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Synthesis and Characterization of Novel Quasiaromatic Zinc–Sulfur Aggregates and Related Zinc–Oxygen Complexes

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Abstract: The synthesis and structural characterization of several alkylzinc alkoxides, aryloxides, and thiolates, many of which have unusual structures, are described. The compounds were synthesized by the simple reaction of the zinc dialkyl, ZnR_2 ($R = CH_2SiMe_3$), with 1 equiv of an alcohol or thiol to afford the products $[RZnOR']_n$ ($n = 2$, $R' = 2,6\text{-}i\text{-}Pr_2C_6H_3$ (**1**) or $2,4,6\text{-}t\text{-}Bu_3C_6H_2$ (**2**); $n = 4$, R' = 1-adamantyl (1-Ad) (**3**) or *t*-Bu (**4**)), or $[RZnSR'']_n$ ($n = 2$, $R'' = -CPh_3$ (**5**); $n = 3$, $R'' = 2,4,6\text{-}i\text{-}Pr_3C_6H_2$ (**6**) or $2,4,6\text{-}t\text{-}Bu_3C_6H_2$ (**7**)). The aggregate $[Zn_3\{O(2,6\text{-}i\text{-}Pr_2C_6H_3)\}_4R_2]$ (**8**) was also obtained. All compounds were characterized by C and H elemental analysis, by ^1H NMR spectroscopy, and, with the exception of **4** (which was only partially structurally characterized), by X-ray crystallography. The main feature of interest in these compounds derives from their structures. For example, the $[RZnSR'']_3$ trimers **6** and **7** possess flattened, almost planar, $Zn_3S_3C_6$ arrays and may be considered to be isoelectronic to the recently synthesized quasiaromatic $Al_3N_3C_6$, $Ge_3N_3C_3$, or $B_3P_3C_6$ ring systems. In contrast, the "antiaromatic" dimer, $[RZnSCPh_3]_2$ (**5**), possesses very pyramidal coordination at the sulfur centers and little apparent delocalization. Attempts to crystallize a compound having a planar $Zn_3O_3C_6$ array analogous to **6** and **7** have not been successful to date. The reaction between ZnR_2 and HOR′ gave either dimers or tetramers that feature Zn_2O_2 or Zn_4O_4 cores as exemplified by compounds **1**–**4**. An alkylzinc alkoxide product, **8**, featuring three zinc centers was obtained when the stoichiometry of the reactants was changed slightly. However, the product did not possess a six-membered-ring structure. Instead, an almost linear Zn_3 array, in which the zinc centers are linked by bridging –OR′ groups and each terminal zinc is also bound to one alkyl group, was obtained.

Some recent work in this laboratory has concerned the synthesis and structural characterization of novel inorganic quasiaromatic ring systems.[1–4] The rings have featured planar, hexagonal cyclic arrays of boron–phosphorus,[2] aluminum–nitrogen,[3] and germanium–nitrogen[4] atoms, whose ring bonding bears a resemblance to the π-system of benzene. These, and a selection of related, isoelectronic cyclic species, are illustrated schematically in Figure 1. Obviously, the rings are expected to display a very wide variation in their degrees of delocalization. For example, if benzene is considered to have perfect delocalization of its π-electrons, then borazine $(HBNH)_3$[5] or the unstable silabenzene rings $[Si_nC_{6-n}H_6]$[6] (n = 1, 2, or 6) are expected to have significantly less delocalization owing to the polarity or the size differences between the atom pairs within the rings. Examples of the ring systems that have been prepared and structurally characterized recently are species such as $[MesBP(C_6H_{11})]_3$,[2] $[MeAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$,[3] or $[GeN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$.[4] In addition, the most recent calculations have shown that the amount of delocalization in these rings is, among other factors, very dependent on the polarity of the ring bonds.[1–7] A surprising feature of the theoretical data is that quasiaromatic rings involving heavier atoms may, in some cases, display greater energies of delocalization than their lighter congeners.[7] For example $(HBPH)_3$ was calculated[7] to have marginally greater energy of delocalization (12.7 vs 11.1 kcal mol^{-1}) than $(HBNH)_3$. On the other hand, $(HAlNH)_3$ was found to possess very little delocalization—only 1.9 kcal mol^{-1}. One of the reasons for the apparent anomaly of the $(HBPH)_3$ ring may be that the BP pair is significantly less polar than BN. Extension of this reasoning has led to a search for other new quasiaromatic rings comprised of pairs of atoms with relatively low polarity. Another objective has been the synthesis of six-membered rings comprised of alternating pairs of atoms from the main group 2 and 6 elements which form part of the isoelectronic series illustrated in Figure 1. These two objectives are combined in the study of the related $(RZnOR')_n$ and $(RZnSR'')_n$ species.

In this paper the synthesis of new examples of quasiaromatic six-membered rings is reported. These rings, of formula $[RZnSR'']_3$, are comprised of zinc and sulfur atoms and possess nearly planar geometries that are consistent with the existence of some delocalization. A four-membered-ring species, $[RZnSCPh_3]_2$, which does not possess planar sulfur centers is also described. In addition, the more polar zinc–oxygen system $[RZnOR']_n$ was investigated in order to study their relationship to the zinc–sulfur ring compounds.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of N_2 in a Vacuum Atmospheres HE 43-2 drybox or by using modified Schlenk techniques. Solvents were freshly distilled from Na/K alloy and degassed twice before use. The compounds $Zn(CH_2SiMe_3)_2$[8] (henceforth ZnR_2), $HS(2,4,6\text{-}i\text{-}Pr_3C_6H_2)$,[9] and $HS(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$[10] were synthesized by literature procedures. The compounds $HO(2,6\text{-}i\text{-}Pr_2C_6H_3)$, HO(1-Ad), $HO(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$, HO(*t*-Bu), and $HSCPh_3$ were purchased from commercial sources and purified by sublimation, HO(1-Ad), distillation, $HO(2,6\text{-}i\text{-}Pr_2C_6H_3)$, or recrystallization from pentane, $HO(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$, or diethyl ether, $HSCPh_3$. ^1H NMR spectra were obtained at 300 MHz in C_6D_6 solvent on a GE QE-300 spectrometer and are referenced to a tetramethylsilane (TMS) standard. All compounds gave satisfactory C and H analyses. The yields were almost quantitative for each reaction.

$[RZnO(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2$ (1). ZnR_2 (0.5 g, 2.2 mmol) and $HO(2,6\text{-}i\text{-}Pr_2C_6H_3)$ (0.4 mL, 2.16 mmol) were mixed with rapid stirring. A gas (TMS) was evolved immediately, and a white solid was also deposited with a concomitant production of heat. After 5 min the remaining volatile material was removed under reduced pressure. Colorless plates of **1** were obtained upon recrystallization from about 10 mL of hexane at −25 °C: mp 115–117 °C; δ ^1H NMR 7.09 (*m*-H), 6.97 (*p*-H), 3.58 (*o*-CH), 1.34 (*o*-CH_3), −0.12 ($SiMe_3$), −0.53 (CH_2).

$[RZnO(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_2$ (2). 2,4,6-Tri-*tert*-butylphenol (0.52 g, 2 mmol) and 0.5 g (2.2 mmol) of bis((trimethylsilyl)methyl)zinc were combined in 50 mL of toluene and refluxed for 1 h. The volatile materials were removed under reduced pressure, and the residue was redissolved in 10 mL of pentane. Crystals of **2** were obtained by cooling this solution in a −25 °C freezer overnight: mp 248–252 °C; δ ^1H NMR 7.48

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(1) Power, P. P. *J. Organomet. Chem.* **1991**, *400*, 49.

(2) Dias, H. V. R.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1270. Dias, H. V. R.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 144.

(3) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699.

(4) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1990**, *112*, 3660.

(5) Stock, A.; Pohland, E. *Chem. Ber.* **1926**, *59*, 2215.

(6) Sax, A.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 651.

(7) Fink, W. H.; Richards, J. *J. Am. Chem. Soc.* Following in this issue.

(8) Moorhouse, S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1974**, 2187.

(9) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1533.

(10) Rundel, W. *Chem. Ber.* **1968**, *101*, 2956.

0002-7863/91/1513-3379$02.50/0

Table I. Abridged Summary of Data Collection, Structure Solution, and Refinement for **1**–**3** and **5**–**8**

	1	**2**	**3**	**5**	**6**	**7**	**8**
formula	$C_{32}H_{56}O_2Si_2Zn_2$	$C_{74}H_{80}O_2Si_2Zn_2$	$C_{56}H_{104}O_4Si_4Zn_4$	$C_{46}H_{52}Si_2S_2Zn_2$	$C_{62}H_{102}Si_3S_3Zn_3$	$C_{66}H_{120}Si_3S_3Zn_3$	$C_{59}H_{96}O_4Si_2Zn_3$
fw	659.73	828.06	1215.31	855.90	1224.0	1290.0	1121.73
T, K	130	130	130	130	130	130	130
cryst system	orthorhombic	monoclinic	tetragonal	triclinic	monoclinic	triclinic	triclinic
a, Å	8.797 (6)	9.344 (2)	21.307 (10)	9.396 (3)	18.135 (8)	10.376 (3)	12.229 (3)
b, Å	19.016 (17)	18.872 (4)		10.609 (4)	13.035 (5)	15.543 (6)	12.465 (3)
c, Å	22.437 (18)	13.056 (5)	13.365 (8)	11.765 (4)	30.923 (10)	26.475 (7)	22.161 (5)
α, deg				113.88 (3)		103.04 (3)	103.97 (2)
β, deg		92.38 (3)		94.15 (3)	96.34 (3)	97.35 (2)	90.23 (2)
γ, deg				92.89 (3)		101.15 (1)	106.93 (2)
V, Å^3	3753 (2)	2300 (1)	6067 (5)	1065.4 (6)	7265 (4)	4015 (2)	3126 (1)
space group	$P2_12_12_1$	$P2_1/a$	$I4_1/a$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Z	4	2	4	1	4	2	2
$D_{(calc)}$, g/cm^3	1.17	1.20	1.33	1.33	1.12	1.082	1.19
λ	Mo Kα	Mo Kα	Mo Kα	Cu Kα	Cu Kα	Cu Kα	Mo Kα
linear abs coeff	13.9 cm^{-1}	11.49 cm^{-1}	17.2 cm^{-1}	3.08 mm^{-1}	1.17 mm^{-1}	2.443 mm^{-1}	12.4 cm^{-1}
2θ range, deg	0–45	0–45	0–50	0–115	0–115	0–115	0–50
obs refl	1530 [$I > 2\sigma(I)$]	1980 [$I > 2\sigma(I)$]	2019 [$I > 2\sigma(I)$]	2647 [$I > 2\sigma(I)$]	8400 [$I > 2\sigma(I)$]	8614 [$I > 2\sigma(I)$]	7817 [$I > 2\sigma(I)$]
no. of variables	215	152	163	235	640	681	682
R, R_w	0.059, 0.054	0.056, 0.041	0.038, 0.039	0.054, 0.064	0.067, 0.075	0.084, 0.095	0.041, 0.041

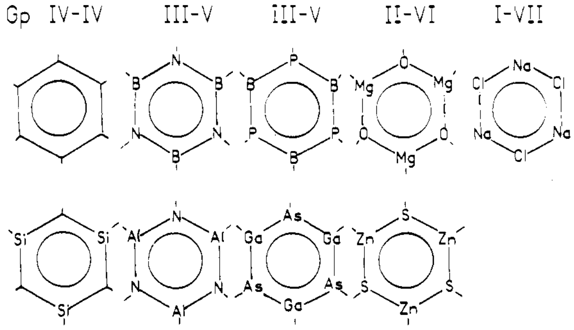

Figure 1. Schematic diagrams of some probable and improbable delocalized ring systems.

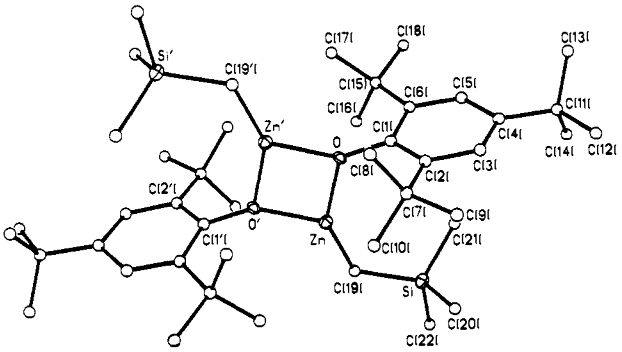

Figure 2. Computer-generated plot of the structure of **2**. Zinc and silicon are shown as 45% probability thermal ellipsoids and carbon and oxygen are shown as spheres of arbitrary radius. H atoms have been omitted for clarity.

(*m*-H), 1.67 (*o*-*t*-Bu), 1.36 (*p*-*t*-Bu), −0.14 ($SiMe_3$), −0.55 (CH_2).

[RZnO(1-Ad)]$_4$ (3). 1-Adamantanol (0.30 g, 2 mmol) dissolved in 50 mL of hexane was added to 0.50 g (2.2 mmol) of bis((trimethylsilyl)methyl)zinc and heated slightly. After 15 min of stirring, a white precipitate formed, which was stirred for an additional 1 h. The mixture was then allowed to settle and the supernatant liquid was removed via cannula. The precipitate was recrystallized from boiling toluene (10 mL). On cooling the solution to room temperature, **1** was recovered as colorless crystals: Mp >200 °C dec; δ ^{1}H NMR 2.11, 1.61, 1.44 (adamantyl), 0.30 ($SiMe_3$), −0.33 (CH_2).

[RZnO(*t*-Bu)]$_4$ (4). *tert*-Butyl alcohol (0.14 g, 2 mmol) was added dropwise to an equimolar amount of neat zinc dialkyl. This afforded a reaction which was accompanied by the evolution of heat and gas (TMS) and the formation of a white crystalline solid. The solid was dissolved in hexane (15 mL) and cooled to −20 °C to give colorless crystals of **4**: mp 144–152 °C. The tetrameric structure of this compound was established by X-ray crystallography which showed the presence of a Zn_4O_4 core. Disorder problems among the (trimethylsilyl)methyl groups did not permit a satisfactory refinement of the data.

[RZnSCPh$_3$]$_2$ (5). Triphenylmethanethiol (0.55 g, 2 mmol) dissolved in 30 mL of a hexane–toluene 1:1 mixture was added dropwise to 0.5 g (2.2 mmol) of neat zinc dialkyl and the mixture was stirred for 30 min. The volatile materials were removed under reduced pressure and the residue was redissolved in 5 mL of toluene. Upon addition of 15 mL of hexane and cooling to −20 °C overnight, colorless crystals of **5** were obtained: mp 120–124 °C; δ ^{1}H NMR 7.44 (*o*-H), 7.07 (*m*-H), 6.96 (*p*-H), 0.09 ($SiMe_3$), −1.02 (CH_2).

[RZnS(2,4,6-*i*-Pr$_3$C$_6$H$_2$)]$_3$ (6). Triisopropylthiophenol (0.71 g, 3 mmol) was added dropwise to an equimolar amount of zinc dialkyl with results similar to those described for the preparation of **1** and **4**. In this case, the resultant solid was redissolved in 2 mL of pentane. Cooling for 2 days in a −20 °C freezer gave a nearly quantitative yield of colorless plates of **6**: mp 110–118 °C dec; δ ^{1}H NMR 7.09 (*m*-H), 4.09 (*o*-CH), 2.72 (*p*-CH), 1.39 (*o*-CH_3), 1.16 (*p*-CH_3), −0.25 ($SiMe_3$), −0.55 (CH_2).

[RZnS(2,4,6-*t*-Bu$_3$C$_6$H$_2$)]$_3$ (7). Tri-*tert*-butylthiophenol (0.56 g, 2 mmol) was dissolved in 10 mL of pentane and added dropwise to 0.5 g (2.2 mmol) of neat bis((trimethylsilyl)methyl)zinc and the mixture was stirred for 2 h. The volatile materials were removed, and the residue was redissolved in 4 mL of pentane. Cooling to −20 °C afforded colorless needles of **7**: mp >200 °C dec; δ ^{1}H NMR 7.56 (*m*-H), 1.81 (*o*-*t*-Bu), 1.28 (*p*-*t*-Bu), −0.17 ($SiMe_3$), −0.65 (CH_2).

[Zn$_3${O(2,6-*i*-Pr$_2$C$_6$H$_3$)}$_4$R$_2$] (8). Bis((trimethylsilyl)methyl)zinc (0.72 g, 3 mmol) was added dropwise to 0.72 g (4 mmol) of diisopropylphenol in 40 mL of hexane. The solution was refluxed for 10 min and then the volume was reduced to ca. 5 mL and the solution cooled to −20 °C to yield colorless parallellepipeds of **8**: mp 154–158 °C.

X-ray Data Collection and Solutions and Refinement of Structures. Compounds **1**–**3** and **8** were collected with the use of a Syntex P2$_1$ diffractometer equipped with a graphite monochromator and a locally modified LT-1 device for low-temperature work. Crystallographic programs used were those of SHELXTL, Version 5, installed on a Data General Eclipse computer. Compounds **5**–**7** were collected with the use of a Siemens R3m/V diffractometer equipped with a graphite monochromator and a locally modified Enraf Nonius universal low-temperature device for low-temperature work. Crystallographic programs used for the structure solutions and refinements were those of SHELXTL PLUS installed on a MicroVax 3200 computer. Scattering factors were from common sources.[11] An absorption correction was applied with use of the method described in ref 12. All compounds were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fiber with silicone grease, and immediately placed in the low-temperature nitrogen cold stream. Table I summarizes the crystal data and refinement for **1**–**3** and **5**–**8**. Important bond distances and angles for **1**–**3** and **8** and **5**–**7** are presented in Tables II and III. Full details are provided in the supplementary material.

Results and Discussion

Structural Descriptions. [RZnO(2,6-*i*-Pr$_2$C$_6$H$_3$)]$_2$ (1) and [RZnO(2,4,6-*t*-Bu$_3$C$_6$H$_2$)]$_2$ (2). The structures of compounds **1** and **2** may be illustrated by the thermal ellipsoidal drawing of

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(11) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(12) Program XABS: Hope, H.; Moezzi, B. University of California, Davis. The program obtains an absorption tensor from $F_o - F_c$ differences. Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987.

Table II. Selected Bond Distances (Å) and Angles (deg) for **1**–**3** and **8**

		$[RZnO(2,6\text{-}i\text{-}Pr_2C_6H_3)]_2$ (**1**)			
Zn(1)–O(1)	1.975 (11)	Zn(2)–O(2)	1.940 (11)	Zn(2)–C(5)	1.923 (17)
Zn(1)–O(2)	1.944 (10)	Zn(1)–C(1)	1.961 (18)	O(1)–C(9)	1.397 (18)
Zn(2)–O(1)	1.934 (10)			O(2)–C(21)	1.420 (19)
O(1)–Zn(1)–O(2)	79.2 (4)	Zn(1)–O(2)–Zn(2)	100.7 (4)		
O(1)–Zn(1)–C(1)	137.2 (6)	Zn(1)–O(2)–C(21)	130.1 (9)		
O(2)–Zn(1)–C(1)	143.6 (6)	Zn(2)–O(2)–C(21)	128.2 (9)		
Zn(1)–C(1)–Si(1)	114.5 (9)	O(1)–Zn(2)–O(2)	80.3 (4)		
Zn(1)–O(1)–Zn(2)	99.8 (5)	O(1)–Zn(2)–C(5)	143.4 (6)		
Zn(1)–O(1)–C(9)	128.5 (9)	O(2)–Zn(2)–C(5)	136.2 (6)		
Zn(2)–O(1)–C(9)	129.8 (10)	Zn(2)–C(5)–Si(2)	115.8 (9)		
		$[RZnO(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_2$ (**2**)			
Zn–O	1.958 (4)	Zn–C(19)	1.948 (6)		
Zn–O′	2.021 (4)	O–C(4)	1.387 (7)		
O–Zn–O′	81.6 (2)	Zn–O–C(1)	118.3 (3)		
O–Zn–C(19)	144.4 (2)	C(1)–O–Zn′	143.0 (4)		
C(19)–Zn–O′	133.8 (2)	Zn–C(19)–Si	122.7 (3)		
Zn–O–Zn′	98.4 (2)				
		$[RZnO(1\text{-}Ad)]_4$ (**3**)			
Zn–O	2.098 (2)	Zn–C(1)	1.988 (4)		
Zn–O′	2.048 (2)	O–C(5)	1.458 (4)		
Zn–O″	2.121 (3)				
O–Zn–O′	83.9 (1)	Zn–O–Zn′	97.5 (1)		
O–Zn–O″	82.2 (1)	Zn′–O–Zn″	97.7 (1)		
O′–Zn–O″	82.0 (1)	C(5)–O–Zn	122.6 (1)		
C(1)–Zn–O	121.3 (1)	C(5)–O–Zn′	117.0 (2)		
C(1)–Zn–O′	143.6 (1)	C(5)–O–Zn″	121.0 (2)		
C(1)–Zn–O″	124.1 (1)	Zn–C(1)–Si	131.9 (2)		
Zn–O–Zn′	95.3 (1)				
		$[Zn_3\{O(2,6\text{-}i\text{-}Pr_2C_6H_3)\}_4R_2]$ (**8**)			
Zn(1)–O(1)	1.950 (2)	Zn(2)–O(3)	1.980 (2)	O(1)–C(5)	1.390 (4)
Zn(1)–O(2)	1.968 (2)	Zn(2)–O(4)	1.955 (2)	O(2)–C(17)	1.378 (4)
Zn(1)–C(1)	1.933 (3)	Zn(3)–O(3)	1.950 (2)	O(3)–C(29)	1.383 (4)
Zn(2)–O(1)	1.985 (2)	Zn(3)–O(4)	1.969 (2)	O(4)–C(41)	1.383 (4)
Zn(2)–O(2)	1.954 (2)	Zn(3)–C(53)	1.948 (3)		
O(1)–Zn(1)–C(1)	147.1 (1)	O(2)–Zn(2)–O(4)	141.6 (1)		
O(2)–Zn(1)–C(1)	132.3 (1)	O(3)–Zn(2)–O(4)	80.1 (1)		
O(1)–Zn(1)–O(2)	80.3 (1)	Zn(2)–O(3)–C(29)	139.2 (2)		
Zn(1)–O(1)–C(5)	118.3 (2)	C(29)–C(3)–Zn(3)	120.5 (2)		
Zn(1)–O(1)–C(5)	99.6 (1)	Zn(2)–O(3)–Zn(3)	100.0 (1)		
C(5)–O(1)–Zn(2)	140.2 (2)	Zn(2)–O(4)–C(41)	136.9 (2)		
Zn(1)–O(2)–C(17)	120.4 (2)	C(41)–O(4)–Zn(3)	121.6 (2)		
Zn(1)–O(2)–Zn(2)	100.1 (1)	Zn(2)–O(4)–Zn(3)	100.2 (1)		
C(17)–O(2)–Zn(2)	139.2 (2)	O(3)–Zn(3)–O(4)	80.1 (1)		
O(1)–Zn(2)–O(2)	79.8 (1)	O(3)–Zn(3)–C(53)	145.7 (1)		
O(1)–Zn(2)–C(3)	145.8 (1)	O(4)–Zn(3)–C(53)	134.1 (1)		
O(1)–Zn(2)–O(4)	114.3 (1)	Zn(1)–C(1)–Si(1)	121.1 (2)		
O(2)–Zn(2)–O(3)	109.2 (1)	Zn(3)–C(53)–Si(2)	121.2 (2)		

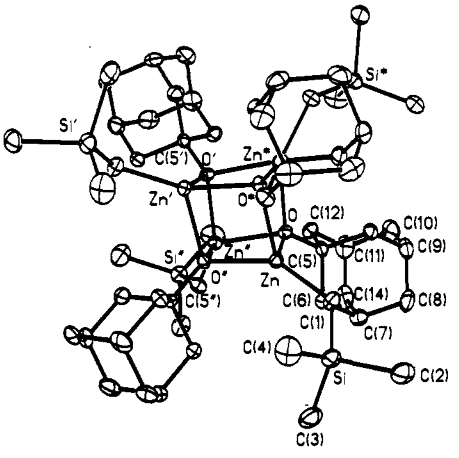

Figure 3. Computer-generated plot of the structure of **3** (50% ellipsoids). H atoms have been omitted for clarity.

Table III. Bond Lengths (Å) and Angles (deg) for Compounds **5**–**7**

		$[RZnSCPh_3]_2$ (**5**)			
Zn–S	2.381 (1)	Zn–SA	2.416 (1)		
Zn–C(1)	1.976 (4)	S–C(5)	1.878 (4)		
S–Zn–C(1)	135.1 (1)	Zn–S–C(5)	103.5 (1)		
S–Zn–SA	96.8 (1)	Zn–S–ZnA	83.2 (1)		
C(1)–Zn–SA	127.1 (1)	C(5)–S–ZnA	98.9 (1)		
		$[RZnS(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]_3$ (**6**)			
Zn(1)–S(1)	2.317 (2)	Zn(2)–S(3)	2.327 (2)	Zn(3)–C(9)	1.956 (6)
Zn(1)–S(2)	2.289 (2)	Zn(2)–C(5)	1.957 (7)	S(1)–C(13)	1.797 (6)
Zn(1)–C(1)	1.957 (6)	Zn(3)–S(2)	2.324 (2)	S(2)–C(28)	1.796 (6)
Zn(2)–S(1)	2.298 (2)	Zn(3)–S(3)	2.294 (2)	S(3)–C(43)	1.786 (6)
S(1)–Zn(1)–S(2)	103.1 (1)	Zn(2)–S(1)–C(13)	106.8 (2)		
S(1)–Zn(1)–C(1)	123.1 (2)	Zn(1)–S(2)–Zn(3)	130.2 (1)		
S(2)–Zn(1)–C(1)	132.7 (2)	Zn(1)–S(2)–C(28)	107.9 (2)		
S(1)–Zn(2)–S(3)	101.6 (1)	Zn(3)–S(2)–C(28)	107.4 (2)		
S(1)–Zn(2)–C(5)	136.7 (2)	Zn(2)–S(3)–Zn(3)	131.8 (1)		
S(3)–Zn(2)–C(5)	121.3 (2)	Zn(2)–S(3)–C(43)	108.0 (2)		
S(2)–Zn(3)–S(3)	104.1 (1)	Zn(3)–S(3)–C(43)	108.0 (2)		
S(2)–Zn(3)–S(3)	104.1 (1)	Zn(1)–C(1)–Si(1)	111.5 (3)		
S(2)–Zn(3)–C(9)	121.4 (2)	Zn(2)–C(5)–Si(2)	118.4 (4)		
S(3)–Zn(3)–C(9)	134.6 (2)	Zn(3)–C(9)–Si(3)	118.4 (3)		
Zn(1)–S(1)–Zn(2)	129.0 (1)				
Zn(1)–S(1)–C(13)	102.1 (2)				
		$[RZnS(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_3$ (**7**)			
Zn(1)–S(1)	2.325 (2)	Zn(2)–S(3)	2.356 (3)	Zn(3)–C(9)	1.954 (10)
Zn(1)–S(2)	2.311 (2)	Zn(2)–C(5)	1.950 (7)	S(1)–C(13)	1.789 (8)
Zn(1)–C(1)	1.966 (7)	Zn(3)–S(2)	2.372 (2)	S(2)–C(31)	1.802 (8)
Zn(2)–S(1)	2.316 (2)	Zn(3)–S(3)	2.291 (2)	S(3)–C(49)	1.812 (6)
S(1)–Zn(1)–S(2)	95.4 (1)	Zn(2)–S(1)–C(13)	102.1 (2)		
S(1)–Zn(1)–C(1)	139.6 (3)	Zn(1)–S(2)–Zn(3)	145.0 (1)		
S(2)–Zn(1)–C(1)	125.0 (3)	Zn(1)–S(2)–C(31)	114.0 (2)		
S(1)–Zn(2)–S(3)	105.0 (1)	Zn(3)–S(2)–C(31)	99.5 (2)		
S(1)–Zn(2)–C(5)	135.0 (2)	Zn(2)–S(3)–Zn(3)	133.9 (1)		
S(3)–Zn(2)–C(5)	119.3 (2)	Zn(2)–S(3)–C(49)	118.1 (3)		
S(2)–Zn(3)–S(3)	99.0 (1)	Zn(3)–S(3)–C(49)	105.3 (3)		
S(2)–Zn(3)–C(9)	114.0 (2)	Zn(1)–C(1)–Si(1)	121.9 (5)		
S(3)–Zn(3)–C(9)	147.0 (2)	Zn(2)–C(5)–Si(2)	128.1 (4)		
Zn(1)–S(1)–Zn(2)	138.0 (1)	Zn(3)–C(9)–Si(3)	125.1 (5)		
Zn(1)–S(1)–C(13)	113.0 (2)				

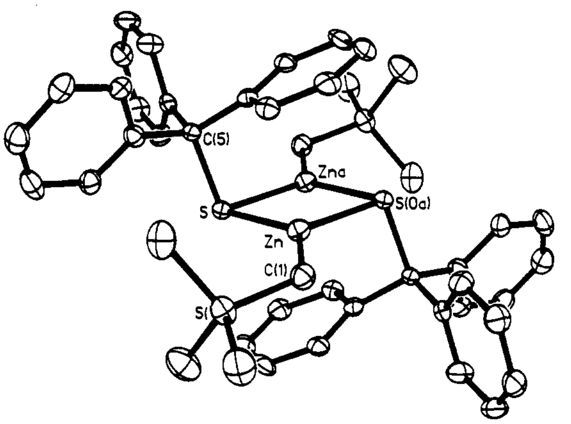

Figure 4. Computer-generated plot of the structure of **5** (50% ellipsoids). H atoms have been omitted for clarity.

2 in Figure 2. Both **1** and **2** are formed by the dimerization, through aryloxo bridges, of the alkylzinc aryloxide monomers. This results in the formation of a planar Zn_2O_2 core. The geometries at the zinc and oxygen centers in both compounds are also planar and the Zn–C bond lengths are very similar in each compound: 1.944 Å in **1** and 1.948 Å in **2**. The Zn–O distances in **1**, which average 1.948 Å, are uniform, whereas the Zn–O distances in **2** are asymmetric and have the values of 1.958 (4) and 2.021 (4) Å. The remaining interatomic distances within the ligands are unremarkable and fall within normal ranges.

$[RZnO(1\text{-}Ad)]_4$ (3). The structure of **3** is illustrated in Figure 3. It consists of well-separated tetramers of high symmetry that possess two mutually perpendicular, crystallographically imposed, 2-fold rotation axes per molecular unit. The main structural feature of **3** is the distorted Zn_4O_4 cubane core. Both Zn and O possess highly distorted tetrahedral coordination. The angles within the cube average 82.7 (8)° at Zn and 95.9 (8)° at O. The external angles, 129.7 (12.1)° at Zn and 120.2 (2.9)° at O, are correspondingly higher. Zinc–oxygen bond lengths in **3** average 2.09 (3) Å and vary from 2.048 to 2.121 Å.

$[RZnSCPh_3]_2$ (5). The structure of **5** is shown in Figure 4. The dimeric stoichiometry bears a superficial resemblance to that observed in **1** and **2**. The molecule possesses a center of symmetry and thus planarity is required for the Zn_2S_2 array. In this

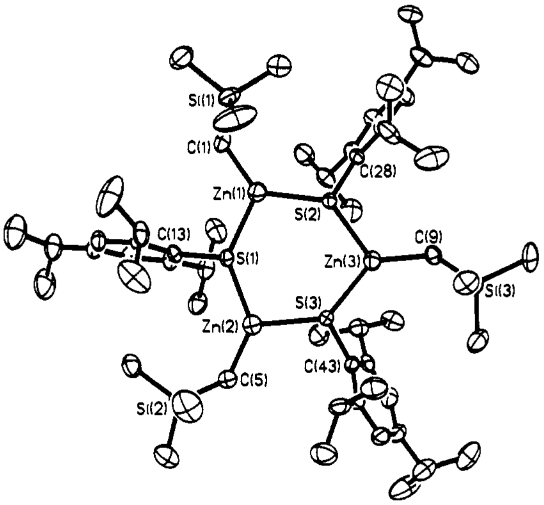

Figure 5. Computer-generated plot of the structure of **6** (50% ellipsoids). H atoms have been omitted for clarity.

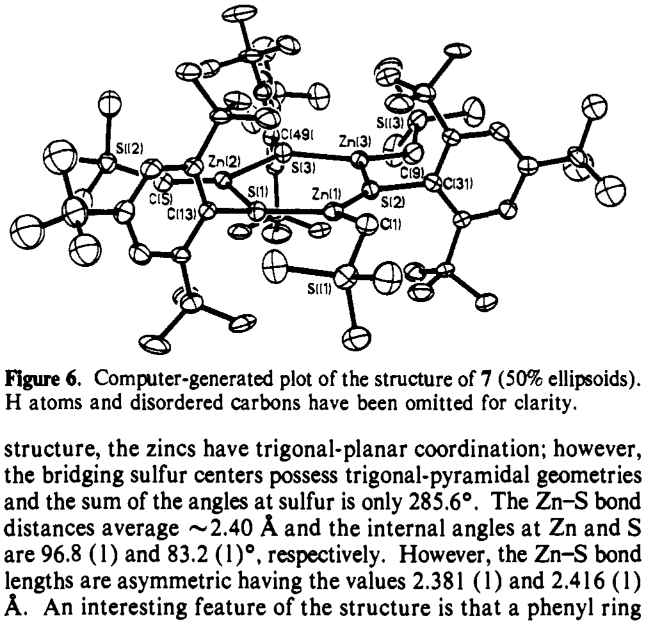

Figure 6. Computer-generated plot of the structure of **7** (50% ellipsoids). H atoms and disordered carbons have been omitted for clarity.

structure, the zincs have trigonal-planar coordination; however, the bridging sulfur centers possess trigonal-pyramidal geometries and the sum of the angles at sulfur is only 285.6°. The Zn–S bond distances average ~2.40 Å and the internal angles at Zn and S are 96.8 (1) and 83.2 (1)°, respectively. However, the Zn–S bond lengths are asymmetric having the values 2.381 (1) and 2.416 (1) Å. An interesting feature of the structure is that a phenyl ring (the C(6) ring) from the $(C_6H_5)_3C$ group is oriented over the Zn_2S_2 core to form a sandwich-like arrangement of one Zn_2S_2 and two phenyl rings. In addition, the SC(5)C(6) angle, 104.2 (3)°, is about 6° smaller than the SC(5)C(12) or SC(5)C(18) angles.

$[RZnS(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]_3$ (6) and $[RZnS(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_3$ (7). The structures of **6** and **7** are formed by the trimerization, through thiolate bridges, of alkylzinc thiolate monomers. The cores of **6** and **7** consist of six-membered rings that are comprised of alternating zinc and sulfur atoms. These structures are illustrated in Figures 5 and 6. The $(Zn–S)_3$ ring in **6** has a structure that deviates from strict planarity toward a chair conformation. Each zinc and sulfur center has trigonal coordination, but whereas the Zn centers have planar geometries, the sulfurs deviate toward pyramidicty (Σ° at S (av) 343.7 (5.2)°). The mean deviation of Zn or S from the plane of the Zn_3S_3 ring is near 0.2 Å. The internal ring angles at sulfur average 130.3 (1.4)°, while at zinc the average is 102.9 (1.2)°. The Zn–S bond lengths in **6** are 2.31 Å. The ring planes of the aromatic sulfur substituents are arranged essentially perpendicular to the average plane of the $(Zn–S)_3$ ring. In **7** the $(Zn–S)_3$ ring is much closer to planarity (the mean Zn and S deviation from a calculated average plane is about 0.1 Å). The zincs remain planar, and the average sum of the angles at the sulfurs is 356.3 (2.8)°. Internal ring angles are much larger at sulfur (139.0 (5.6)°) and less obtuse at zinc (99.8 (3.9)°). The average Zn–S bond length in **7** (2.33 Å) is marginally longer than those in **6** (2.3 Å).

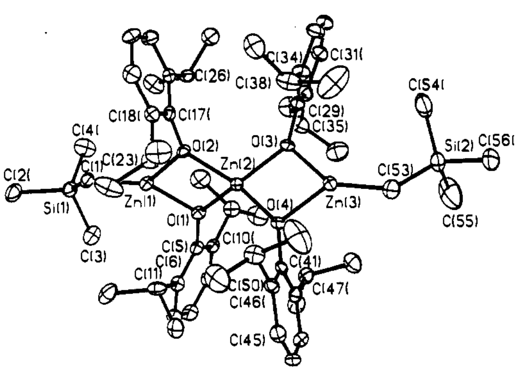

Figure 7. Computer-generated plot of the structure of **8** (50% ellipsoids). H atoms have been omitted for clarity.

$[Zn_3\{O(2,6\text{-}i\text{-}Pr_2C_6H_3)\}_4R_2]$ (8). The structure of **8** is illustrated in Figure 7. The molecular unit is comprised of an almost linear array of three zinc atoms (∠Zn··Zn··Zn = 175.7 (1)°) that are bridged by four diisopropylphenoxy groups. Each of the terminal zincs is further coordinated to one alkyl group. The central zinc has a distorted tetrahedral geometry whereas the two terminal zincs have a trigonal-planar coordination. The Zn–O bond distances in **8** average 1.969 (2) Å for the central zinc and 1.959 (2) Å for the outer zincs. The Zn–C bond lengths average 1.940 (3) Å.

Discussion

General Considerations. The syntheses of compounds **1–8** were performed with the objective of forming novel, potentially delocalized, six-membered rings comprised of the arrays $(Zn–O)_3$ and or $(Zn–S)_3$. These reactions were prompted by the recent synthesis of molecules such as $[(C_6H_{11})PBMes]_3$,[2] $[MeAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$,[3] and $[GeN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$,[4] which are isoelectronic, in terms of the valence electrons, to the corresponding zinc–oxygen or zinc–sulfur six-membered rings. Structural relationships had already been established between these classes of compounds for the higher aggregates. For example, quite a wide range of iminoalanes of formula $(RAlNR')_n$ (n = 4–16; R and R′ = alkyl or aryl group) has been known for a number of years.[13] They possess a wide variety of interesting cage structures. Moreover, their structures find a close parallel in the corresponding $(RZnER')_n$ (E = O or S) compounds. Thus, $(MeZnOMe)_4$[14] possesses a cubane structure that closely resembles that of $(PhAlNPh)_4$.[15] Similarly, the octamer $[HAlN(i\text{-}Pr)]_8$[16] has an Al–N framework that is very similar to that found for the species $[MeZnS(i\text{-}Pr)]_8$.[17] The structure of an interesting pentameric compound $[MeZnS(t\text{-}Bu)]_5$[18] has also appeared but no iminoalane counterpart with a similar Al–N framework is known at present.

The lower aggregates (n = 1–3) of the B–P, Al–N, Ga–N, and Zn–S species are interesting for a number of reasons. The major one is that multiple bonding may be observed between B and P,[19] Al or Ga and N, or Zn and S. This is exemplified by the, as yet unknown, monomers RBPR′, RAlNR′, or GeNR′ (R and R′ = alkyl or aryl) which would be expected to have B–P, Al–N, or Ge–N double or triple bonding. For dimeric and trimeric species some degree of multiple bonding is also expected. In these cases,

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(13) Cesari, M.; Cucinella, S. *The Chemistry of Inorganic Homo- and Heterocycles*; Academic Press: New York, 1982; Vol. 1, Chapter 6.

(14) Shearer, H. M. M.; Spencer, C. B. *J. Chem. Soc., Chem. Commun.* **1966**, 194. Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2046.

(15) McDonald, T. R. R.; McDonald, W. S. *Acta Crystallogr., Sect. B* **1972**, *28*, 1619.

(16) Del Piero, G.; Cesari, M.; Perego, G.; Cucinella, S.; Cerma, E. *J. Organomet. Chem.* **1977**, *129*, 289.

(17) Adamson, G. W.; Shearer, H. M. M. *J. Chem. Soc., Chem. Commun.* **1969**, 897.

(18) Adamson, G. W.; Bell, N. A.; Shearer, H. M. M. *Acta Crystallogr., Sect. B* **1982**, *B38*, 462.

(19) Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 449.

(20) (a) Frankland, E. *Jahresber. Fortschr. Chem. Verw. Theile Anderer Wiss.* **1857**, 418. (b) Butlerow, A. M. *Ibid.* **1864**, 467.

Table IV. Comparison of Radii,[a] Electronegativity,[b] and ΔH_{HDR}[c] for Benzene and Several Possible Quasiaromatic Systems

	O	N	B	P	S	Zn	Ge	Al
covalent radius, Å	0.73	0.75	0.9	1.1	1.02	1.2	1.22	1.3
electronegativity	3.44	3.04	2.04	2.19	2.58	1.65	2.01	1.61

atom-pair	Δradius	ΔEN	ΔH_{HDR},[c] kcal mol^{-1}
Al–N	0.55	1.43	1.9
Ge–N	0.47	1.03	
Zn–O	0.47	1.78	
B–N	0.15	1.00	11.1
B–P	0.20	0.15	12.7
Zn–S	0.18	0.93	
C–C	0.00	0.00	22.1

[a] Covalent radii estimated from bond lengths in: Sutton, L. Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Spec. Publ. Nos. 11 and 18; Chem. Soc. (London), 1958, 1965. See also: Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; p 258. [b] Pauling electronegativities. [c] ΔH_{HDR} = energy of the homodesmotic reaction $C_6H_6 + 3C_2H_4 \rightarrow 3C_4H_6$ or the analogous BN, AlN, or BP systems. The energy values thus calculated give an index of the stabilization and delocalization of the C_6H_6, $B_3N_3H_6$, $Al_3N_3H_6$, and $B_3P_3H_6$ ring systems. The term homodesmotic has been used to indicate that the number, hybridization, and bonding of the atoms on each side of the equation are the same. The energy difference is then taken to be the result of the delocalization. For further discussion see ref 7.

if a two-dimensional structure is assumed, both the metal and the heteroatom will be three coordinate and also have adjacent empty and filled p-orbitals arranged in either a four- or six-membered ring. This is illustrated by the case of the "alumazene" and "germanazene" molecules, $(MeAlNAr)_3$[3] and $(GeNAr)_3$[4] (Ar = 2,6-*i*-$Pr_2C_6H_3$), or the boron–phosphorus ring species $((C_6H_{11})PBMes)_3$[2] which possess planar $(Al–N)_3$, $(Ge–N)_3$, or $(B–P)_3$ rings and a set of six p-orbitals perpendicular to the ring plane. The obvious similarity of these rings to both benzene and borazine has given rise to speculation on the degree of delocalization within the rings. Calculations[7] have indicated that, in the case of the "alumazene" species, there is negligible delocalization; therefore it is highly probably that the "germanazene" ring is also not delocalized since the Ge–N bond is of similar polarity to Al–N. In contrast, for the isoelectronic system $B_3P_3H_6$, exemplified by the stable ring species $[(C_6H_{11})PBMes]_3$,[2] the delocalization is calculated to be greater than that of borazine.[1,7] These trends in delocalization can be traced to the polarity of the ring atom pairs and to the size match between the ring constituents. In this respect, the pair B–P is much more evenly matched than the Al–N pair in terms of both electronegativity and size. In order to maximize the ring delocalization the covalency should be kept as high as possible and the atoms should be as close as possible in size. The data in Table IV show that the Al–N and Ge–N pairs have the maximum polarity and size difference and, in the case of the $(Al–N)_3$ ring, the lowest stabilization as calculated by using a homodesmotic reaction.[7] In contrast, the borazine and the $(B–P)_3$ rings have much smaller size differences and lower polarity and have stabilization energies of about half that of benzene. An interesting feature of Table IV is the position of the Zn–S pair which has about the same size discrepancy but lower polarity than borazine. On the basis of these data the Zn–S ring trimer should have a delocalization energy that falls between those of borazine and the $(HAlNH)_3$ species. On the other hand, a very ionic and non-delocalized structure is predicted for the corresponding Zn–O ring system.

Syntheses. The synthesis of compounds **1**–**8** was effected with use of the alkane elimination process

$$ZnR_2 + R'EH \rightarrow (RZnER')_n + RH$$

$$(E = O \text{ or } S)$$

which is one of the oldest known classes of organometallic reactions.[19] This reaction proceeds, either in hydrocarbon solvent or neat solution, to give essentially quantitative yields of the desired products. The volatility of the TMS side product serves to drive the equilibrium to the right. The formation or relatively strong Zn–E and C–H bonds, at the expense of breaking the E–H and a relatively weak Zn–C bond, ensures favorable reaction energetics. The formation of aggregates, though not favored entropically, may also favor the reaction. All the products, except **3**, are soluble in hydrocarbon solvents such as hexane. The low solubility of **3** in most hydrocarbons (with the exception of refluxing toluene) is, to some degree, expected since 1-adamantanol is also only sparingly soluble in these solvents.

Zn–O Compounds. The structures of the alkylzinc alkoxide or aryloxide compounds **1**–**3** and **8** follow fairly well established patterns that can be rationalized mainly on the basis of steric considerations. The cubane Zn_4O_4 core observed in the tetrameric species $[RZnO(1\text{-}Ad)]_4$ (**3**) is very close to the structures observed for cubane species $[MeZnOMe]_4$[14] (**9**) and for the compound $[Zn(OMe)_2\cdot(EtZnOMe)_6]$ (**10**),[21] which possesses two Zn_4O_4 cubane units with a common corner at a Zn. The metric features in **3** are the same, within experimental error, as those observed in **9**. The only remarkable aspect of the structure of **3** is its high degree of aggregation in view of the fairly large 1-adamantyl and CH_2SiMe_3 substituents.

Increasing the size of the oxygen substituents to 2,6-*i*-$Pr_2C_6H_3$ and 2,4,6-*t*-$Bu_3C_6H_2$ affords the dimeric species **1** and **2**. These products may be considered to be one-half of the cubane structure observed in **3**. The lower coordination number observed at both Zn and O in these compounds results in shorter Zn–O and Zn–C bond distances. Both the zinc and oxygen centers possess planar geometries, but this is not necessarily indicative of any multiple bonding or delocalization within the Zn_2O_2 ring. The shortened distances may be explained on the basis of an increased ionic attraction between Zn and O since the number of oxygens coordinated to zinc has been decreased from three to two. The changes in hybridization of the zinc and oxygen bonding orbitals (sp^3 to sp^2) may also account for the shorter bonds. Planarity at oxygen may be readily achieved because of its very low inversion barrier. This is decreased further by the presence of two relatively electropositive zinc substituents at the oxygens. The influence of electropositive substituents on inversion barriers has been adequately established elsewhere.[21,22] The inequality of the Zn–O distances in **2** appears to indicate that a slight increase in the size of the alkyl substituent at zinc might effect its complete dissociation into monomers. The only structure comparable to **1** and **2** that has been published concerns the unusual dimer $[(Me_2PhSi)_3CZnOH]_2$.[24] In this case the Zn_2O_2 ring is also planar and the Zn–O distance is very short indeed (1.889 (9) Å). This is probably due to the increased donor strength of OH and the less stringent steric requirements of the H atom relative to the bulky aryl groups in **1** and **2**. Short Zn–O distances, which average 1.887 (7) Å in length, have also been observed in the mononuclear compound $[Zn\{O(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2(THF)_2]$.[25] In this case, however, the aryloxo group is a terminal instead of a bridging ligand, so that a somewhat shorter Zn–O bond is to be expected.

Although no trimeric ring structures were observed for the various combinations of zinc and oxygen substituents used in this work, trimeric aggregates have been reported in the solution phase.[26] For example, the species $[t\text{-}BuZnO(t\text{-}Bu)]_3$ was reported to be a trimer in benzene.[27] In addition, a six-membered (Zn_3O_3) ring of formula $[\{\eta^2\text{-}H_2B(3\text{-}t\text{-}BuPz)_2\}Zn(\mu\text{-}OH)]_3$ (Pz = pyrazolyl)

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(21) Ishimori, M.; Hagiwara, T.; Tsuruta, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1165.

(22) Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 4759.

(23) Abel, W. E.; Bhargava, S. K.; Orrell, K. G. *Prog. Inorg. Chem.* **1984**, *32*, 1.

(24) Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Robert, A. T. L.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 908.

(25) Geerts, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1986**, *25*, 1803.

(26) Boersma, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E., Stone, F. G. A., *Eds.*; Pergamon: Oxford, 1984; Vol. 2. Chapter 16, p 823.

(27) Noltes, J. G.; Boersma, J. *J. Organomet. Chem.* **1968**, *12*, 425.

has been reported recently.[28] However, this features four-coordinate Zn and ring Zn–O bonds that alternate in a short–long (1.909 vs 1.97 Å) fashion. The lack of examples, in the solid state, of six-membered-ring compounds that feature three-coordinate zinc and oxygen is therefore of some interest. It may be that the correct combination of substituents on Zn and O that would afford crystals suitable for X-ray diffraction has not yet been found. No doubt such a trimeric species will be obtained eventually. However, it is the present rarity of its occurrence, in comparison to the dimer or tetramer, that is the most striking feature. It is also notable that it is either the dimer, **1**, or the acyclic species $[Zn_3\{O(2,6\text{-}i\text{-}Pr_2C_6H_3)\}_4R_2]$ (**8**) that is formed instead of a cyclic $(ZnO)_3$ species when ZnR_2 reacts with $2,6\text{-}i\text{-}Pr_2C_6H_3OH$. No ring compound such as $[RZnO(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$, whose steric requirements are close to those of the trimer $[MeAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$ was observed. In this case it is difficult to account for the non-occurrence of the $(ZnO)_3$ ring. One explanation of the observation of trimeric ring compounds in solution may be in the fact that the molecular weight of **8**, i.e. a species of general formula $Zn_3(OR')_4R_2$, is actually very close to that of $(RZnOR')_3$ if the R and R′ groups are either the same or of similar molecular weight. Although this could account for the apparent trimeric structure of $[t\text{-}BuZnO(t\text{-}Bu)]_3$ it does not readily explain the trimeric formulation of $[EtZnOCHPh_2]_3$[29] in benzene. There is, however, a further possibility that either or both of these compounds be mixtures of dimers or tetramers in solution which could account for the trimeric formulation. Conclusive proof of the existence of alkylzinc alkoxide or aryloxide trimers still awaits a structural determination of such a compound.

Zn–S Compounds. Inspection of the data in Table IV shows that the Zn–S pair is much less polar and more closely matched in size than Zn and O. After the B–P system it is, in fact, the second least polar moiety. Although the numbers in Table IV are encouraging, there are problems in forming rings comprised of planar arrays of zinc and sulfur. The major one is the large inversion barrier at the sulfur center which is manifested in its preference for the pyramidal configuration as a μ_2-SR bridging thiolate ligand.[30,31] It is to be expected that the inversion barrier would be greatly reduced by having two, relatively electropositive, metal substituents at sulfur. ^{1}H NMR studies of the inversion barriers in μ_2-SR thiolate transition-metal complexes afford values that are generally in the range 11–15 kcal mol^{-1},[22] whereas the calculated inversion barrier in $[SH_3]^+$ is ~32 kcal mol^{-1}.[32] Nonetheless, it is a fact that, in the vast majority of cases, thiolates that bridge two metals remain pyramidal. The rare planar stereochemistry for a doubly bridging thiolate has been observed only in the complexes $[(Ph_3P)_2Cu(\mu\text{-}SAr)_2Cu(PPh_3)_2]$[33] and $[Fe_3(\mu_2\text{-}SR)_3X_6]^{3-}$[34] (X = Cl or Br). The planar sulfur in the former compound has been attributed to the high degree of steric crowding. The planarity in the latter species has not been fully explained, although it was established that it is an intrinsic property of the ring and not a result of packing arrangements. In addition, it was suggested that transannular repulsions between halides may play a role in the setting of the planar structure. The Fe–S distances (~2.35 Å) in the rings, which were structurally characterized, are not shortened in comparison to other Fe–(μ_2-SR) mean values.

The trimers **6** and **7**, in addition to having almost planar rings, bear a further resemblance to the $[Fe_3(\mu\text{-}SR)_3X_6]^{3-}$ structure[34] because of the extremely wide internal ring angles at the sulfurs. The Zn–S–Zn angles for the doubly bridging thiolates have the average values of about 130° in **6** and about 139° in **7**. These wide angles conform approximately to an established pattern that involves a relationship between the internal bridge angle (θ) on sulfur and the angle of inclination (φ) between the S–C bond and SM_2 plane.[33] The data obtained so far indicate that a bridge angle (θ) of ~140° corresponds to a φ angle of 0°, i.e. planarity at sulfur. The θ and φ values measured for **5**–**7** are provided in Table V. These indicate a somewhat similar θ–φ pattern to that previously observed. The wide θ angles observed in **7** correpond to the almost planar sulfurs and relatively low φ angle. In sharp contrast, the acute θ angle in **5** is matched by a φ angle which shows that, in this case, the S–C vector is not far from perpendicularity to the Zn_2S_2 plane.

Table V. θ and φ Angles for Compounds **5**–**7** and the Dimeric Transition-Metal Thiolates $[M(SAr)_2]_2$[36] (Ar = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$; M = Mn, Fe, Co)

	θ	φ	$\sum$° at S (bridging)[a]
5	83.2	74.5	285.6
6			
S(1)	129.00	54.6	343.7 (av)
S(2)	130.2	43.9	
S(3)	131.8	40.9	
7			
S(1)	138.0	32.5	356.3 (av)
S(2)	145.0	16.4	
S(3)	133.9	18.7	
$[M(SAr)_2]_2$			
M = Mn	93.3	36.3	340.3
M = Fe	87.2	43.2	330.8
M = Co	76.8	52.4	313.2

[a] $\sum$° at S = sum of the angles at S.

The wide angles and the flatter sulfur coordination observed in **6** and **7** may be partly explained on the basis of the high steric requirements of the aryl substituents. Yet, this can hardly be the whole story. If the steric requirements were the sole determining factor for the structures of **6** and **7** then lower aggregates such as the dimeric species **5** should be observed. Dimers are normally less sterically crowded than the trimers and their formation is the most obvious way in which steric interference could be reduced. Nonetheless, **6** and **7** remain trimeric. The Zn–S distances in **6** and **7** are 2.31 and 2.33 Å long, whereas in the dimer **5**, the Zn–S distance is about 2.4 Å in length. The shorter Zn–S distances observed in **6** and **7** may be due to rehybridization of the Zn–S bond from Zn(sp^2)–S(p) overlap to a Zn(sp^2)–S(sp^2) overlap in **6** and **7**. Significantly, in the three compounds the Zn–C distances remain fairly constant, which is in agreement with the unchanged (~sp^2) hybridization at zinc.

An alternative explanation for the shorter Zn–S distances observed in **6** and **7** involves the overlap of the remaining p orbitals on adjacent Zn and S atoms and the proposal of a quasiaromatic delocalized π-system. This hypothesis fits very well with the non-planarity of the sulfurs in the Zn_2S_2 four-membered ring in **5**. In addition, the Zn–S bonds in **5** have different lengths. The Zn_2S_2 core in **5** is, in some ways, analogous to antiaromatic cyclobutadiene. Consequently, it is not expected to delocalize to the same extent as a six-membered Zn_3S_3 ring, which is analogous to benzene. In this respect, the structure of **5**, with its pyramidal sulfur coordination, resembles the four-membered B_2P_2 ring compounds such as $(thexylBPMes)_2$[2,19] (thexyl = $-CMe_2CHMe_2$) or $[MesBP(1\text{-}Ad)]_2$[35] which also have pyramidal phosphorus centers.

The metric features of the four-membered-ring species **5** bring to mind the θ–φ correlation mentioned earlier.[33] The implication here is that a less obtuse or more acute ring angle θ at sulfur in the four-membered Zn_2S_2 ring necessarily correlates with a larger φ angle or greater pyramidicity at that sulfur center. But how true is this assertion? The data in Table V certainly support the correlation but the agreement is much less close than that seen in the data published earlier. For example, in the case of **7**, θ does indeed average ~139° but φ averages almost 22.5° and not 0°.

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(28) Gorrell, I. B.; Looney, A.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 4068.

(29) Coates, G. E.; Ridley, D. *J. Chem. Soc. A* **1966**, 1064.

(30) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.

(31) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121.

(32) Dixon, D. A.; Marynick, J. *Chem. Phys.* **1979**, *71*, 2860.

(33) Dance, I. G.; Fitzpatrick, L. J.; Scudder, M. L. *J. Chem. Soc., Chem. Commun.* **1983**, 546.

(34) Hagen, K. S.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5496. Whitener, M. A.; Bashkin, J. K.; Hagen, K. S.; Girerd, J.-J.; Gamp, E.; Edelstein, N.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 5607.

(35) Dias, H. V. R.; Pestana, D. C.; Petrie, M.; Power, P. P. *Phosphorus, Sulfur and Silicon* **1990**, *51/52*, 87.

Similarly, in **6**, θ averages 130.3° but φ is 46.5°. These values are well outside the range predicted in ref 33. Other compounds display even more dramatic deviations from that correlation. For example, in the recently synthesized dimers $[\mathrm{M(SAr)_2}]_2$ (Ar = 2,4,6-*t*-$\mathrm{Bu_3C_6H_2}$; M = Mn, Fe, or Co),[36] and θ and φ angles for the sulfurs in the $\mathrm{M_2S_2}$ cores are as follows: Mn, θ = 93.3°, φ = 36.3°; Fe, θ = 87.2°, φ = 43.2°; Co, θ = 76.8°, φ = 52.4°. These data demonstrate that θ values which differ by about 40° can have similar φ values as illustrated by compounds **6** and $[\mathrm{Fe(SAr)_2}]_2$. On the basis of these data it is not possible to argue that an acute angle within an $\mathrm{M_2S_2}$ ring necessarily implies a very pyramidal sulfur. This suggests that the sulfur centers in **5**, **6**, or **7** are not required to be either very pyramidal or nearly planar by the internal ring angle. Clearly, there is a tendency, but not a requirement, to adopt a particular sulfur geometry on the basis of the internal ring angles. In short the data allow for the possibility that some delocalization may indeed occur in the six-membered $\mathrm{Zn_3S_3}$ rings.

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Supplementary Material Available: Full tables of crystallographic data, summary of data collection and refinement, positional parameters for non-hydrogen atoms, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (57 pages); listing of observed and calculated structure factors (163 pages). Ordering information is given on any current masthead page.

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(36) Power, P. P.; Shoner, S. C. *Angew. Chem., Int. Ed. Engl.* In press.

Reactions of Trimethylaluminum or Trimethylgallium with Bulky Primary Amines: Structural Characterization of the Thermolysis Products

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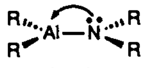
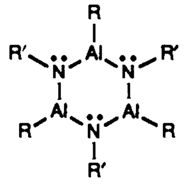
Abstract: The reaction of trimethylaluminum or trimethylgallium with bulky primary amines affords, in the first instance, dimeric aminoalkylalanes and gallanes via the elimination of 1 equiv of methane. Additional loss of methane may be accomplished by further heating of the aminometallanes to give either associated iminoalanes, orthometalated aminoalanes, or orthometalated aminogallanes. The aminometallane compounds $(\mathrm{Me_2MNHDipp})_2$ (Dipp = 2,6-*i*-$\mathrm{Pr_2}$-$\mathrm{C_6H_3}$; M = Al (**1**) or Ga (**2**)), $[\mathrm{Me_2MNH(1\text{-}Ad)}]_2$ (1-Ad = 1-adamantyl; M = Al (**3**) or Ga (**4**)), and $(\mathrm{Me_2GaNHPh})_2$ (**5**) were isolated by the treatment of $\mathrm{MMe_3}$ (M = Al or Ga) with 1 equiv of the primary amine in refluxing toluene. Each compound has been structurally and spectroscopically characterized by X-ray crystallography and/or ^{1}H, ^{13}C, and ^{27}Al NMR spectroscopy. The structures of **1–5** are all dimeric with bridging amide groups and distorted tetrahedral geometries at the metal. The aluminum and gallium compounds are invariably isomorphous. The bulky substituents present in **1** and **2** induce a remarkable 4-coordinate geometry at the nitrogen in which three of the substituents are coplanar with nitrogen and the fourth substituent occupies one of the axial positions of the pseudo-trigonal-bipyramidal arrangement. Further heating of the aluminum species **1** resulted in the isolation of the unique "alumazene" trimer $(\mathrm{MeAlNDipp})_3$ (**6**), whereas the corresponding reaction in the case of the gallium analogue **2** afforded the orthometalated species $[\overline{\mathrm{GaMe}\{\mu\text{-}\mathrm{NHC_6H_3}\text{-}i\text{-}\mathrm{Pr\text{-}6\text{-}CMeHC}}\mathrm{H_2\text{-}2}\}]_2$ (**7**). Heating $\mathrm{H_2NMes}$ with $\mathrm{AlMe_3}$ or $\mathrm{GaMe_3}$ to a higher temperature resulted in the direct isolation of the cubane species $(\mathrm{MeAlNMes})_4 \cdot 3\mathrm{C_7H_8}$ (**8**) or the orthometalated compounds $[\overline{\mathrm{GaMe}\{\mu\text{-}\mathrm{NHC_6H_2Me_2\text{-}4,6\text{-}C}}\mathrm{H_2\text{-}2}\}]_2$ (**9**) and $\mathrm{Ga}[\overline{\{\mathrm{NHC_6H_2Me_2\text{-}4,6,13,15\text{-}C}}\mathrm{H_2\text{-}2,11}\}_2\mu\text{-}\mathrm{GaMe_2}]$ (**10**). These products were also fully characterized by X-ray crystallography and/or ^{1}H, ^{13}C, and ^{27}Al NMR spectroscopy. The data reveal remarkable differences in the reactivity of aluminum and gallium. Thus, whereas the aluminum compounds eliminate a second equivalent of methane to afford the iminoalanes $(\mathrm{MeAlNR})_n$ (n = 3, 4), the gallium analogues prefer to eliminate methane by the activation of a C–H bond and subsequent cyclometalation. Compounds **3** and **4** exhibited remarkable stability and did not eliminate a second equivalent of methane below 300 °C. Compound **5** sublimed upon heating without further elimination of methane. The structure of **3** is currently the sole example of a trimeric iminoalane wherein both the aluminum and the nitrogen are three coordinate. It is, in effect, the aluminum analogue of borazine. The structure of **8** is one of a handful of structurally characterized tetrameric iminoalanes. The structures of **7**, **9**, and **10** are the first well-characterized cyclometalated gallium amide compounds.

In comparison to boron–nitrogen compounds the analogous species involving Al–N, Ga–N, In–N, or Tl–N bonds have received much less attention.[1] At present, for example, there are many classes of B–N compounds for which no heavier congeners involving the elements Al–Tl are structurally characterized. Simple examples include monomeric aminometallanes ($\mathrm{R_2MNR_2'}$, M = Al–Tl; R, R′ = alkyl or aryl), monomeric iminometallanes (RMNR′), and, until recently, aluminum analogues of borazine. These species, which may be illustrated schematically by are of interest because of the lower coordination numbers (3 and 2) of Al and N and/or the presence of adjacent nitrogen lone pairs and empty metal p-orbitals which may enable multiple bonding to occur. In fact, very few compounds that have bonding between


aminoalane


iminoalane


"alumazene"

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(1) Lappert, M. F.; Sanger, A. R.; Srivastava, R. C.; Power, P. P. *Metal and Metalloid Amides*; Ellis-Horwood: Chichester, U.K., 1980.

0002-7863/91/1513-3385$02.50/0