they were oriented *gauche* on the organic cyclohexyl framework.

At -50°C , the ¹H NMR spectrum of a solution prepared by dissolving the 1:4 tetrahydrofuran adduct of bidentate zirconium trichloride alkoxide **8** in $CDCl_3$ showed the presence of free tetrahydrofuran. We were tempted to conclude that the *trans* diequatorial conformer of compound **8** had been formed in solution, allowing the two electrophilic sites to be bridged by chlorine or by tetrahydrofuran and permitting tetrahydrofuran to be re-

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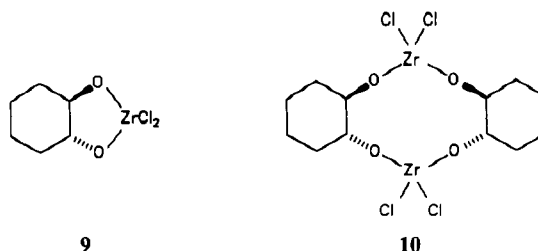
Table III. Atomic Coordinates ($\times 10^4$ for O, C; $\times 10^5$ for Zr, Cl) and Equivalent Isotropic Temperature Factors ($\times 10^3$) for the Non-Hydrogen Atoms of the 1:4 Tetrahydrofuran Adduct of Bidentate Zirconium Trichloride Alkoxide **8**

atom	x	y	z	$U_{eq}, \text{\AA}^2$
Zr(1)	64239 (4)	15260 (7)	75044 (3)	41
Zr(2)	95905 (4)	14934 (6)	62908 (3)	43
Cl(11)	48037 (11)	15499 (21)	66000 (8)	70
Cl(12)	62576 (13)	-6122 (17)	77569 (9)	70
Cl(13)	67119 (13)	37392 (17)	74921 (10)	74
Cl(21)	86392 (14)	16533 (21)	51714 (8)	75
Cl(22)	96212 (13)	-7609 (16)	62617 (9)	64
Cl(23)	99585 (14)	37126 (16)	64537 (10)	74
Cl(31) ^a	4151 (6)	1693 (9)	-120 (4)	149
Cl(32) ^a	3082 (13)	2503 (20)	11 (7)	184
Cl(33) ^a	3246 (10)	141 (11)	140 (5)	175
Cl(34) ^a	2636 (4)	385 (6)	-30 (2)	139
Cl(35) ^a	4582 (21)	502 (26)	273 (12)	210
Cl(36) ^a	4364 (12)	891 (16)	-40 (7)	163
Cl(37) ^a	3792 (16)	2365 (19)	-63 (9)	163
Cl(38) ^a	2777 (23)	1229 (19)	118 (9)	203
O(1)	7128 (3)	1104 (5)	7130 (2)	64
O(2)	8584 (3)	1605 (4)	6451 (2)	58
O(10)	7791 (2)	1494 (4)	8437 (2)	45
O(20)	10683 (3)	1296 (4)	7306 (2)	54
O(30)	5822 (3)	2031 (4)	8117 (2)	47
O(40)	10978 (3)	1378 (4)	6252 (2)	60
C(1)	7727 (5)	737 (7)	6879 (3)	63
C(2)	7821 (5)	1887 (6)	6591 (3)	62
C(3)	6886 (5)	2243 (8)	6000 (4)	84
C(4)	6467 (6)	1154 (11)	5550 (4)	134
C(5)	6299 (7)	122 (11)	5848 (5)	140
C(6)	7237 (6)	-309 (7)	6406 (4)	87
C(11)	7906 (5)	981 (6)	9008 (3)	54
C(12)	8980 (5)	696 (7)	9409 (3)	62
C(13)	9449 (4)	1648 (7)	9203 (3)	62
C(14)	8739 (4)	1731 (7)	8509 (3)	59
C(21)	10642 (5)	2029 (8)	7776 (3)	82
C(22)	11383 (6)	1515 (8)	8385 (3)	83
C(23)	12002 (6)	734 (9)	8256 (4)	105
C(24)	11392 (6)	331 (8)	7614 (4)	101
C(31)	6028 (5)	3151 (7)	8488 (3)	64
C(32)	5663 (6)	2864 (9)	8918 (4)	95
C(33)	4801 (6)	2069 (9)	8526 (4)	108
C(34)	5040 (5)	1341 (8)	8119 (4)	81
C(41)	11075 (6)	562 (8)	5824 (4)	90
C(42)	11874 (7)	1086 (9)	5771 (5)	119
C(43)	12254 (8)	2032 (11)	6176 (7)	199
C(44)	11849 (5)	2134 (8)	6571 (4)	88
C(300)	3803 (12)	1395 (13)	366 (6)	240

^a Disordered chlorine atoms, coordinates $\times 10^4$.

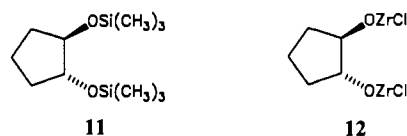
leased. This may indeed occur, but it appears to trigger a reversible redistribution reaction that converts the tetrahydrofuran adduct of bidentate zirconium trichloride alkoxide **8** into the 1:2 tetrahydrofuran adduct **3** of ZrCl_4 . The redistribution is complete at 0.01 M in CDCl_3 , since only the characteristic signals of free tetrahydrofuran and the *cis* and *trans* isomers of adduct **3**^{2a} could be observed in the low-field region of the ^1H NMR spectrum at -50°C . At higher concentrations, however, two minor signals of equal intensity appeared at δ 4.37 and 4.43 and could be assigned to the nonequivalent molecules of tetrahydrofuran in the 1:4 *mer* complex of bidentate zirconium trichloride alkoxide **8** itself. Crystallization of the 1:4 tetrahydrofuran adduct of bidentate zirconium trichloride alkoxide **8** from similar solutions is therefore fortuitously selective and does not reflect the actual composition of the mixtures.

The other products of this redistribution are presumably oligomers formally derived from hypothetical zirconium dichloride dialkoxide **9**. The unfavorable *trans* fusion and nonlinear $\text{Zr}-\text{O}-\text{C}$ angles of structure **9** would make its conversion into dimer **10** or related structures significantly exothermic. Support for this hypothesis is provided by the observation that similar titanium chloride alkoxides undergo analogous redistribution reactions.⁸ Since redistribution of the 1:4 tetrahydrofuran adduct of bidentate zirconium trichloride alkoxide **8** liberates 2 equiv of tetrahydro-

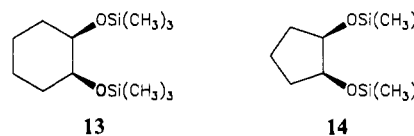


furan, dimer **10** does not bind tetrahydrofuran strongly in solution, perhaps because it exists as larger aggregates.

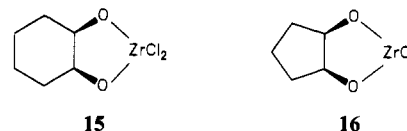
The reaction of the bis(trimethylsilyl) ether **11**¹⁰ of racemic *trans*-1,2-cyclopentanediol with 2 equiv of the 1:2 tetrahydrofuran adduct **3** of ZrCl_4 gave a soluble but noncrystalline product, presumably the 1:4 tetrahydrofuran adduct of bidentate zirconium trichloride alkoxide **12**. This material was not characterized in



detail, but the low-field region of its ^1H NMR spectrum in CD_2Cl_2 (0.04 M) at -80°C showed the characteristic signals of free tetrahydrofuran and the *cis* and *trans* isomers of the 1:2 tetrahydrofuran adduct **3** of ZrCl_4 . Like its bidentate homologue **8**, compound **12** therefore appears to undergo extensive redistribution in solution. Two smaller signals of equal intensity appeared at δ 4.24 and 4.34 and could be assigned to the nonequivalent molecules of tetrahydrofuran in the 1:4 *mer* complex of bidentate zirconium trichloride alkoxide **12** itself. Integration of the spectrum showed approximately 60% redistribution under these conditions. The corresponding reactions of bis(trimethylsilyl) ethers **13**¹⁰ and **14**¹⁰ of *cis*-1,2-cyclohexanediol and *cis*-1,2-



cyclopentanediol with 2 equiv of the 1:2 tetrahydrofuran adduct **3** of ZrCl_4 yielded only insoluble precipitates, possibly oligomers derived from zirconium dichloride dialkoxides **15** and **16**.



This study of zirconium trichloride alkoxides shows that strong multidentate Lewis acids can be prepared by using very simple reactions to attach electrophilic sites to an organic framework. The great versatility of this strategy makes us confident that we will be able to construct multidentate Lewis acids that actually bind basic substrates cooperatively. Multiple binding by a chiral Lewis acid is particularly promising, since it should restrict conformational mobility and make subsequent reactions of the substrate highly enantioselective.

Experimental Section

Our general experimental procedures have been described elsewhere.^{2a} Isopropyl trimethylsilyl ether (**4**),³ the bis(trimethylsilyl) ethers¹⁰ of *cis*- and *trans*-1,2-cyclohexanediol and -cyclopentanediol, and the 1:2 tetrahydrofuran adduct **3**^{2b} of ZrCl_4 were prepared by published procedures. All other reagents were commercial products of the highest purity available.

Preparation of the 1:2 Tetrahydrofuran Adduct **5 of Zirconium Trichloride Isopropoxide.** A stirred solution of the 1:2 tetrahydrofuran adduct **3**^{2b} of ZrCl_4 (500 mg, 1.33 mmol) in dichloromethane (5 mL) was treated dropwise at 25°C under dry N_2 with a solution of isopropyl trimethylsilyl ether³ (**4**; 176 mg, 1.33 mmol) in dichloromethane (1 mL). The resulting mixture was stirred at 25°C for 24 h and filtered. Removal of volatiles from the filtrate in vacuo left a white solid residue of the 1:2 tetrahydrofuran adduct of zirconium trichloride isopropoxide (**5**;

510 mg, 1.27 mmol, 95.5%): mp 95 °C, IR (Nujol) 1125, 1015, 1000, 840, 315 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.39 (d, 6 H), 2.05 (m, 8 H), 4.37 (m, 8 H), 4.66 (septet, 1 H). Anal. Calcd for C₁₁H₂₃Cl₃O₃Zr: C, 32.95; H, 5.79. Found: C, 31.21; H, 5.62.

Preparation of the 1:4 Tetrahydrofuran Adduct of Bidentate Zirconium Trichloride Alkoxide 8. A stirred solution of the 1:2 tetrahydrofuran adduct 3^{2b} of ZrCl₄ (600 mg, 1.59 mmol) in dichloromethane (2 mL) was treated dropwise at 25 °C under dry N₂ with a solution of the bis(trimethylsilyl) ether ⁷10 of racemic *trans*-1,2-cyclohexanediol (207 mg, 0.795 mmol) in dichloromethane (1 mL). The resulting mixture was stirred at 25 °C for 24 h and filtered into a test tube. A layer of pentane (3 mL) was carefully added, and the tube was kept at -25 °C for several days. This produced a crop of colorless needles contaminated with a small amount of white powder. The crystals were separated mechanically and shown by X-ray crystallography to be a 1:1 dichloromethane solvate of the 1:4 tetrahydrofuran adduct of bidentate zirconium alkoxide 8 (400 mg, 0.453 mmol, 57.0%): mp 86-88 °C; IR (Nujol) 1160, 1090, 990, 830, 730, 315 cm⁻¹. Anal. Calcd for C₂₂H₄₂Cl₆O₆Zr₂·CH₂Cl₂: C, 31.29; H, 5.03. Found: C, 30.29; H, 4.97.

Crystallographic Data for the 1:4 Tetrahydrofuran Adduct of Bidentate Zirconium Trichloride Alkoxide 8. Crystals suitable for an X-ray study were grown by crystallization from dichloromethane/pentane. The sample selected for analysis had the following dimensions: 0.27 × 0.35 × 0.39 mm. Other crystallographic data are summarized in Table I.

Crystallographic Measurements and Structure Resolution. An Enraf-Nonius CAD-4 diffractometer was used to collect a set of intensity data according to a procedure described elsewhere.¹⁴ Seven standard reflections checked every 1 h showed random fluctuations of less than ±3.0% about their respective means. A set of 14518 Mo Kα reflections (2θ ≤ 50°) was collected at 220 K over half the Laue sphere (±h, ±k, ±l). Of these, 3699 (I ≤ 3σ(I)) were retained for structure resolution and refinement after averaging to Laue 2/m symmetry. These measurements were corrected for the Lorentz effect and polarization but not

for absorption. The structure was solved by using direct methods (EEMS) and difference-Fourier calculations (SHELX), and it was refined on |F_o| by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. For disordered CH₂Cl₂, occupancies were initially refined by using common isotropic temperature factors, and then the occupancies were fixed and anisotropic temperature factors were used. Refinement converged to R = 0.042 and R_w = 0.042, and the goodness-of-fit ratio S was 1.88 for 407 parameters refined. The final ΔF map was essentially featureless, with a general background below ±0.20 e Å⁻³, seven peaks of 0.25-0.37 e Å⁻³ within 0.94 Å from Zr, and four peaks of 0.21-0.23 e Å⁻³ within 1.2 Å from Cl. The scattering curves for the non-hydrogen atoms¹⁵ and hydrogen atoms¹⁶ were taken from standard sources. Contributions of Zr and Cl to anomalous dispersion were included.¹⁷

Selected interatomic distances and bond angles are listed in Table II, and atomic coordinates and isotropic temperature factors are provided in Table III. Tables of anisotropic temperature factors and structure factors are included as supplementary material.

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Supplementary Material Available: For the 1:4 tetrahydrofuran adduct of bidentate zirconium trichloride alkoxide 8, Table SI, containing anisotropic temperature factors (2 pages); Table SII, containing structure factors (24 pages). Ordering information is given on any current masthead page.

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New Low-Dimensional Zinc Compounds Containing Zinc-Oxygen-Phosphorus Frameworks: Two-Layered Inorganic Phosphites and a Polymeric Organic Phosphinate

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Two new zinc phosphites have been prepared by reaction of zinc chloride with either calcium or strontium phosphite in aqueous phosphorous acid. The compounds have been characterized by single-crystal X-ray diffraction techniques. ZnCa(HPO₃)₂(H₂O)₂: P2₁/n, a = 7.131 (2) Å, b = 7.766 (2) Å, c = 14.479 (2) Å, β = 97.30 (2)°, V = 795.3 (3) Å³, Z = 4, R(F_o) = 0.045 for 1063 observations (I > 3σ(I)) and 109 variables. ZnSr(HPO₃)₂(H₂O)₂: P1̄, a = 7.728 (2) Å, b = 7.967 (2) Å, c = 7.448 (2) Å, α = 99.56 (2)°, β = 107.93 (2)°, γ = 100.51 (2)°, V = 416.6 (2) Å³, Z = 2, R(F_o) = 0.034 for 1187 observations (I > 3σ(I)) and 109 variables. Both compounds have layered structures in which the zinc atoms are tetrahedrally coordinated and the Ca or Sr atoms are 8-coordinate. In each case, the interlayer region is lined with water molecules coordinated to the alkaline-earth-metal ion. The modes in which Ca and Sr bridge the phosphite groups are different, however, resulting in layers with different topographies. These results, together with earlier work on Na⁺, K⁺, and Ba²⁺, are discussed in terms of the effect of the alkali or alkaline-earth metals on the observed structural trends. A new polymeric zinc phenylphosphinate has also been synthesized and its structure determined. Crystal data for Zn(O₂PHC₆H₅)₂: C2/c, a = 15.763 (2) Å, b = 11.162 (2) Å, c = 8.272 (2) Å, β = 109.34 (2)°, V = 1373.2 (6) Å³, Z = 4, R(F_o) = 0.047 for 480 observations (I > 3σ(I)) and 105 variables. The structure is compared with known phosphinates and phosphonates.

Introduction

As an outgrowth of our continuing interest in transition-metal phosphates with framework structures,^{1,2} we recently reported the synthesis of a novel series of zinc phosphites containing alkali or alkaline-earth metals.³ Each of the compounds prepared (containing Na⁺, K⁺, and Ba²⁺, respectively) had a different structure that was highly dependent on the coordination requirements of

the alkali- or alkaline-earth-metal ion. In order to further examine the structural trends in these materials, we have prepared and characterized two new zinc phosphites of calcium and strontium. In addition, we have been exploring the chemistry of organic derivatives⁴⁻⁷ of layered transition-metal phosphates and recently

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