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Triangular Phenoxide Aggregates of Calcium, Strontium, and Barium: A Comparison

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The synthesis, solid-state structure, and solution (NMR) characterization of $[Ca_3(OPh)_5(HMPA)_6][OPh\cdot 2PhOH]$ (**1**), $Sr_3(OPh)_6(HMPA)_5$ (**2**), and $Ba_6(OPh)_{12}(TMEDA)_4$ (**3**) are reported (HMPA = $OP(NMe_2)_3$; TMEDA = $Me_2NC_2H_4NMe_2$). All share an $M_3(\mu_3\text{-}OPh)_2(\mu_2\text{-}OPh)_3$ core structure, with different distributions of anionic and neutral ligands. In the barium compound, two Ba_3 triangles are linked together by phenoxide bridges so as to make the coordination number of one metal 7, rather than 6, as observed for both the calcium and strontium compounds. All three molecules are fluxional in toluene solvent, with evidence of the hydrogen-bonded anion $[OPh\cdot 2PhOH]^-$ displacing (at equilibrium) some HMPA from the calcium compound. Thermogravimetric analysis of the calcium compound shows thermolysis processes, but no significant volatility (1 atm of He). Crystal data: for **1**, a = 17.595(18) Å, b = 34.160(35) Å, c = 18.521(19) Å, β = 94.93(3)° at −155 °C with Z = 4 in space group Cc; for **2**, a = 23.133(7) Å, b = 27.126 Å, c = 15.789(5) Å, α = 92.10(1)°, β = 96.19(1), γ = 94.36(1) at −131 °C with Z = 4 in space group $P\bar{1}$; for **3**, a = 15.049(2) Å, b = 16.775 Å, c = 24.819 Å, β = 98.80(1)° at −171 °C with Z = 4 in space group $P2_1/c$.

Introduction

A considerable amount of early research in the chemistry of groups I and IIA has been carried out in liquid ammonia.[1] HMPA, $OP(NMe_2)_3$, is an aprotic solvent with similar a Gutmann donor number[2] which has seen increasing recent application in group IA chemistry.[3] In comparison to the instability and difficulty of isolation of adducts of NH_3, those of HMPA are generally more kinetically resistant to loss of donor molecules, are easier to isolate, and offer potentially useful spectroscopic probes (e.g., ^1H, ^{13}C and ^{31}P NMR). Our interest in establishing general principles of group IIA alkoxide chemistry requires efforts to inhibit polymerization via alkoxide bridging, a common occurrence which has the consequence of complicating purification and crystallization. In order to unambiguously establish the general principles of preferred coordination number and structure, it is necessary to obtain X-ray diffraction data, and we anticipated that HMPA would prevent polymerization and provide physical properties conducive to crystallization. Finally, the polarity of HMPA is known to facilitate electron transfer (thus, the alkali metals themselves dissolve, with electron transfer, in HMPA).[4] Since synthesis of metal alkoxide from bulk metal and alcohol is a particularly attractive (redox) methodology, HMPA would seem to offer an additional advantage. On the basis of these ideas, we report here a comparative study of seemingly analogous calcium and strontium chemistries. We also report a related barium compound. The resulting compounds are revealing as much by their differences as they are by their similarities.[5]

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of argon by using Schlenk techniques. Toluene and pentane were purified by distillation from sodium benzophenone ketyl and stored under an argon atmosphere. Hexamethylphosphoramide was dried over 4-Å molecular sieves, phenol was sublimed before use, and calcium hydride and calcium and strontium metals were obtained from commercial suppliers and used without further purification. **Warning**: *Hexamethylphosphoramide is highly toxic and a suspected carcinogen*! IR spectra were recorded on a Perkin-Elmer 283 spectrometer. A Bruker AM 500 spectrometer was used to obtain ^1H, $^{13}C\{^1H\}$, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra. The ^1H, $^{13}C\{^1H\}$, and ^{13}C spectra employed C_7D_8 as the internal reference, and $^{31}P\{^1H\}$ data were referenced to 85% H_3PO_4. Elemental analyses were performed by Oneida Laboratories. Thermogravimetric analyses were performed inside a glovebox on a Du Pont 951 TGA instrument using a platinum boat, with a helium gas flow at a heating rate of 3 °C/min.

Preparation of $[Sr_3(OPh)_6(HMPA)_5]\cdot PhMe\cdot C_5H_{12}$ (2). Strontium metal granules (870 mg, 10 mmol) and PhOH (1.84 g, 20 mmol) were suspended in a mixture of HMPA (3.5 mL, 20 mmol) and toluene (8 mL). The resulting mixture was gradually brought to reflux and the temperature maintained for 3 h. During this time, the strontium metal slowly dissolved to yield a pale yellow solution. The reaction mixture was filtered hot to yield a yellow filtrate; this was subsequently layered with pentane (15 mL), and the temperature was lowered to −20 °C. After 14 days, a large crop of colorless crystals were obtained (2.93 g); a further crop was obtained after a further 2 days (2.56 g). Total yield of product: 5.49 g, 86%. IR (cm^{-1}, Nujol mull) shows the presence of coordinated HMPA. Observed mp: 127–130 °C. Microanalytical data for $Sr_3O_{11}P_5N_{15}C_{66}H_{120}$ are as follows. (The crystals were pumped under vacuum for 2 h to remove pentane and toluene present in the crystal; see X-ray study. Otherwise, a variable analysis was obtained.) Anal. Calcd: C, 46.12; H, 6.98; N, 12.23; P, 9.03; Sr, 15.37. Found: C, 46.26; H, 7.12; N, 12.41; P, 10.05; Sr, 15.07.

Single-Crystal X-ray Diffraction Study of $Sr_3(OPh)_6(HMPA)_5\cdot PhMe\cdot C_5H_{12}$. A crystal of suitable size was mounted in a nitro-

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Table I. Crystallographic Data for $Sr_3(OPh)_6[OP(NMe_2)_3]_5{\cdot}C_7H_8{\cdot}C_5H_{12}$

formula	$C_{78}H_{140}N_{15}O_{11}P_5Sr_3$	fw	2046.08
a, Å	23.133(7)	space group	$P\bar{1}$
b, Å	27.126(8)	T, °C	–133
c, Å	15.789(5)	λ, Å	0.710 69
α, deg	92.10(1)	ρ_{calcd}, g cm^{-3}	1.385
β, deg	96.19(1)	μ(Mo Kα), cm^{-1}	17.2
γ, deg	94.36(1)	R	0.1226
V, Å^3	9810.75	R_w	0.1186
Z	4		

Table II. Selected Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $Sr_3(OPh)_6[OP(NMe_2)_3]_5$

	x	y	z	$10B_{iso}$, Å^2
Sr(1A)	3404(1)	2465(1)	9509(2)	35
Sr(2A)	3019(1)	1432(1)	7903(2)	36
Sr(3A)	3885(1)	2548(1)	7349(2)	35
O(4A)	3954(8)	1912(7)	8524(12)	30(5)
O(11A)	2931(8)	2362(7)	7958(12)	25(4)
O(18A)	2854(9)	1619(8)	9391(13)	38(5)
O(25A)	3436(9)	1751(8)	6595(14)	44(6)
O(32A)	4017(8)	3040(7)	8705(13)	33(5)
O(39A)	2891(10)	3048(8)	10176(14)	49(6)
O(46A)	4033(10)	2335(8)	10781(14)	50(6)
P(47A)	4414(5)	2357(4)	11619(8)	46(3)
O(57A)	3297(9)	580(8)	7918(14)	40(5)
P(58A)	3428(5)	76(4)	8173(7)	43(3)
O(68A)	2038(10)	1097(8)	7367(15)	53(6)
P(69A)	1435(5)	995(4)	6953(7)	43(3)
O(79A)	4847(9)	2574(8)	6879(14)	42(5)
P(80A)	5292(5)	2325(4)	6410(8)	52(3)
O(90A)	3756(9)	3266(8)	6501(14)	47(6)
P(91A)	3536(5)	3747(5)	6201(8)	59(3)
Sr(1B)	1634(2)	7425(1)	6649(2)	41
Sr(2B)	1330(1)	6453(1)	8154(2)	37
Sr(3B)	498(1)	7552(1)	8105(2)	35
O(4B)	706(9)	6879(8)	7024(14)	39(5)
O(11B)	1590(9)	7388(7)	8238(13)	35(5)
O(18B)	1971(9)	6601(8)	7093(14)	41(5)
O(25B)	548(9)	6771(7)	8916(13)	39(5)
O(32B)	923(9)	8041(8)	7032(14)	46(6)
O(39B)	2483(11)	7913(9)	6381(17)	67(7)
O(46B)	1384(11)	7190(9)	5197(16)	61(7)
P(47B)	1347(5)	7072(5)	4269(9)	60(3)
O(57B)	877(10)	5603(8)	7955(14)	48(6)
P(58B)	570(5)	5099(4)	7961(8)	50(3)
O(68B)	2055(9)	6127(7)	9164(13)	37(5)
P(69B)	2585(5)	6022(4)	9742(7)	44(3)
O(79B)	–556(9)	7632(8)	7852(13)	39(5)
P(80B)	–1195(4)	7600(3)	7791(6)	31(2)
O(90B)	557(10)	8240(8)	9159(15)	50(6)
P(91B)	639(5)	8671(5)	9763(8)	57(3)

[a] Fractional coordinates are ×10^4. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Sr_3(OPh)_6[OP(NMe_2)_3]_5$

	molecule A	molecule B
Sr(1)–O(4)	2.614(20)	2.646(21)
Sr(1)–O(11)	2.569(19)	2.527(21)
Sr(1)–O(18)	2.529(22)	2.521(23)
Sr(1)–O(32)	2.500(20)	2.534(23)
Sr(1)–O(39)	2.336(26)	2.37(3)
Sr(1)–O(46)	2.401(23)	2.354(27)
Sr(2)–O(4)	2.522(20)	2.540(22)
Sr(2)–O(11)	2.545(19)	2.557(21)
Sr(2)–O(18)	2.461(23)	2.379(25)
Sr(2)–O(25)	2.526(24)	2.469(23)
Sr(2)–O(57)	2.448(22)	2.452(23)
Sr(2)–O(68)	2.429(24)	2.427(21)
Sr(3)–O(4)	2.578(20)	2.561(22)
Sr(3)–O(11)	2.524(19)	2.587(21)
Sr(3)–O(25)	2.522(23)	2.518(22)
Sr(3)–O(32)	2.458(21)	2.433(24)
Sr(3)–O(79)	2.417(23)	2.454(21)
Sr(3)–O(90)	2.424(23)	2.440(25)
Sr(1)–O(4)–Sr(2)	92.2(7)	90.8(7)
Sr(1)–O(4)–Sr(3)	91.2(6)	90.5(7)
Sr(2)–O(4)–Sr(3)	92.5(7)	92.0(7)
Sr(1)–O(11)–Sr(2)	92.7(6)	93.2(7)
Sr(1)–O(11)–Sr(3)	93.4(6)	92.7(7)
Sr(2)–O(11)–Sr(3)	93.3(6)	91.0(7)
Sr(1)–O(18)–Sr(2)	95.7(8)	97.8(9)
Sr(2)–O(25)–Sr(3)	93.8(8)	94.7(8)
Sr(1)–O(32)–Sr(3)	96.8(7)	96.3(8)
Sr(1)–O(39)–O(40)	169.1(25)	175.(3)
Sr(1)–O(46)–P(47)	168.9(15)	168.9(17)
Sr(2)–O(57)–P(58)	164.2(14)	171.4(15)
Sr(2)–O(68)–P(69)	167.8(15)	167.6(13)
Sr(3)–O(79)–P(80)	149.1(13)	169.7(14)
Sr(3)–O(90)–P(91)	160.2(15)	175.0(15)

gen atmosphere glovebag using silicone grease and was then transferred to a goniostat where it was cooled to –133 °C for characterization and data collection (Table I). A systematic search of a limited hemisphere of reciprocal space revealed no symmetry or systematic absences. An initial choice of space group $P\bar{1}$ was confirmed by the solution of the structure. Because of the unusually large number of unique data ($6° \leq 2\theta \leq 40°$), a scan speed of 15°/min was used for the collection of intensity data. Four standards measured every 300 data showed no significant trends. No correction was made for absorption.

The structure was solved by a combination of direct methods and Fourier techniques. The Sr positions were obtained from the initial *E* map, and the remainder of the atoms were gradually found after many iterations of least-squares refinement and difference Fourier calculations. The outer portions of the molecule, notably the methyl groups on the HMPA ligands, have large thermal motion and/or disorder. In addition to *two* Sr_3 molecules, the asymmetric unit contains solvent molecules. One complete toluene molecule and three other fragments of either toluene or pentane were found for a total of 20 additional atoms. Since the peaks were weak, the occupancies for the solvent atoms were estimated at 0.5. For the purpose of density calculation, the structure was assumed to initially contain two molecules of toluene and two molecules of pentane per asymmetric unit. No attempt was made to include the hydrogen atoms.

In the final cycles of least-squares refinement, the Sr atoms were refined with anisotropic thermal parameters, the other nonsolvent atoms were refined with isotropic thermal parameters, and the solvent atoms were refined with fixed thermal parameters and occupancies. In the final difference map the largest residual peak was 0.9 e/Å^3. All of the residual peaks could be attributed to a small amount of disorder in the existing atoms; i.e., there was no evidence of additional solvent atoms.

The results are shown in Tables II and III and Figure 1. Further details are available as supplementary material.

Preparation of $[Ca_3(OPh)_5(HMPA)_6][OPh{\cdot}2PhOH]{\cdot}PhMe$ (1). (a) From CaH_2. CaH_2 (402 mg, 10 mmol) and PhOH (1.84 g, 20 mmol) were suspended in a mixture of HMPA (3.5 mL, 20 mmol) and toluene (8 mL). The resulting mixture was gradually brought to reflux and the temperature maintained for 30 h. During this time, the CaH_2 slowly dissolved to yield a yellow-green solution. The reaction mixture was filtered hot to yield a yellow-green filtrate; this was subsequently layered with pentane (15 mL), and the temperature was lowered to –20 °C. After 5 days, a large crop of colorless crystals was obtained (3.008 g); a further crop was obtained after a further 2 days (1.211 g). Total yield of product: 4.22 g, 81%. IR (cm^{-1}, Nujol mull) shows the presence of coordinated HMPA and a broad absorption centered at 3230 cm^{-1} for an OH group. Observed mp: 78–80 °C. Anal. Calcd for $Ca_3O_{14}P_6N_{18}C_{91}H_{158}$: C, 53.73; H, 7.78; N, 12.39; P, 9.15; Ca, 5.92. Found: C, 53.96; H, 8.01; N, 12.63; P, 9.33; Ca, 5.78.

(b) From Calcium Metal. Calcium metal powder (400 mg, 10 mmol) and phenol (2.50 g, 26.6 mmol) were suspended in a mixture of 6 mL of toluene and 3.5 mL (20 mmol) of HMPA. This mixture was refluxed for 80 h to yield a turbid gray solution which was filtered twice to yield a pale green filtrate. Layering this solution with 15 mL of *n*-pentane and storage at –20 °C for 1 week yielded 4.03 g (55% yield) of colorless crystals.

Thermogravimetric Analysis. Percent weight loss (°C temperature range; assigned groups lost, calculated percent weight loss): 7.13 (50–130; 1.5 PhOH, 7.1); 24.27 (130–220; 0.5 PhOH + 2 HMPA + toluene, 24.4); 53.26 (220–375; 4 HMPA + 4 PhOH, 53.4); 8.86 (380–470; Ph_2O, 7.8). Final residue is 8.1% (expected for CaO, 8.45%).

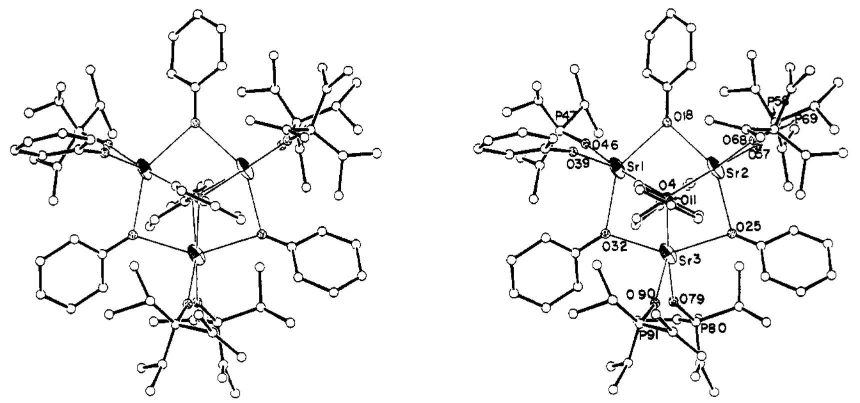


Figure 1. Stereo ORTEP drawing (50% probability ellipsoids) of molecule "A" of $Sr_3(OPh)_6[OP(NMe_2)_3]_5$, showing selected atom labeling. Open spheres are C, N, or P, and oxygens are stippled. Oxygens O(4) and O(11) of the μ_3-phenoxides are obscured by a phenyl group.

Table IV. Crystallographic Data for $[Ca_3(OPh)_5(HMPA)_6][OPh\cdot 2PhOH]\cdot PhMe$

formula	$C_{91}H_{158}N_{18}O_{14}P_6Ca_3$	space group	*Cc*
a, Å	17.595(18)	*T*, °C	−155
b, Å	34.160(35)	λ, Å	0.710 69
c, Å	18.521(19)	ρ_{calcd}, g cm^{-3}	1.218
β, deg	94.93(3)	μ(Mo Kα), cm^{-1}	2.90
V, Å^3	11090.9	*R*	0.0613
Z	4	R_w	0.0573
fw	2034.44		

Table V. Selected Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $[Ca_3(OPh)_5(HMPA)_6][OPh\cdot 2PhOH]\cdot PhMe$

	x[c]	*y*	*z*	$10B_{iso}$, Å^2
Ca(1)	7758[c]	1282(1)	5976[c]	17
Ca(2)	6911(2)	2175(1)	6188(2)	15
Ca(3)	5936(2)	1332(1)	6524(2)	15
O(4)	6589(5)	1585(2)	5515(4)	17
O(11)	7151(4)	1615(2)	6940(4)	14
O(18)	8120(4)	1941(2)	5934(5)	18
O(25)	5699(5)	2006(2)	6502(5)	21
O(32)	6834(5)	842(2)	6301(5)	24
O(39)	8063(5)	995(2)	4913(5)	23
P(40)	8092(3)	727(1)	4295(3)	48
O(50)	8940(5)	1053(2)	6432(5)	24
P(51)	9752(2)	1075(1)	6723(2)	27
O(61)	7042(5)	2710(2)	6973(4)	19
P(62)	7104(2)	3037(1)	7506(2)	20
O(72)	6837(5)	2611(2)	5248(4)	18
P(73)	6646(2)	2882(1)	4633(2)	21
O(83)	5552(5)	1158(2)	7622(4)	20
P(84)	5351(2)	1049(1)	8355(2)	21
O(94)	4802(5)	1080(2)	6015(5)	26
P(95)	3985(2)	992(1)	5755(2)	20
O(105)	1317(5)	9656(3)	6096(5)	35
O(112)	12171(5)	−381(3)	5106(5)	30
O(119)	13455(5)	−720(3)	5323(5)	34

[a] Fractional coordinates are $\times 10^4$. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609. [c] Not varied.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[Ca_3(OPh)_5(HMPA)_6][OPh\cdot 2PhOH]\cdot PhMe$

Ca(1)–O(4)	2.393(8)	Ca(2)–O(25)	2.331(8)
Ca(1)–O(11)	2.441(8)	Ca(2)–O(61)	2.335(8)
Ca(1)–O(18)	2.343(8)	Ca(2)–O(72)	2.286(8)
Ca(1)–O(32)	2.331(9)	Ca(3)–O(4)	2.434(9)
Ca(1)–O(39)	2.304(9)	Ca(3)–O(11)	2.412(8)
Ca(1)–O(50)	2.313(8)	Ca(3)–O(25)	2.338(9)
Ca(2)–O(4)	2.413(8)	Ca(3)–O(32)	2.363(8)
Ca(2)–O(11)	2.382(8)	Ca(3)–O(83)	2.277(8)
Ca(2)–O(18)	2.357(8)	Ca(3)–O(94)	2.300(9)
Ca(1)–O(4)–Ca(2)	91.15(28)	Ca(1)–O(32)–C(33)	134.5(7)
Ca(1)–O(4)–Ca(3)	91.2(3)	Ca(3)–O(32)–C(33)	130.4(8)
Ca(2)–O(4)–Ca(3)	90.25(27)	Ca(1)–O(39)–P(40)	163.1(6)
Ca(1)–O(11)–Ca(2)	90.7(3)	Ca(1)–O(50)–P(51)	157.2(6)
Ca(1)–O(11)–Ca(3)	90.60(27)	Ca(2)–O(61)–P(62)	176.7(5)
Ca(2)–O(11)–Ca(3)	91.54(27)	Ca(2)–O(72)–P(73)	170.2(5)
Ca(1)–O(18)–Ca(2)	93.8(3)	Ca(3)–O(83)–P(84)	176.5(5)
Ca(2)–O(25)–Ca(3)	94.7(3)	Ca(3)–O(94)–P(95)	167.4(6)
Ca(1)–O(32)–Ca(3)	94.58(28)		

Bulk Thermolysis of $[Ca_3(OPh)_5(HMPA)_6][OPh\cdot 2PhOH]$. An all-glass apparatus was designed for thermolysis under a helium flow with the minimum contamination by water or oxygen. The apparatus was silanated prior to use, using Sulfasil (Pierce Chemical Co.) (1–10% in *n*-pentane) and then thoroughly rinsed with *n*-pentane. The glassware was then dried for 12 h at 150 °C, before being assembled, and flame-dried under vacuum (three times) over a period of 3 h.

A freshly prepared (via crystallization) calcium aryloxide–hexamethylphosphoramide complex was placed into a boat, and the material was decomposed (2 h) under helium gas flows inside a furnace at temperatures between 450 and 600 °C. The volatile organic materials were trapped inside a U-shaped trap filled with glass beads (presilanated), which was attached to an NMR tube. The remaining white solid was transferred to the glovebox for characterization by powder X-ray diffraction. In the U-shaped trap were found phenol and hexamethylphosphoramide, by ^1H and ^{13}C NMR studies in benzene-d_6. From 2.0 g of reagent was obtained 145 mg of colorless solid, whose powder pattern matched that of CaO.

X-ray Diffraction Study of $[Ca_3(OPh)_5(OP(NMe_2)_3)_6][OPh\cdot 2PhOH]\cdot PhMe$. A suitable crystal was located and transferred to the goniostat using standard inert-atmosphere handling techniques and cooled to −155 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to a *C*-centered monoclinic space group, either *C*2/*c* or *Cc* (Table IV). Subsequent solution and refinement of the structure confirmed the noncentrosymmetric choice, *Cc*. Data were collected using a continuous θ–2θ scan with fixed backgrounds ($6° \leq 2\theta \leq 45°$). Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. After all non-hydrogen atoms were located and identified, a difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions were therefore calculated using idealized geometries and d(C–H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement, which showed the crystal to be of better quality than that of the Sr compound. All hydrogens are included except for the two associated with oxygen of the phenol solvent molecules. Because of the size of the molecule, no attempt was made to determine the absolute structure. No absorption correction was deemed necessary, although a correction was made for extinction. A final difference Fourier map was featureless, the largest peak being 0.58 e/Å^3. The results of the structure determination are shown in Tables V and VI and Figures 2 and 3. Further details are available as supplementary material.

$Ba_6(OPh)_{12}(TMEDA)_4$. Barium metal granules (1.37 g, 10 mmol), PhOH (1.86 g, 20 mmol), and TMEDA (4.8 mL, 30 mmol) were combined in toluene (10 mL). The reaction was left to stir (at 25 °C) for 80 min, during which time the metal all dissolved with evolution of hydrogen. Subsequently, the solution was filtered to yield a yellow filtrate, which was left overnight at room temperature. A large crop of colorless, well-formed crystals was isolated. Yield: 3.76 g (75.1%). Mp: 96–99 °C to yield a colorless liquid. ^1H NMR (500 MHz, at 25 °C in toluene-d_8):

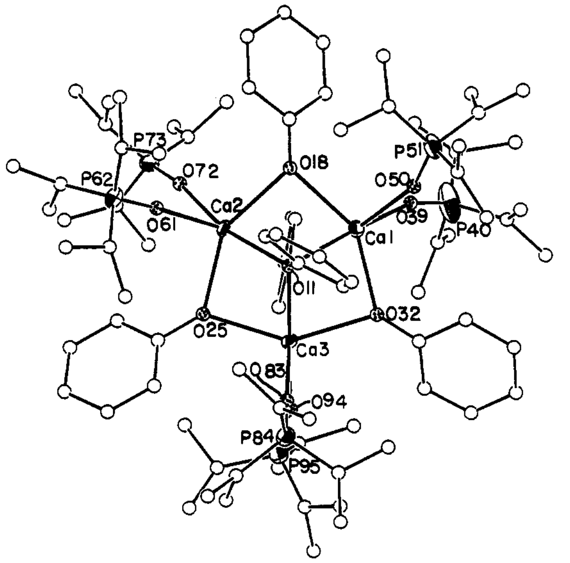


Figure 2. ORTEP drawing (50% probability ellipsoids) of the non-hydrogen atoms of the cation $Ca_3(OPh)_5[OP(NMe_2)_3]_6^+$, showing selected atom labeling. Open spheres are carbon or nitrogen. Oxygens O(4) and O(11) of the μ_3-phenoxides are obscured by their phenyl rings.

Table VII. Crystallographic Data for $Ba_6(OPh)_{12}(Me_2NC_2H_4NMe_2)_4{\cdot}4PhMe$

formula	$C_{62}H_{78}Ba_3N_4O_6$	space group	$P2_1/c$
a, Å	15.049(2)	T, °C	−171
b, Å	16.775(2)	λ, Å	0.710 69
c, Å	24.819(5)	ρ_{calcd}, g cm^{-3}	1.488
β, deg	98.80(1)	μ(Mo Kα), cm^{-1}	19.35
V, Å^3	6191.80	R	0.0333
Z	4	R_w	0.0387
fw	1387.34		

δ 2.03 (s, 4H, CH_2), 2.08 (s, 12H, NMe_2), 6.94 (s, Ph), 6.96 (s, Ph), 7.05 (s, Ph). ^{13}C NMR (at 25 °C in C_7D_8): δ 31.41 (s, CH_3), 46.28 (s, CH_2), 115.28 (s, Ph), 130.62 (s, Ph), 166.37 (s, Ph). Low-temperature NMR studies were precluded by the poor solubility of this complex below 0 °C. Elemental analysis follows for material pumped in vacuum for 24 h, to remove lattice solvent. Anal. Calcd for $Ba_6O_{12}N_8C_{124}H_{156}$: C, 53.62; H, 5.62; N, 4.04. Found: C, 53.40; H, 5.74; N, 4.15.

X-ray Diffraction Study of $Ba_6(OPh)_{12}(TMEDA)_4{\cdot}4$(toluene). A suitable crystal was selected in an N_2-atmosphere glove bag and transferred to the goniostat where it was cooled to −171 °C for characterization and data collection.[6] A computerized systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic (2/m) symmetry and systematic extinctions consistent with the space group $P2_1/c$. Data collection (6° ≤ 2θ ≤ 45°) was undertaken as detailed in Table VII of this report. All of the unique reflections were used in the subsequent computations. No correction for absorption was made. The structure was solved using the usual combination of direct methods and Fourier techniques. The three unique Ba atoms were located in the initial E map, and the remaining non-hydrogen atoms were located in successive difference Fourier maps phased with the already located atoms. The asymmetric unit contains half of the Ba_6 molecule, as well as two molecules of toluene solvent. The solvent molecules are numbered C(62) through C(75). Almost all of the hydrogen atoms were evident in a later difference map; they were introduced in idealized fixed positions during the final cycles of full-matrix least-squares refinement. All non-hydrogen atoms were refined using anisotropic thermal parameters. The final difference map was essentially featureless; the largest peak was 1.01 e/Å^3 in the vicinity of C(72) (toluene). The results of the structure determination are shown in Tables VIII and IX and Figures 4 and 5.

Table VIII. Selected Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $Ba_6(OPh)_{12}(Me_2NC_2H_4NMe_2)_4{\cdot}4PhMe$

	x	y	z	$10B_{iso}$, Å^2
Ba(1)	7727.4(2)	1913.5(2)	8733.8(1)	15
Ba(2)	9836.9(2)	2142.5(2)	9948.1(1)	12
Ba(3)	8615.7(2)	28.0(2)	9638.0(1)	14
O(4)	9329(2)	1185(2)	9067(1)	16
O(11)	8086(2)	1554(2)	9806(1)	17
O(18)	9814(2)	681(2)	10427(1)	16
O(25)	8905(2)	3008(2)	9184(1)	19
O(32)	11439(2)	1473(2)	9940(1)	18
O(39)	7363(2)	396(2)	8818(1)	22
N(46)	7194(3)	2330(2)	7569(2)	20
N(49)	5859(3)	2543(2)	8422(2)	21
N(54)	11083(3)	3444(2)	10301(2)	20
N(57)	9233(3)	3383(2)	10693(2)	19

[a] Fractional coordinates are ×10^4. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Results

Synthesis. Reaction at reflux in toluene of polymeric, insoluble commercial CaH_2 with stoichiometric phenol, in the presence of 2 mol of HMPA/mol of Ca, proceeds slowly to consume all CaH_2. If the resulting homogeneous solution is layered with 2 volumes of pentane and the mixture cooled, an 81% yield of crystals of empirical formula $Ca(OPh)_2(HMPA)_2(PhOH)_{2/3}(toluene)_{1/3}$ is obtained. The same product is obtained if CaH_2 is replaced by calcium metal in this procedure.

If the entirely analogous procedure is followed using metallic strontium, an 86% yield of colorless crystals of empirical formula $Sr(OPh)_2(HMPA)_{5/3}(toluene)_{1/3}(pentane)_{1/3}$ is obtained.

When barium metal, phenol, and tetramethylethylenediamine (TMEDA) are combined in toluene, there is a reaction at 25 °C, with hydrogen evolution. Even with 50% more TMEDA than HMPA employed above (i.e., 3 mol of chelate/mol of barium), the resulting high-yield product has a formula, $Ba_6(OPh)_{12}(TMEDA)_2$, with a lower neutral ligand:metal ratio than in the calcium and strontium/HMPA cases.

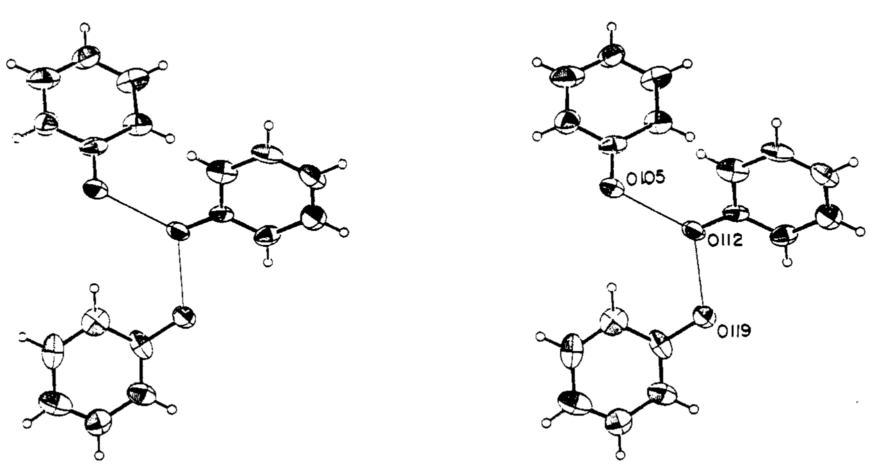


Figure 3. Stereo ORTEP drawing of the hydrogen-bonded unit $H_2(OPh)_3^-$.

Table IX. Selected Bond Distances (Å) and Angles (deg) for $Ba_6(OPh)_{12}(Me_2NC_2H_4NMe_2)_4$

Ba(1)–O(4)	2.715(3)	Ba(3)–O(4)	2.719(3)
Ba(1)–O(11)	2.702(3)	Ba(3)–O(11)	2.733(3)
Ba(1)–O(25)	2.676(3)	Ba(3)–O(18)′	2.672(3)
Ba(1)–O(39)	2.619(3)	Ba(3)–O(18)	2.685(3)
Ba(1)–N(46)	2.962(4)	Ba(3)–O(32)′	2.733(3)
Ba(1)–N(49)	2.992(4)	Ba(3)–O(39)	2.627(3)
Ba(2)–O(4)	2.726(3)	O(4)–C(5)	1.340(5)
Ba(2)–O(11)	2.786(3)	O(11)–C(12)	1.320(5)
Ba(2)–O(18)	2.726(3)	O(18)–C(19)	1.347(5)
Ba(2)–O(25)	2.619(3)	O(25)–C(26)	1.323(5)
Ba(2)–O(32)	2.662(3)	O(32)–C(33)	1.324(6)
Ba(2)–N(54)	2.924(4)	O(39)–C(40)	1.322(6)
Ba(2)–N(57)	3.015(4)		
Ba(1)–O(4)–Ba(2)	96.11(10)	Ba(2)–O(18)–C(19)	100.38(25)
Ba(1)–O(4)–Ba(3)	94.44(9)	Ba(3)–O(18)–Ba(3)′	106.01(10)
Ba(1)–O(4)–C(5)	94.12(23)	Ba(3)–O(18)–C(19)	139.71(27)
Ba(2)–O(4)–Ba(3)	95.00(9)	Ba(3)′–O(18)–C(19)	103.75(24)
Ba(2)–O(4)–C(5)	125.30(27)	Ba(1)–O(25)–Ba(2)	99.72(10)
Ba(3)–O(4)–C(5)	137.46(28)	Ba(1)–O(25)–C(26)	104.19(25)
Ba(1)–O(11)–Ba(2)	95.05(9)	Ba(2)–O(25)–C(26)	155.53(28)
Ba(1)–O(11)–Ba(3)	94.44(9)	Ba(2)–O(32)–Ba(3)′	107.78(10)
Ba(1)–O(11)–C(12)	108.78(26)	Ba(2)–O(32)–C(33)	158.1(3)
Ba(2)–O(11)–C(12)	131.45(27)	Ba(3)′–O(32)–C(33)	90.99(25)
Ba(3)–O(11)–C(12)	124.9(3)	Ba(1)–O(39)–Ba(3)	98.98(10)
Ba(2)–O(18)–Ba(3)	95.79(9)	Ba(1)–O(39)–C(40)	119.24(28)
Ba(2)–O(18)–Ba(3)′	107.70(10)	Ba(3)–O(39)–C(40)	141.8(3)

Since the spectroscopic data for these three compounds are not definitive of structure, we temporarily defer discussion of these data.

Solid-State Structures. (a) Strontium Compound. The unit cell of $Sr(OPh)_2(HMPA)_{5/3}(toluene)_{1/3}(pentane)_{1/3}$ contains two crystallographically-independent $Sr_3(OPh)_6(HMPA)_5$ molecules and noninteracting solvent molecules filling cavities in the solid. These Sr_3 molecules are essentially identical, and thus only one is portrayed in Figure 1. Metric parameters of the two molecules are displayed side-by-side in Table III to facilitate comparison. The trinuclear molecules adopt the $M_3(\mu_3\text{-}X)_2(\mu_2\text{-}X)_3L_6$ structural type,[7] which furnishes coordination number 6 to each metal. Since divalent cations require six anionic ligands in a neutral molecule, this structural type leaves one phenoxide to occupy a terminal position, with the consequence that only five neutral ligands are needed. This odd number of terminal Lewis bases reduces the potential 3-fold rotational symmetry of an M_3 triangle to the observed (idealized) mirror symmetry. The unique metal, Sr(1), carries a terminal phenoxide (and one HMPA), while Sr(2) and Sr(3) each have two terminal HMPA ligands.

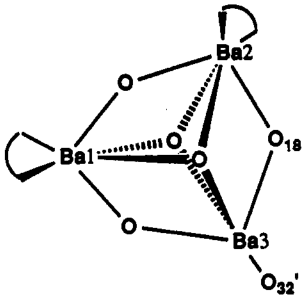
Within the metal coordination sphere, cis O–Sr–O angles are as small as 65.9(6)° (μ_3-O/Sr/μ_3-O) and trans O–Sr–O angles are as small as 142.1(7)° (μ_2-O/Sr/μ_2-O). Sr–O bonds[8] to μ_3-O (2.52(2)–2.65(2) Å) are longer than those to μ_2-O (2.38(3)–2.53(2) Å), which are only slightly longer than those to the HMPA oxygens (2.35(3)–2.45(2) Å). Sr–O distances to the terminal phenoxides (2.34(3) and 2.37(3) Å) are shorter still. The angles at oxygens of the terminal phenoxides are 169.1(25) and 175.(3)°, while those at the oxygens of the HMPA ligands range from 149.1(13) to 175.0(15)°.

(b) Calcium Compound. The solid-state structure of material with empirical formula $Ca(OPh)_2(HMPA)_2\cdot{}^2/_3PhOH\cdot{}^1/_3$toluene comprises equal quantities of $Ca_3(OPh)_5(HMPA)_6^+$ cations (Figure 2), $(OPh)(HOPh)_2^-$ anions (Figure 3), and toluene molecules.

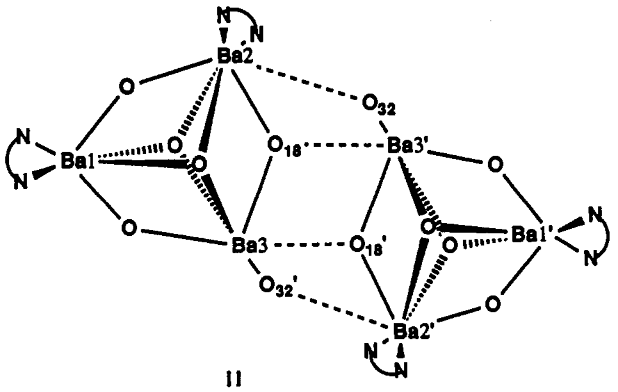
The cation may be written $Ca_3(\mu_3\text{-}OPh)_2(\mu_2\text{-}OPh)_3(HMPA)_6^+$ and is thus of the now-standard M_3L_{11} stoichiometry and structure, which confers coordination number 6 on each metal. The Ca/Ca separations range from 3.432 to 3.449 Å. The coordination geometry may be described as distorted octahedral, with cis O–Ca–O angles as small as 68.9(3)° (μ_3-O/Ca/μ_3-O) and trans O–Ca–O angles as small as 144.6(3)° (μ_2-O/Ca/μ_2-O). Ca–O bond lengths to μ_3-O (2.38(1)–2.44(1) Å) are longer than those to μ_2-O (2.33(1)–2.36(1) Å), which are both longer than those to the HMPA oxygens (2.28(1)–2.34(1) Å). Ca–O–P angles range from 157.2(6) to 176.7(5)°.

The anion contains two phenol molecules hydrogen-bonded to one phenoxide (Figure 3) with O/O distances of 2.471 and 2.540 Å and an O(105)–O(112)–O(119) angle of 119.66°. While the hydroxyl hydrogens were not located in the X-ray data, one proton is assumed to span each of the two O/O vectors in the open (i.e., V-shaped) three-oxygen unit. The three C–O distances are identical to within 3 esd's.

(c) Barium Compound. The structural study (Figures 4 and 5) shows that the six metals are *not* arranged at the apices of an octahedron but instead are arranged as two $Ba_3(OPh)_6(TMEDA)_2$ triangles connected along one edge of each triangle by a total of four phenoxide bridges. The two Ba_3 triangles are related by a crystallographic center of symmetry. One $Ba_3(OPh)_6(TMEDA)_2$ triangle is represented schematically as I and bears an obvious relationship to the calcium and strontium structure discussed above. The major difference is that one metal, designated Ba(3), is unsaturated (five-coordinate) in this structure. The six phenoxide and two TMEDA ligands furnish only ten of the eleven ligands needed for the M_3L_{11} structural prototype. Two of these units (I) thus dimerize to give the observed product, but they do so via *two* alkoxide groups (O(18) and O(32)′) of I and thus not only increase the coordination number of Ba(3) to 6 but also increase that of Ba(2) to 7. The highly acute (~64°) N–Ba–N angles leave the coordination sphere around Ba(2) relatively open and thus facilitate that metal becoming seven-coordinate. The "docking" of two units I forms a centrosymmetric dimer as shown in II. As a consequence of this dimerization to a Ba_6 unit, the structure contains *no* terminal phenoxides.



I



II

The dimeric molecule shows (Figure 5) considerable evidence for crowding along the juncture of the two Ba_3 components. Phenyl rings on oxygens 25 and 39 bend away from the junction (and towards Ba(1)), as do those on the μ_3-oxygens, O(4) and O(11). These distortions occur primarily in the phenyl groups, with retention of the oxygens in their idealized locations displayed by

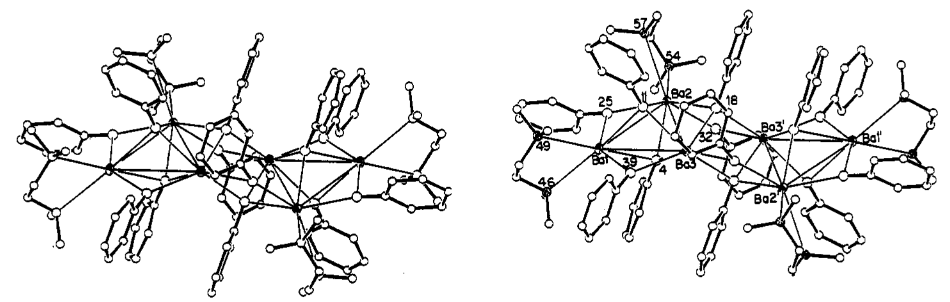


Figure 4. Stereo ORTEP drawing of the non-hydrogen atoms of $Ba_6(OPh)_{12}(TMEDA)_4$, showing selected atom labeling. Numbers indicate oxygen (open circles) or nitrogen (stippled circles). Unlabeled atoms are carbon. Lines connecting metals (large open circles) are not bonds but are for visual clarity only.

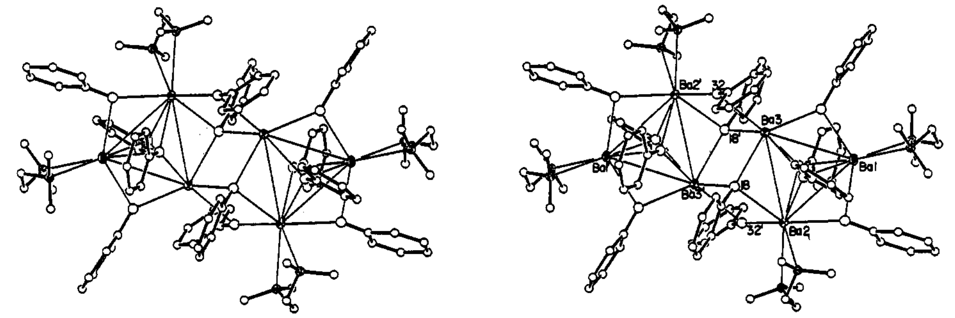
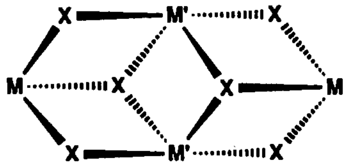


Figure 5. Stereo ORTEP drawing of $Ba_6(OPh)_{12}(TMEDA)_4$, showing the phenoxide bridging of the two Ba_3 triangles. This view is nearly perpendicular to the plane of the metal triangles.

the calcium and strontium prototypes: the μ_2-oxygens O(25) and O(39) lie within 0.07 Å of the Ba_3 plane, and the μ_3-oxygens O(4) and O(11) lie ±1.44 Å from the Ba_3 plane. Even the Ba/O bond lengths show only modest asymmetry. The Ba–(μ_2-O) distances vary from 2.619(3) to 2.676(3) Å, while the Ba–(μ_3-O) distances vary from 2.702(3) to 2.786(3) Å. Concerning O(18) and O(32), the ligand atoms which link the two Ba_3 groups, the μ_2 atom is quite asymmetric (Ba(2)–O(32) = 2.662(3) Å and Ba(3)′–O(32) = 2.733(3) Å). The short distance is associated with a very large angle Ba–O–C (158.1(3)°), and the long distance is the longest bond length to the six-coordinate Ba(3)′. The triply-bridging O(18) is fairly symmetrically positioned (Ba–O distances range from 2.672(3) to 2.726(3) Å). This oxygen is displaced 0.38 Å from the Ba_3 plane by becoming μ_3 in the dimerization.

The structural motif of the bridging between the two Ba_3 units (III) resembles that found frequently for M_4 units.[9] Since other examples involve metals as diverse as Li and Y, this is evidently a very versatile geometric form which can accommodate metals of greatly varying size and coordination number.



III

Solution NMR Studies. The complex [$Ca_3(\mu_3\text{-OPh})_2(\mu_2\text{-OPh})_3(HMPA)_6$] [OPh·2PhOH]·PhMe (**1**) exhibits very complex behavior in solution as observed by NMR spectroscopy. Fluxional behavior is observed in both ^1H and $^{13}C\{^1H\}$ NMR; even at 210 K, the different phenoxide environments are not frozen out. The six equivalent HMPA ligands are observed as a ^1H NMR doublet (2.37 ppm) at 298 K, in accord with the solid-state structure. On cooling, the situation becomes more complex with additional resonances appearing at δ 2.11, 2.15, 2.24, and 2.29. At 210 K, the resonances are observed in a ratio of 1:2:1:1:2. This behavior was observed to be reversible, and on warming, a single doublet was again observed.

To clarify the complex behavior observed in the low-temperature ^1H NMR spectrum, we investigated the phosphorus environments. The $^{31}P\{^1H\}$ NMR spectrum of **1** in C_7D_8 at 298 K exhibits a single broad peak at δ 22.79, in accord with the HMPA ligands all being equivalent. On gradual cooling of a solution of **1** to 213 K, four peaks are observed in a ratio of 2:1:3, which is in accord with the increased complexity of the ^1H NMR spectra at low temperature.

These observations are consistent with partial HMPA dissociation (eq 1) with the open coordination site being replaced by a phenoxide ligand from the counterion. Such a reaction would be promoted by hydrogen bonding between HMPA and the liberated phenol.

$$Ca_3(\mu_3\text{-OPh})_2(\mu_2\text{-OPh})_3(HMPA)_6^+ + H_2(OPh)_3^- \rightleftharpoons Ca_3(\mu_3\text{-OPh})_2(\mu_2\text{-OPh})_3(OPh)(HMPA)_5 + HMPA + 2PhOH \quad (1)$$

The complex $Sr_3(\mu_3\text{-OPh})_2(\mu_2\text{-OPh})_3(OPh)(HMPA)_5$ (**2**) has also been investigated by multinuclear NMR. Variable-temperature NMR studies on **2** in toluene revealed that, as for **1**, the different phenoxide environments and HMPA environments could not be frozen out by ^1H and $^{13}C\{^1H\}$ NMR. Hence, we again used $^{31}P\{^1H\}$ NMR as a probe of structural dynamics in solution. At 298 K, a single broad resonance is observed, indicating that the three types of HMPA ligands in the solid-state structure are undergoing rapid site exchange. On cooling to 243 K, three signals are observed in an approximate ratio of 2:1:2, consistent with that expected from the solid-state structure.

For $Ba_6(OPh)_{12}(TMEDA)_4$, both the ^1H and ^{13}C NMR spectra in toluene at 25 °C show only signals for one type of TMEDA and one type of phenyl and are thus clearly simpler than required for the solid-state structure. Although a fluxional (site exchange) process is implied, low solubility at reduced temperatures prevented further definition of the process. The low solubility, however, does suggest that the Ba_6 unit remains intact in toluene solvent.

Discussion

The two triangular structural units in the calcium and strontium compounds are clearly very similar, and this structure with a large number of bridging ligands is adopted in response to a comparative deficiency of donor ligands (i.e., insufficient to form an $M(OAr)_2L_n$ monomer where $n \geq 4$). The adoption, by a seemingly weak donor like phenoxide, of μ_3-bridging sites is unusual but not unprecedented.[10] Because of the close similarity of the structures of $Ca_3(OPh)_5(HMPA)_6^+$ and $Sr_3(OPh)_6(HMPA)_5$, it is possible to use structurally-analogous bonds to gauge the difference in metal size. By this criterion, strontium is larger than calcium by 0.14 and 0.21 Å (μ_3-OPh), 0.05 and 0.17 Å (μ_2-OPh), or 0.07 and 0.11 Å (HMPA). Their ionic radii differ by 0.18 Å.[11]

It remains to understand how two closely-related syntheses (eqs 2 and 3) can lead to a salt in one case and a molecular species

$$3CaH_2 + 8PhOH + 6HMPA \rightarrow [Ca_3(OPh)_5(HMPA)_6][OPh\cdot 2PhOH] + 6H_2 \quad (2)$$

$$3Sr + 6PhOH + 5HMPA \rightarrow Sr_3(OPh)_6(HMPA)_5 + 3H_2 \quad (3)$$

in the second. These reactions (in toluene/pentane) were executed with identical (2:2:1) ratios of PhOH:HMPA:metal. We doubt that the smaller size of calcium makes it impossible to have a terminal phenoxide between two μ_2- and two μ_3-phenoxides. A possible thermodynamic origin is that Ca^{2+} in the triangle is less electrophilic than are 2 mol of phenol toward the final phenoxide ion. Finally, however, it may be possible that the saltlike character of the calcium-containing product causes its ready precipitation from solution, even if such a solution contains some of the neutral $Ca_3(OPh)_6(HMPA)_5$. Indeed, our NMR studies suggest that this is in fact the case.

The progression from M_3 to M_6 molecularity on going from the lighter alkaline earth elements to barium is due partly to the increase in size and attendant preferred coordination number. In the three examples reported here, the difference is accentuated by the progressive change in the number of uncharged donor ligands per metal: 2.0 for calcium, $^5/_3$ for strontium, but only $^2/_3$ for barium. The number for barium is so low that ligands from a second Ba_3 unit are required and aggregation occurs. The Ba_3 parentage of the resulting dimer is clearly evident, however.

The occurrence of a six-metal array which is *not* an octahedron for $Ba_6(OPh)_6(TMEDA)_4$ is noteworthy. We propose that a Ba_6 octahedron is unsuitable since the strong desire for coordination number greater than or equal to 6 necessitates a monatomic ligand at the center of the octahedron.[12] Without this, it becomes impossible to give all metals a coordination number of 6 or larger. This is evident from the Mo_6Cl_{12} structure, which forms a polymer by halide bridging between Mo_6 octahedra but nevertheless fails to exceed metal coordination number 5.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Tables giving full crystallographic details, anisotropic thermal parameters, fractional coordinates, and bond distances and angles for the three molecules reported (24 pages). Ordering information is given on any current masthead page.

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