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Synthesis and Structural Characterization of the Alkaline Earth Aryloxide Aggregates $H_2Ba_8(\mu_5\text{-}O)_2(OPh)_{14}(HMPA)_6$ and $H_2Sr_6Ba_2(\mu_5\text{-}O)_2(OPh)_{14}(HMPA)_6$. A New Structural Type Displaying Metal Ion Site Selectivity

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The reaction of barium metal granules with phenol and hexamethylphosphoramide (HMPA) in toluene at 25 °C yields a novel eight-metal atom aggregate. The reaction of $Sr_3(OPh)_6(HMPA)_5$ with barium metal and phenol yields a structurally related species. The two aggregates have been characterized by IR and ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectroscopy and single-crystal X-ray studies and shown to consist to two square-based pyramidal $M_5(\mu_5\text{-}O)$ fragments sharing a common basal edge. The structure is completed by μ_3- and μ_2-phenoxide and terminal HMPA ligands. The selectivity for barium in the two polyhedral sites where the square-based pyramids are joined originates in the higher coordination number there. Crystal data: for $H_2Ba_8O_2(OPh)_{14}(HMPA)_6\cdot 2PhMe$ (−172 °C), $a = 16.379(3)$ Å, $b = 19.504(4)$ Å, $c = 26.763(5)$ Å, $\beta = 100.90(0)°$ with $Z = 2$ in space group $P2_1/n$; for $H_2Sr_6Ba_2O_2(OPh)_{14}(HMPA)_6\cdot 2PhMe$ (−158 °C), $a = 17.797(2)$ Å, $b = 17.421(2)$ Å, $c = 26.624(3)$ Å, $\beta = 107.62(0)°$ with $Z = 2$ in space group $P2_1/n$.

Introduction

The interest in the formation and chemistry of main group alkoxides and aryloxides has undergone a renaissance over the last few years. There are many reasons for this surge of interest in such compounds, many of which until recently were either poorly characterized or not known at all.[1,2] One such stimulus is the discovery of superconducting ceramics[3] containing alkaline earth ions. The classical heat-and-sinter preparative technique for such superconductors can suffer from poor reproducibility, incorporation of ionic impurities, and multi-phase products. In addition, the use of metal oxides as reagents in this methodology generally necessitates very high temperatures before reaction rates become useful. The use of hydrocarbon soluble (molecular) alkoxide precursors has been advocated.[4] The advantage of this technique is that the desired stoichiometry may be achieved on the molecular level by selective formation of a binary or ternary metallic alkoxide, e.g., $M_xM'_yM''_z(OR)_n$, and the resulting molecule subsequently thermolyzed (and/or hydrolyzed) to yield the desired ceramic product.

Considerable research has already been undertaken on the requisite lanthanide[5] and copper alkoxides,[6] but to date, little research has focused on the characterization of the heavier alkaline earth aryloxide precursors. There have been only a few preliminary reports on the alkoxides of strontium and barium, perhaps due in part to the insolubility of the alkoxides obtained.[7,8] This behavior is in marked contrast to the extensive studies on the alkoxides and aryloxides of Be and Mg by Coates and other workers.[9,10] The insoluble nature of the metal alkoxides in the parent alcohols, suggests that they may be polymeric. Indeed, X-ray powder diffraction studies on $M(OR)_2$ (M = Ca, Sr, Ba; R = Me, Et, Pr^i) yielded hexagonal unit cells with structures proposed to be similar to the corresponding metal hydroxides (e.g, a CaF_2 type of lattice).[8]

In the interest of making volatile, yet molecular, species, we chose to use a simple aryloxide, in this case phenoxide. To minimize the degree of oligomerization, we have used a very strong, sterically-hindered Lewis base, hexamethylphosphoramide ($[NMe_2]_3PO$, HMPA). This Lewis base has been extensively used in group 1A[11] and more recently in group 2A chemistry.[12]

We report in this paper the preparation and characterization of the first examples of molecular aggregates of barium and a mixed strontium–barium species supported by phenoxide and HMPA ligands.[13]

Experimental Section

The manipulations of all reactants and products were carried out under an argon atmosphere (Schlenk line), helium atmosphere (glovebox) or in vacuo, with rigorous exclusion of moisture and air. The solvents n-pentane and toluene were dried and distilled prior to use, and stored over 4A molecular sieves under an atmosphere of nitrogen or argon. Barium and strontium granules were obtained from Alfa Products and hexamethylphosphoramide was purchased from the Aldrich Chemical Co. and dried over 4A molecular sieves. NMR data were obtained on a Bruker WM-500 NMR spectrometer, using the proton impurities of the deuterated solvents as reference for ^1H NMR and the ^{13}C NMR resonances of the solvent as a reference for ^{13}C NMR. $^{31}P\{^1H\}$ NMR

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spectra were recorded at 202 MHz and are referenced to H_3PO_4 as 0 ppm. Infrared spectra were recorded on a Nicolet 510P FTIR spectrometer. Elemental analyses were performed by Oneida Research Services.

Preparation of $[H_2Ba_8(\mu_5\text{-}O)_2(\mu_3\text{-}OPh)_8(\mu_2\text{-}OPh)_6(HMPA)_6]\cdot 2PhMe$ (I). Barium metal granules (1.37 g, 10 mmol) and PhOH (1.84 g, 20 mmol) were suspended in a mixture of HMPA (1.35 mL, 7.5 mmol) and toluene (10 mL). The resulting mixture was stirred at room temperature for 20 min, during which time all the metal was consumed in an exothermic reaction to yield a pale brown solution. The reaction mixture was filtered hot to yield a brown filtrate that was layered with pentane (15 mL), and subsequently left to crystallize at −20 °C. Large, regular shaped, colorless crystals were obtained after 7 days in 81% yield (2.88 g). Anal. Calcd (found) for $Ba_8P_6O_{22}N_{18}C_{134}H_{196}$: C, 42.33 (42.6); H, 5.22 (5.30); N, 6.99 (7.26); P, 5.17 (5.28). IR (Nujol): ν(OH) 3400 cm^{-1}. Mp: 217–220 °C. ^1H NMR (500 MHz, C_7D_8, 25 °C): δ 2.42 (d, 9.5 Hz, Me_2N), 4.06 (s, br, OH), 6.88 (t, Ph), 7.28 (m, Ph), 7.43 (m, Ph). The spectrum remains essentially unchanged on cooling to 193 K. $^{13}C\{^1H\}$ NMR (C_7D_8): δ 36.33 (s, Me_2N), 113.83 (s, Ph), 119.99 (s, Ph), 130.10 (s, Ph), 166.84 (s, Ph, ipso carbon), unchanged on cooling to 193 K. $^{31}P\{^1H\}$ NMR (C_7D_8): δ +24.96 (s); remains unchanged over the temperature range 193–293 K.

Preparation of $\{H_2Ba_2Sr_6(\mu_5\text{-}O)_2(\mu_3\text{-}OPh)_8(\mu_2\text{-}OPh)_6(HMPA)_6\}\cdot 2PhMe$ (II). 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 at 90 °C and the temperature maintained for three hours. During this time, the strontium metal slowly reacted to yield a pale yellow solution. The reaction mixture was filtered hot to yield a yellow filtrate containing essentially pure $Sr_3(\mu_3\text{-}OPh)_2(\mu_2\text{-}OPh)_3(OPh)(HMPA)_5$.[14] To this solution were then added barium metal granules (1.37 g, 10 mmol) and phenol (1.84 g, 20 mmol), and the resulting mixture was held at reflux for 5 h. During this time, the solution gradually turned a dark chocolate-brown with consumption of 60% of the barium metal. After this time, the solution was filtered hot, layered with pentane (15 mL), and subsequently left to crystallize at −20 °C. Large, regular hexagonally-shaped crystals were obtained after 5 days in 58% yield (5.05 g). Anal. Calcd (found) for $Sr_6Ba_2P_6O_{22}N_{18}C_{134}H_{196}$: C, 46.15 (45.98); H, 5.69 (5.84); N, 7.63 (7.46); P, 5.63 (5.88). IR (Nujol): ν(OH) 3150 (br). Mp: 311–314 °C. ^1H NMR (500 MHz, C_7D_8, 25 °C): δ 2.46 (d, 9.8 Hz, Me_2N), 4.14 (s, br, OH), 7.17–7.46 (m, Ph). The spectrum remains essentially unchanged on cooling to 193 K. $^{13}C\{^1H\}$ NMR (C_7D_8): δ 36.31 (s, Me_2N), 113.09 (s, Ph), 119.03 (s, Ph), 128.92 (s, Ph), 166.09 (s, Ph, ipso carbon); unchanged on cooling to 193 K. $^{31}P\{^1H\}$ NMR (C_7D_8): δ +24.71 (s); remains unchanged over the temperature range 193–293 K. Differential scanning calorimetry: broad peak centered at 182 °C (0.228 J/g). This is possibly due to chemical change, i.e., loss of toluene, phenol and/or HMPA from the complex. Thermogravimetric analysis: first weight loss of 21% (25–300 °C), −PhOH − PhMe − 3HMPA (calculated 21%); second weight loss of 18% (310–460 °C), −3HMPA − PhOH (calculated 19%); third weight loss of 6% (470–670 °C) $-Ph_2O$ (calculated 5%). This leaves a black solid corresponding to 55% (calculated for $HSr_6Ba_2(O)_3(OPh)_{11}$ 55%).

X-ray Diffraction Structure Determinations. $H_2Ba_8O_2(OPh)_{14}(HMPA)_6\cdot 2PhMe$. A suitable crystal was transferred to the goniostat using inert atmosphere handling techniques and was cooled to −172 °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 the unique monoclinic space group $P2_1/n$. Subsequent solution and refinement of the structure confirmed this choice. Data were collected (6° ≤ 2θ ≤ 45°) in the usual manner[15] using a continuous θ–2θ scan with fixed backgrounds. Data (Table I) were reduced to a unique set of intensities and associated sigmas and the structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions associated with carbon atoms were therefore calculated using idealized geometries and d(C–H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement. There was no crystallographic evidence for hydrogen atoms on any oxygen atom. Six peaks corresponding to a crude hexagon was located in an earlier difference map. Since the solvent used was toluene, it is assumed that a disordered toluene is present. There was no evidence for the methyl group. There was no crystallographic evidence for hydrogen atoms on any oxygen atom. A final difference Fourier was featureless, with the largest peak being 0.45 e/Å^3. No absorption correction was performed. The results of the structural study are shown in Table II and Figure 1. Additional details are available as supplementary material.

Table I. Crystallographic Data

	$H_2Ba_8O_2(OPh)_{14}(HMPA)_6\cdot 2PhMe$		
chem formula	$Ba_8C_{120}H_{178}N_{18}O_{22}P_6\cdot 2C_7H_8$	fw	3694.4
		space group	$P2_1/a$
a, Å	16.379(3)	T, °C	−172 °C
b, Å	19.504(4)	λ Å	0.710 69
c, Å	26.763(5)	ρ_{calcd}, g cm^{-3}	1.353
β, deg	100.90(0)	μ(Mo Kα), cm^{-1}	15.0
V, Å^3	8394.98	R	0.0680
Z	2	R_w	0.0717
	$H_2Ba_2Sr_6O_2(OPh)_{14}(HMPA)_6\cdot 2PhMe$		
chem formula	$C_{120}H_{178}Ba_2N_{18}O_{22}P_6Sr_6\cdot 2C_7H_8$	fw	3395.36
		space group	$P2_1/n$
a, Å	17.797(2)	T, °C	−158 °C
b, Å	17.421(2)	λ Å	0.710 69
c, Å	26.624(3)	ρ_{calcd}, g cm^{-3}	1.433
β, deg	107.62(0)	μ(Mo Kα), cm^{-1}	25.7
V, Å^3	7867.27	R	0.148
Z	2	R_w	0.157

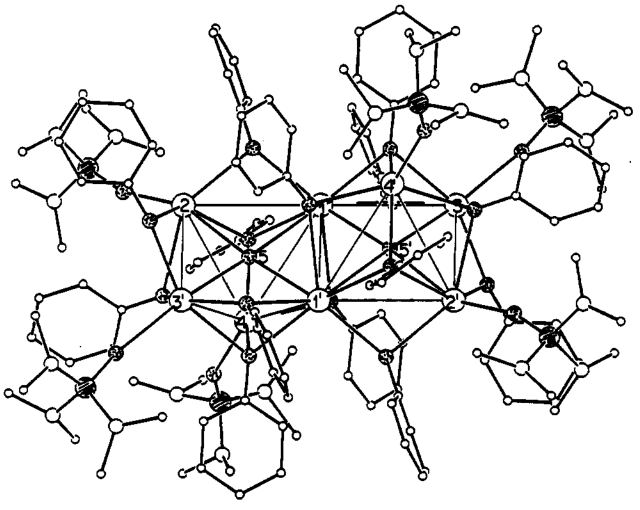

Figure 1. ORTEP drawing the non-hydrogen atoms of $H_2Ba_8O_2(OPh)_{14}[OP(NMe_2)_3]_6$, showing selected atom labeling. A center of symmetry lies between Ba1 and Ba1′. Only the metals and the oxide oxygens are labeled. Oxygen atoms are stippled, phosphorus atoms are hatched, and nitrogen and carbon atoms are open circles. Lines between metals are visual aids, not bonds.

$H_2Ba_2Sr_6O_2(OPh)_{14}[OP(NMe_2)_3]_6\cdot$2toluene. A rather large single crystal was selected and transferred to the goniostat using inert atmosphere handling techniques. The crystal was cooled to −158 °C for characterization and data collection.[15] A systematic search of a limited hemisphere of reciprocal space yielded a set of 14 reflections which exhibited monoclinic (2/m) Laue symmetry. The systematic extinction of h0l for h + l = 2n + 1 and of 0k0 for k = 2n + 1 uniquely identified the space group as $P2_1/n$ (Table II). Data collection (6° < 2θ < 45°) yielded only 4084 reflections by the criterion $F > 3.0\sigma(F)$, an indication that the quality of the data was poor, possibly due to disorder problems and/or large thermal motion. A plot of the standards did not indicate any systematic trends. The structure was solved by the usual combination of direct methods and Fourier techniques. All reflections were used in this procedure. The best E-map from MULTAN revealed four large peaks, located around a center of symmetry so that an eight-atom core was formed. Successive difference-maps phased with known atoms gradually revealed all of the oxygen atoms in the central core. Difficulties were encountered in locating the outer atoms in the molecule due to high thermal parameters and disorder of two phenyl rings and most of the NMe_2 groups. A molecule of toluene solvent was also located in the asymmetric unit. The final refinement model was anisotropic for all metal, O and P atoms. Rigid-body phenyl (B = 10) and NMe_2 (B = 15) groups were also used. The final difference Fourier map contained several

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Table II. Selected Bond Distances (Å) and Angles (deg) for $H_2Ba_8O_2(OPh)_{14}(HMPA)_6$

Ba(1)–Ba(2)	4.011(6)	Ba(2)–O(6)	2.626(12)
Ba(1)–Ba(3)′	4.026(5)	Ba(2)–O(13)	2.697(13)
Ba(1)–Ba(1)′	4.039(6)	Ba(2)–O(34)	2.743(13)
Ba(1)–Ba(4)	4.115(6)	Ba(2)–O(5)	2.764(12)
Ba(1)–Ba(4)′	4.139(5)	Ba(2)–O(41)	2.792(13)
Ba(2)–Ba(3)	3.967(5)	Ba(3)–O(13)	2.581(12)
Ba(2)–Ba(4)	3.999(5)	Ba(3)–O(66)	2.593(13)
Ba(3)–Ba(4)	3.987(6)	Ba(3)–O(20)	2.599(12)
Ba(1)–O(6)	2.629(12)	Ba(3)–O(41)	2.735(13)
Ba(1)–O(20)′	2.752(13)	Ba(3)–O(48)	2.778(13)
Ba(1)–O(48)′	2.844(13)	Ba(3)–O(5)	2.779(13)
Ba(1)–O(34)	2.858(13)	Ba(4)–O(77)	2.610(11)
Ba(1)–O(5)	2.878(11)	Ba(4)–O(27)	2.619(11)
Ba(1)–O(5)′	2.939(13)	Ba(4)–O(48)	2.645(12)
Ba(1)–O(27)	2.900(12)	Ba(4)–O(34)	2.656(11)
Ba(1)–O(27)′	2.901(13)	Ba(4)–O(41)	2.663(11)
Ba(2)–O(55)	2.589(13)	Ba(4)–O(5)	2.755(12)

O(6)–Ba(1)–O(20)	126.52(4)	O(6)–Ba(2)–O(41)	142.24(3)
O(6)–Ba(1)–O(48)′	99.01(4)	O(13)–Ba(2)–O(34)	139.05(4)
O(6)–Ba(1)–O(34)	72.10(5)	O(13)–Ba(2)–O(5)	74.52(4)
O(6)–Ba(1)–O(5)′	144.95(4)	O(13)–Ba(2)–O(41)	74.33(4)
O(6)–Ba(1)–O(27)′	81.61(4)	O(34)–Ba(2)–O(5)	66.54(5)
O(6)–Ba(1)–O(27)	136.55(5)	O(34)–Ba(2)–O(41)	78.39(4)
O(6)–Ba(1)–O(5)	76.75(4)	O(5)–Ba(2)–O(41)	65.49(5)
O(20)–Ba(1)–O(48)	69.67(3)	O(13)–Ba(3)–O(20)	112.33(4)
O(20)–Ba(1)–O(34)	102.91(4)	O(13)–Ba(3)–O(41)	77.17(3)
O(20)–Ba(1)–O(5)	78.05(4)	O(13)–Ba(3)–O(48)	140.58(3)
O(20)–Ba(1)–O(27)	136.40(3)	O(13)–Ba(3)–O(5)	76.09(4)
O(20)–Ba(1)–O(27)′	86.87(4)	O(66)–Ba(3)–O(20)	108.63(4)
O(20)–Ba(1)–O(5)	149.71(4)	O(66)–Ba(3)–O(41)	99.18(4)
O(48)–Ba(1)–O(34)	162.40(4)	O(66)–Ba(3)–O(48)	104.61(5)
O(48)–Ba(1)–O(5)	63.58(3)	O(66)–Ba(3)–O(5)	163.11(4)
O(48)–Ba(1)–O(27)	73.76(4)	O(20)–Ba(3)–O(41)	144.28(3)
O(48)–Ba(1)–O(27)′	120.32(4)	O(20)–Ba(3)–O(48)	73.89(4)
O(48)–Ba(1)–O(5)	131.15(3)	O(20)–Ba(3)–O(5)	82.45(5)
O(34)–Ba(1)–O(5)	131.88(4)	O(41)–Ba(3)–O(48)	78.83(4)
O(34)–Ba(1)–O(27)	118.50(4)	O(41)–Ba(3)–O(5)	66.05(5)
O(34)–Ba(1)–O(27)′	73.86(4)	O(48)–Ba(3)–O(5)	65.70(4)
O(34)–Ba(1)–O(5)	62.79(3)	O(77)–Ba(4)–O(27)	129.82(3)
O(5)–Ba(1)–O(27)	64.73(4)	O(77)–Ba(4)–O(48)	114.29(3)
O(5)–Ba(1)–O(27)′	58.07(4)	O(77)–Ba(4)–O(34)	107.79(3)
O(5)–Ba(1)–O(5)′	92.07(4)	O(77)–Ba(4)–O(41)	92.53(3)
O(27)–Ba(1)–O(27)′	91.74(4)	O(77)–Ba(4)–O(5)	159.64(4)
O(27)–Ba(1)–O(5)	57.41(5)	O(27)–Ba(4)–O(48)	81.82(3)
O(27)–Ba(1)–O(5)′	63.96(4)	O(27)–Ba(4)–O(34)	81.99(3)
O(55)–Ba(2)–O(6)	116.13(4)	O(27)–Ba(4)–O(41)	137.57(3)
O(55)–Ba(2)–O(13)	115.10(5)	O(27)–Ba(4)–O(5)	70.22(5)
O(55)–Ba(2)–O(34)	95.35(4)	O(48)–Ba(4)–O(34)	135.64(3)
O(55)–Ba(2)–O(5)	152.51(3)	O(48)–Ba(4)–O(41)	82.52(3)
O(55)–Ba(2)–O(41)	91.48(4)	O(48)–Ba(4)–O(5)	67.83(4)
O(6)–Ba(2)–O(13)	111.78(4)	O(34)–Ba(4)–O(41)	82.26(3)
O(6)–Ba(2)–O(34)	74.05(4)	O(34)–Ba(4)–O(5)	67.84(3)
O(6)–Ba(2)–O(5)	79.97(4)	O(41)–Ba(4)–O(5)	67.35(4)

Table III. Selected Bond Distances (Å) and Angles (deg) for $H_2Ba_2Sr_6O_2(OPh)_{14}(HMPA)_6$

Ba(1)–Ba(1)′	4.037(5)	Sr(2)–O(13)	2.62(4)
Ba(1)–Sr(2)	3.987(5)	Sr(2)–O(34)	2.69(3)
Ba(1)–Sr(3)	4.018(5)	Sr(2)–O(41)	2.71(3)
Ba(1)–Sr(4)	3.986(6)	Sr(2)–O(55)	2.57(3)
Ba(1)–Sr(4)′	4.009(5)	Sr(3)′–Sr(4)	3.816(6)
Sr(2)–Sr(3)′	3.874(6)	Sr(3)–O(13)′	2.57(5)
Sr(2)–Sr(4)	3.821(6)	Sr(3)–O(20)	2.52(3)
Sr(3)–O(5)′	2.711(27)	Sr(3)–O(41)′	2.74(3)
Ba(1)–O(5)	2.926(27)	Sr(3)–O(48)	2.76(3)
Ba(1)–O(5)′	2.943(23)	Sr(3)–O(66)	2.45(5)
Ba(1)–O(6)	2.66(3)	Sr(4)–O(5)	2.572(28)
Ba(1)–O(20)	2.61(3)	Sr(4)–O(27)	2.522(27)
Ba(1)–O(27)	2.86(3)	Sr(4)–O(34)	2.492(27)
Ba(1)–O(27)′	2.869(28)	Sr(4)–O(41)	2.516(28)
Ba(1)–O(34)	2.861(25)	Sr(4)–O(48)′	2.45(3)
Ba(1)–O(48)	2.85(3)	Sr(4)–O(77)	2.38(3)
Sr(2)–O(5)	2.690(22)	O(5)–O(27)′	2.83(5)
Sr(2)–O(6)	2.58(5)		

Ba(1)′–Ba(1)–Sr(2)	88.99(12)	O(5)′–Sr(3)–O(13)′	77.9(11)
Ba(1)′–Ba(1)–Sr(3)	88.69(10)	O(5)′–Sr(3)–O(20)	78.2(9)
Ba(1)′–Ba(1)–Sr(4)	59.95(10)	O(5)′–Sr(3)–O(41)′	65.0(8)
Ba(1)′–Ba(1)–Sr(4)′	59.40(9)	O(5)′–Sr(3)–O(48)	64.9(8)
Sr(2)–Ba(1)–Sr(3)	177.59(12)	O(5)′–Sr(3)–O(66)	178.2(13)
Sr(2)–Ba(1)–Sr(4)	57.27(10)	O(13)′–Sr(3)–O(20)	112.4(13)
Sr(2)–Ba(1)–Sr(4)′	121.32(12)	O(13)′–Sr(3)–O(41)′	75.0(11)
Sr(3)–Ba(1)–Sr(4)	121.87(12)	O(13)′–Sr(3)–O(48)	139.9(12)
Sr(3)–Ba(1)–Sr(4)′	56.76(9)	O(13)′–Sr(3)–O(66)	102.4(15)
Sr(4)–Ba(1)–Sr(4)′	119.35(9)	O(20)–Sr(3)–O(41)′	140.2(10)
O(5)–Ba(1)–O(5)′	93.1(7)	O(20)–Sr(3)–O(48)	75.1(11)
O(5)–Ba(1)–O(6)	76.6(11)	O(20)–Sr(3)–O(66)	100.1(13)
O(5)′–Ba(1)–O(6)	148.6(9)	O(41)′–Sr(3)–O(48)	76.1(8)
O(5)′–Ba(1)–O(20)	72.6(9)	O(41)′–Sr(3)–O(66)	116.9(13)
O(5)–Ba(1)–O(20)	145.1(10)	O(48)–Sr(3)–O(66)	115.3(13)
O(5)–Ba(1)–O(27)	63.7(8)	Ba(1)′–Sr(4)–Ba(1)	60.65(9)
O(5)–Ba(1)–O(27)′	58.4(8)	Ba(1)′–Sr(4)–Sr(2)	91.78(12)
O(5)′–Ba(1)–O(27)	58.3(7)	Ba(1)–Sr(4)–Sr(2)	61.38(10)
O(5)′–Ba(1)–O(27)′	63.4(7)	Ba(1)–Sr(4)–Sr(3)′	92.36(13)
O(5)–Ba(1)–O(34)	60.9(8)	Ba(1)′–Sr(4)–Sr(3)′	61.75(10)
O(5)′–Ba(1)–O(34)	130.8(8)	Sr(2)–Sr(4)–Sr(3)′	60.97(12)
O(5)–Ba(1)–O(48)	128.9(8)	O(5)–Sr(4)–O(27)	73.7(9)
O(5)′–Ba(1)–O(48)	60.9(8)	O(5)–Sr(4)–O(34)	70.7(8)
O(6)–Ba(1)–O(20)	130.8(12)	O(5)–Sr(4)–O(41)	70.2(9)
O(6)–Ba(1)–O(27)	134.9(11)	O(5)–Sr(4)–O(48)′	71.5(10)
O(6)–Ba(1)–O(27)′	86.4(9)	O(5)–Sr(4)–O(77)	168.9(10)
O(6)–Ba(1)–O(34)	69.7(11)	O(27)–Sr(4)–O(34)	84.9(9)
O(6)–Ba(1)–O(48)	102.6(12)	O(27)–Sr(4)–O(41)	143.9(10)
O(20)–Ba(1)–O(27)	82.0(11)	O(27)–Sr(4)–O(48)′	83.1(10)
O(20)–Ba(1)–O(27)′	132.0(9)	O(27)–Sr(4)–O(77)	117.2(11)
O(20)–Ba(1)–O(34)	104.5(10)	O(34)–Sr(4)–O(41)	82.8(10)
O(20)–Ba(1)–O(48)	72.1(10)	O(34)–Sr(4)–O(48)′	142.2(11)
O(27)–Ba(1)–O(27)′	90.4(8)	O(34)–Sr(4)–O(77)	106.9(10)
O(27)–Ba(1)–O(34)	72.5(8)	O(41)–Sr(4)–O(48)′	86.2(10)
O(27)′–Ba(1)–O(34)	118.2(8)	O(41)–Sr(4)–O(77)	98.9(11)
O(27)–Ba(1)–O(48)	118.5(8)	O(48)′–Sr(4)–O(77)	110.6(12)
O(27)′–Ba(1)–O(48)	70.5(8)	Ba(1)′–O(5)–Ba(1)	86.9(7)
O(34)–Ba(1)–O(48)	167.0(8)	Ba(1)–O(5)–Sr(2)	173.4(11)
Ba(1)–Sr(2)–Sr(3)′	91.46(10)	Ba(1)–O(5)–Sr(3)′	90.5(7)
Ba(1)–Sr(2)–Sr(4)	61.35(10)	Ba(1)–O(5)–Sr(4)	93.0(7)
Sr(3)′–Sr(2)–Sr(4)	59.45(11)	Sr(2)–O(5)–Sr(3)′	91.7(8)
O(5)–Sr(2)–O(6)	82.4(9)	Sr(2)–O(5)–Sr(4)	93.1(8)
O(5)–Sr(2)–O(13)	77.5(11)	Sr(3)′–O(5)–Sr(4)	92.4(9)
O(5)–Sr(2)–O(34)	66.0(8)	Ba(1)–O(6)–Sr(2)	99.2(12)
O(5)–Sr(2)–O(41)	65.7(8)	Sr(2)–O(13)–Sr(3)′	96.5(16)
O(5)–Sr(2)–O(55)	171.4(11)	Ba(1)′–O(20)–Sr(3)′	103.1(11)
O(6)–Sr(2)–O(13)	118.2(11)	Ba(1)′–O(27)–Ba(1)	89.6(8)
O(6)–Sr(2)–O(34)	73.7(10)	Ba(1)–O(27)–Sr(4)	95.9(9)
O(6)–Sr(2)–O(41)	142.5(9)	Ba(1)′–O(27)–Sr(4)	95.4(8)
O(6)–Sr(2)–O(55)	105.1(13)	Ba(1)–O(34)–Sr(2)	91.8(8)
O(13)–Sr(2)–O(34)	140.0(12)	Ba(1)–O(34)–Sr(4)	96.0(8)
O(13)–Sr(2)–O(41)	74.8(11)	Sr(2)–O(34)–Sr(4)	94.9(10)
O(13)–Sr(2)–O(55)	102.1(14)	Sr(2)–O(41)–Sr(3)′	90.6(10)
O(34)–Sr(2)–O(41)	75.7(9)	Sr(2)–O(41)–Sr(4)	93.9(10)
O(34)–Sr(2)–O(55)	111.5(11)	Sr(3)′–O(41)–Sr(4)	93.0(9)
O(41)–Sr(2)–O(55)	105.8(11)	Ba(1)′–O(48)′–Sr(3)′	91.4(10)
Ba(1)–Sr(3)–Sr(2)′	90.86(12)	Ba(1)′–O(48)′–Sr(4)	98.0(11)
Ba(1)–Sr(3)–Sr(4)′	61.49(10)	Sr(3)′–O(48)′–Sr(4)	93.9(10)
Sr(2)′–Sr(3)–Sr(4)′	59.58(11)		

peaks of 2–3 e/Å^3 in the vicinity of the metal atoms; many peaks of about 1 e were located in the area of the disordered ligands. The results of the structure determination are shown in Table III and Figure 2.

Results and Discussion

Synthesis. The reaction of barium metal granules with phenol and HMPA in toluene proceeds rapidly at ambient temperature, being complete in 20 min. The reaction of barium metal granules with phenol (but no added HMPA) in the presence of $Sr_3(OPh)_6(HMPA)_5$[14] in toluene takes 5 h at reflux to reach completion; we attribute this slow rate to the absence of free HMPA. In both cases, crystallization from the reaction mixture and layering with *n*-pentane yields colorless crystals. These products are formulated as $H_2Ba_8(\mu_5\text{-}O)_2(\mu_3\text{-}OPh)_8(\mu_2\text{-}OPH)_6(HMPA)_6\cdot 2PhMe$ (I) and the mixed-metal aggregate $H_2Sr_6Ba_2(\mu_5\text{-}O)_2(\mu_3\text{-}OPh)_8(\mu_2\text{-}OPh)_6(HMPA)_6\cdot 2PhMe$ (II) on the basis of single-crystal X-ray diffraction studies.

The two aggregates I and II are effectively HMPA deficient (compare with $Sr_3(OPh)_6(HMPA)_5$[14] or $HBa_5(O)(OPh)_9$-

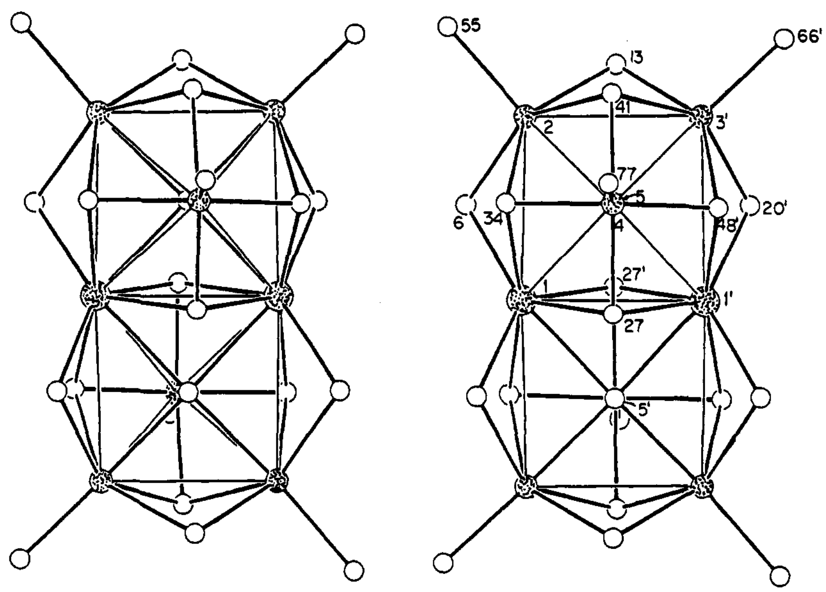


Figure 2. Stereo ORTEP drawing of the $Ba_2Sr_6O_{22}$ portion of $H_2Ba_2Sr_6O_2(OPh)_{14}[OP(NMe_2)_3]_6$ showing selected atom labeling. Ba and Sr atoms are stippled and oxygen atoms are open circles. Primes indicate atoms related by the crystallographic center of symmetry located between Ba1 and Ba1'. Atoms 2–4 are Sr.

$(THF)_8$,[13] with higher terminal ligand:metal ratios) on the two central barium atoms (i.e., <1 HMPA per metal). These metal sites therefore increase their coordination number by being ligated to two extra μ_3-OPh ligands. If 2 equiv of HMPA is used in the preparation of **I** (or if additional HMPA is added in the second step of the synthsis of II), then only an oil is obtained, i.e., either I and II is extremely soluble in this Lewis base, or different, more soluble highly solvated species are produced.

Spectroscopic Data. Compound I and II each exhibited an OH band in their IR spectra. NMR spectroscopic studies in d_8-toluene showed that for both ^1H and ^{13}C it was not possible to freeze out the different phenoxide environments in solution; the different phenoxide environments are involved in a migrational interchange. The $^{31}P\{^1H\}$ NMR spectra of I and II at ambient temperature reveal one sharp peak; on cooling, decoalescence was not observed. A rapid fluxional process is also occurring to equilibrate the two different (see below) HMPA environments.

Since the nature of the complexes I and II could not be fully elucidated by spectroscopic techniques, X-ray single-crystal molecular studies were undertaken to unambiguously identify their structures.

Crystal and Molecular Structures. In each solid, the toluene molecules fill holes in the lattice, and do not interact with the metals. Of particular interest is the structure of the eight-metal aggregates and the question of selectivity vs. positional disorder of the two alkaline earth metals in compound II.

While the crystals are not isomorphous,[16] the molecular structures of I and II are shown in Figures 1 and 2. Since the structures are essentially identical, the two figures in effect represent different perspectives on the same structure. A number of points are worthy of mention:

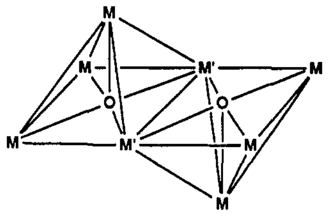
1. The structure contains two square-based pyramidal $M_5(\mu_5\text{-}O)$ units, similar to that in the recently reported $HBa_5(\mu_5\text{-}O)(OPh)_9(THF)_8$,[13] although in the present cases they are Ba_5 in I and Sr_3Ba_2 in II. Both *I* and *II* possess a crystallographically-imposed center of symmetry between Ba1 and Ba1'.

2. The apical metal atoms are bonded to four μ_3-OPh ligands that cap the four triangular faces of the square-based pyramidal core. The metal atoms in the basal plane are connected by these same four μ_3- as well as by three μ_2-OPh groups that project on the side of the basal plane opposite to the apical metal.

3. The two M_5O units are fused along one basal edge, with the apical atoms projecting to the opposite sides of the $M_6(\mu_5\text{-}O)_2$ plane containing the basal metals. The $M_6(\mu_5\text{-}O)_2$ part of these aggregates is essentially planar. Those six metals not involved in the fused edge each bear one terminal HMPA ligand. There are no terminal phenoxides in I or II.

4. The $M_5(\mu_5\text{-}O)$ unit is related to the rock-salt structure of the parent metal oxides and, as such, can be considered a fragment of the parent structure.

5. In both I and II, each metal atom in the two M_3 triangles is coordinated to a terminal HMPA ligand to yield a coordination number of 6. In contrast, the two central (barium) metal atoms (M') achieve a higher coordination number (as expected for a cation as large as Ba^{2+}) through the agency of the oxo groups, four μ_3- and two μ_2-OPh ligands. This yields eight-coordinate metal centers. This site in the fused square pyramids carries no terminal ligand.



6. The six-coordinate Ba–(μ_3-O) bond distances to the apical metal atom in I are notably (≥0.1 Å) shorter than those involving the metal atoms in the basal plane. All Ba–O distances to eight-coordinate barium in I are larger than those to six-coordinate barium. For six-coordinate basal barium, the bond length trend is Ba–(μ_2-O) (average 2.626 Å) < Ba–(μ_3-O) (average 2.762 Å) < Ba–(μ_5-O) (average 2.771 Å). The ability of the metal atoms to synthesize and assemble a ligand set of their choice is evident from the unexpected appearance of the μ_5-oxo moiety in I and II. The partial encapsulation of an oxide (μ_5-O) finds extensive parallel with the encapsulation of light main group atoms (e.g., Be, B, C, N) in the synthesis of transition metal clusters.[17] This

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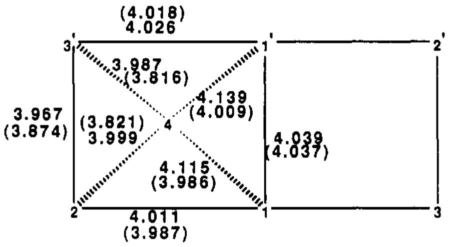
(16) The two compounds are not isomorphous. However, least-squares fits of the two structures (see supplementary material) show the *molecular* structures to differ only in the conformations of the HMPA and the OPh groups.

(17) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 4844. Corbett, J. D. *Acc. Chem. Res.* **1989**, *22*, 256.

is also observed in the recent synthesis of the oxo alkoxides $M_5(\mu_5\text{-}O)(OPr^i)_{13}$ where M = In[18] and Y.[18,19]

7. Shown in the following diagram are the nonbonded metal/metal separations in I and (in parentheses) II. These reflect the (mirror) symmetry of the bonding of the bridging ligands, as well as the near-invariance of the Ba1/Ba1′ separation in I and II. While Sr/Sr separations are 0.10–0.18 Å shorter than Ba/Ba separations in sites 2–4, there is a curious invariance of the 1/2 and 1′/3′ separations when strontium is substituted for barium. The longest M/M separations are consistently from the apical metal to the seven-coordinate barium at the edge fusion site.



I(II)

8. Finally, there is the question of the location of the hydrogens in the two title complexes. It seems quite reasonable to assume that barium is present in an oxidation state of +2 which leads us to formulate the atoms located crystallographically in I and II as $[M_8(\mu_5\text{-}O)_2(OPh)_{14}(HMPA)_6]^{2-}$. Although the protons themselves were not evident in the single-crystal X-ray diffraction studies, they are surely associated with the oxygen atoms. An inspection of the O···O and Ba–O distances and Ba–O–C angles in I and II does provide a possible location for the protons. There is a short O(5)′–O(27) contact distance of 2.80 Å between the oxo group and the μ_3-OPh group in I; in II, this distance is 2.83 Å. Thus, and in spite of the fact the O(5) is already bound to five metal centers, we suggest that there are two hydrogen-bonded groups $[O(5)\text{–}H\text{–}O(27)Ph]^-$ in both I and II. For comparison, the next shortest O/O separation is 3.00 Å between O(5) and O(41).

Final Comments. Rather surprising is the observation that the triangular Sr_3 unit used in the synthesis of II is also found in the product, since the kinetic lability of alkaline earth ions might have been expected to lead to a Ba_2Sr_6 species with disordered metal site occupancies (or even a mixture of Ba_nSr_{8-n} species). It is probable that the obtained compound II is the thermodynamically-favored product, due to the distinct coordination numbers provided by the observed structure. There are thus two "natural" sites for the larger barium ions, and this provides the basis of the observed selectivity in the synthesis. With barium favored at the juncture of the two square pyramids, the preformed Sr_3 triangle is obviously a particularly favorable reagent for this purpose. One can view the aggregate II as formed by the linking of two Sr_3 units to the Ba atoms; linkage occurs via a μ_2-OPh ligand of the Sr_3 triangle, which thus becomes μ_3-coordinated. This fusion is augmented by hydrogen bonding.

Particularly since we have made compound II from a barium source and an Sr_3 compound, it is of interest to speculate on the mechanism of cluster assembly. It is evident that the M_8O_2 structural unit is the fusion of an M_5O square pyramid and an M_3 triangle, but these two species must *each* furnish an oxo (or hydroxo) ligand. That is, the species condensing to form $Ba_8(OH)_2(OPh)_{14}(HMPA)_6$ are $Ba_5(OH)(OPh)_9$ and $Ba_3(OH)(OPh)_5$ (with six additional HMPA molecules). This latter species implies either the presence of a higher OH:Ba ratio than for the synthesis of $Ba_5(OH)(OPh)_9(THF)_8$[13] or the ready conversion of the $Ba_5(OH)(OPh)_9$ unit into $Ba_3(OH)(OPh)_5$ and $[Ba_2(OPh)_4]_n$. We have reported separately[20] two examples of $Ba_2(OR)_4L_n$ species.

Finally, thermogravimetric analysis of II shows that this material decomposes in three stages to yield a material analyzing as $HSr_6Ba_2(O)_3(OPh)_{11}$. It is noteworthy that, even after heating to 680 °C, phenoxide ligands remain in this material. This behavior attests to the remarkable thermal stability of alkaline earth phenoxide complexes.

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Supplementary Material Available: Tables of full crystallographic details, anisotropic thermal parameters, and fractional coordinates and fully labeled figures (9 pages). Ordering information is given on any current masthead page.

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