Formation and Solid State Structure of a Tetranuclear Oxoaryloxide Cluster of Barium, $[Ba_4(\mu_4\text{-}O)(\mu_2\text{-}OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6)_6]\cdot 3(\text{toluene})$

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The tetranuclear oxo–aryloxide cluster, $[Ba_4(\mu_4\text{-}O)(\mu_2\text{-}OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6)_6]\cdot 3(\text{toluene})$, synthesized from the reaction of $K[(OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6]$ and BaI_2 in tetrahydrofuran, crystallizes from toluene as a tetrahedron of barium atoms encapsulating a single oxo ligand, the metal centres coordinated by six μ_2-aryloxide groups and the nitrogen atoms of the *ortho*-dimethylaminomethyl groups.

Barium amides, alkoxides and aryloxides have drawn increasing attention as potential precursors to barium-containing oxides, including the high-T_c superconducting ceramics[1–4] and materials with valuable electronic properties.[5]

The conceptual gap between discrete molecular alkoxides and nonmolecular oxides is bridged to some extent by oxo-alkoxide and -aryloxide complexes.[6] The formation and structure of several barium derivatives have been the subject of recent reports.[7,8] We describe here an oxo–aryloxide of barium derived from the substituted phenol 2,4,6-$(Me_2NCH_2)_3C_6H_2OH$ [(2,4,6-tris(dimethylaminomethyl)-phenol = tamp-OH] that extends the range of synthetic methods applicable to these compounds and introduces several novel structural features.

The reaction of tamp-OH with KH in thf (thf = tetrahydrofuran) generates the salt K(O-tamp), which in turn reacts with one-half equivalent of BaI_2 to produce an immediate precipitate of KI. After filtration to remove the precipitate and evaporation of the filtrate to a small volume, addition of toluene and evaporation to dryness yields the pale-yellow solid $Ba_4O(\text{O-tamp})_6$ in 65% yield.† Attempted sublimation

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† Analysis for C, H, N and Ba is incomplete, but the elemental ratios are consistent with the proposed formulation. ^1H NMR data (400 MHz, C_6D_6): δ 2.01 (s, 6H, CH_3), 2.24 (s, 3H, CH_3), 3.40 (s, 2H, CH_2), 3.43 (s, 2H, CH_2), 3.48 (s, 2H, CH_2). ^{13}C NMR data (50.3 MHz, C_6D_6): δ 45.1 (q, CH_3), 45.3 (q, CH_3), 61.6 (br, CH_2) 64.7 (t, CH_2), 124.6 (d, C_6-3,5); other peaks obscured by C_6D_6 resonance.

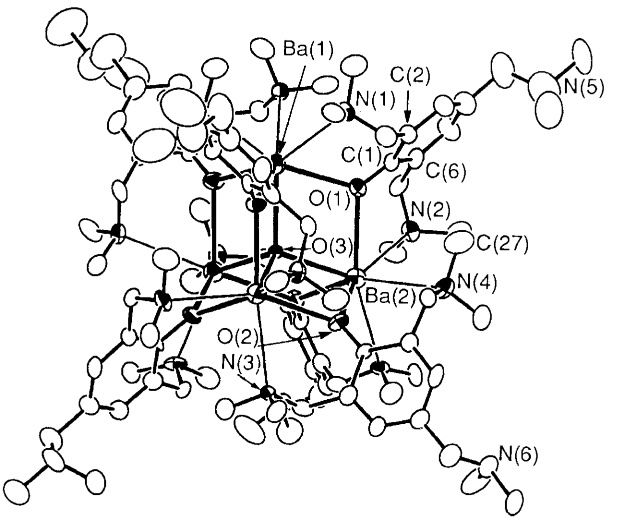

Fig. 1 ORTEP view of $Ba_4O(O\text{-tamp})_6{\cdot}3$ toluene. For clarity, thermal ellipsoids have been drawn at the 40% probability level and hydrogen atoms and the lattice toluenes have been omitted.

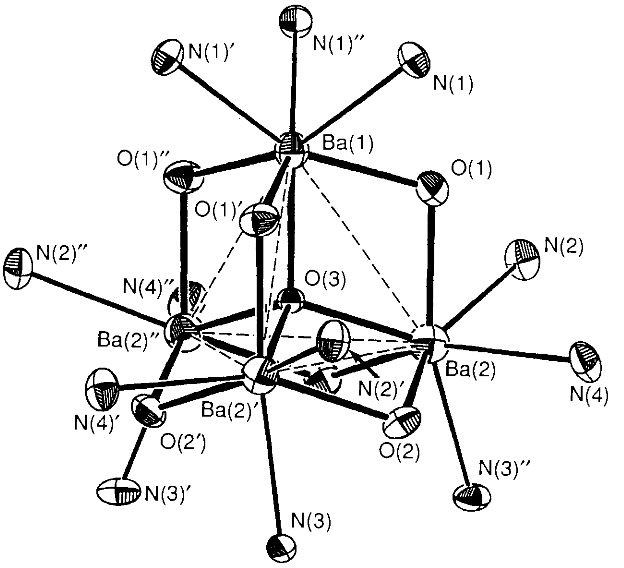

Fig. 2 ORTEP view of the tetranuclear core of $Ba_4O(O\text{-tamp})_6{\cdot}3$ toluene, with thermal ellipsoids drawn at the 50% probability level. The dashed lines drawn between the barium atoms are meant as a visualisation guide, and are not to suggest the presence of metal–metal bonding.

of the complex at 135 °C and 10^{-6} Torr results in decomposition. The origin of the oxo ligand is not yet known, but the reproducibly high yield of the cluster argues against the source being adventitious water.

The structure of the complex was determined by X-ray crystallography on a single crystal grown from toluene, a view of which is presented in Fig. 1.‡ The complex consists of a tetranuclear cluster of barium atoms encapsulating a μ_4-oxo ligand, the simplest polyhedral metal array yet observed among alkaline-earth oxo–alkoxide or –aryloxide complexes. Bridging O-tamp groups span each edge of the tetrahedron, and the nitrogen atoms of the *ortho*-dimethylaminomethyl groups also coordinate to the barium atoms, giving each metal a formal coordination number of seven. Three molecules of toluene per cluster are found in the lattice, but they are no closer than 3.8 Å to the cluster.

Only C_3 crystallographic symmetry is imposed on the complex, with the threefold axis containing the apical Ba(1) and the oxo ligand O(3), but the Ba_4 core is nearly a perfect tetrahedron (Fig. 2). It is slightly compressed, with an apical Ba(1) to basal Ba(2) distance of 4.339(2) Å and a Ba(2)···Ba(2)′ distance of 4.375(2) Å; there is thus, no direct metal–metal interaction. The oxo ligand is situated 2.65(2) Å from the apical barium and 2.675(7) Å from the basal metal atoms.

The aryloxide ligands symmetrically bridge the edges of the Ba_4 tetrahedron, with Ba(1)–O(1), Ba(2)–O(1), and Ba(2)–O(2) distances of 2.70(1), 2.73(1) and 2.74(1) Å, respectively. The *ortho*-dimethylamino nitrogens exhibit greater differences in their approaches to the barium centres. The aryloxide group spanning the apical and basal barium atoms (ring 1) displays N(1)–Ba(1) and N(2)–Ba(2) distances of 3.10(1) and 3.07(1) Å. These are appreciably longer than the distances between four-coordinate Ba and the bridging bis(trimethylsilyl)amido groups in $\{Ba[N(SiMe_3)_2]_2(thf)\}_2$ [2.834(9) Å and 2.903(10) Å],[1] but given the difference in coordination number and the corresponding size of the barium centres, the effective difference in Ba–N length between the complexes is only 0.04–0.14 Å.[9] An analogous comparison can be made with the 2.867(7) Å and 2.937(6) Å contacts found between the seven-coordinate barium and the neutral pyrazine in the $[(Me_5C_5)_2Ba]_2(\mu\text{-}C_6H_4N_2)$ dimers.[10] The orientation of the dimethylamino groups in $Ba_4O(O\text{-tamp})_6$ suggests that the Ba–N distances, despite their length, should still be considered as bonding contacts.

In contrast to ring 1, the Ba–N contacts of the aryloxide joining Ba(2) to Ba(2)′ (ring 2) are clearly unequal, at 3.07(1) Å [N(3)–Ba(2)] and 3.16(1) Å [N(4)–Ba(2)′]. The latter distance is undoubtedly controlled by steric congestion between the aryloxide ligands. The methyl carbon C(27), for example, displays several close contacts to the atoms of ring 1, including a 3.58(3) Å distance to C(2), and a 3.38(3) Å distance to C(1). Such restraints on the methyl positions limit the approach of the nitrogen to the barium centres. It should be pointed out that the differences between ring 1 and 2 do not exist in solution, as the aryloxide groups are equivalent on the NMR time-scale.

The planes of the aryloxide ligands are canted about the Ba_4 core. The tilt angle beween the Ba(1)–Ba(2)–O(3) plane and that defined by the aromatic carbon atoms of ring 1 is 55.8°; that between the basal $Ba(2)_3$ plane and ring 2 is 24.7°. These orientations create a 'propeller-like' arrangement of rings, and the molecule is accordingly chiral.

Several features of the complex are worth noting. (*i*) This oxo–aryloxide is the first formed by the metathetical reaction of an alkali metal aryloxide and a barium halide, rather than beginning with the metal and the free phenol or alcohol. This probably contributes to the cluster's freedom from intermolecular hydrogen bonds or hydroxy groups.[8] (*ii*) The coordination of the barium atoms by both aryloxide oxygens and

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‡ *Crystal data* for $[Ba_4(\mu_4\text{-}O)\{\mu_2\text{-}OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6\}_6{\cdot}3C_7H_8]$: $C_{111}H_{180}Ba_4N_{18}O_7$, trigonal, space group $R3(h)$, $a = b = 27.899(3)$, $c = 13.528(4)$, $\alpha = \beta = 90°$, $\gamma = 120°$, $U = 9119(4)$ Å^3, $Z = 3$, $D_c = 1.326$ g cm^{-3}. Data were collected on a Rigaku AFC6S diffractometer at 293 K using graphite monochromated Cu-Kα-radiation. Continuous $\theta - 2\theta$ scans with fixed backgrounds were used to collect a total of 3361 intensities (3280 unique) in the range $6° < 2\theta < 120°$, of which 2330 had $F > 2\sigma(F)$. Data were reduced to a unique set of intensities and associated σ-values in the usual manner. The structure was solved with a combination of direct methods (MITHRIL, DIRDIF) and Fourier techniques. As not all hydrogen atoms were visible in a difference Fourier synthesis phased on the non-hydrogen parameters, they were inserted in calculated positions with $d = 0.95$ Å, and were fixed in the final cycles of refinement. $R(F) = 0.045$, $R_w(F) = 0.053$. A final difference Fourier was featureless, with the largest peak being 0.5 e Å^{-3}. The absolute configuration of the molecule was determined by inverting the signs of the coordinates and refining to convergence. The originally chosen configuration was judged correct.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

dimethylaminomethyl nitrogens is apparently responsible for the complex's lack of coordinated solvent, despite its synthesis in thf.[8] The amino groups undoubtedly occupy the coordination sites that otherwise would have been filled by thf.

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