Synthesis and structural characterisation of the heavier alkaline earth 2,6-di-iso-propylphenolate complexes†‡

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Redox transmetallation ligand exchange reactions involving a heavy alkaline earth metal, bis(pentafluorophenyl)mercury and 2,6-di-iso-propylphenol (HOdipp) in dme (1,2-dimethoxyethane) afforded alkaline earth aryloxo complexes which were structurally characterised. All complexes obtained were mononuclear, but the ionic radius of the alkaline earth metal was found to influence the number, and binding mode, of ligated dme molecules. Using Ca metal in the reaction afforded [Ca(Odipp)$_2$(dme)$_2$] **1** containing a six coordinate Ca metal atom and the phenolate ligands oriented in a cisoidal arrangement. Using Sr metal in the reaction yielded {3[Sr(Odipp)$_2$(dme)$_2$]·[Sr(Odipp)$_2$(dme)$_3$]} **2** containing both six and seven coordinate Sr metal atoms. The six coordinate species [Sr(Odipp)$_2$(dme)$_2$] contains phenolate ligands positioned in a cisoidal geometry. The seven coordinate species [Sr(Odipp)$_2$(dme)$_3$] contains a unidentate dme ligand, a rare binding mode for dme in alkaline earth chemistry. Using Ba metal in the reaction afforded [Ba(Odipp)$_2$(dme)$_3$] **3**, which contains an eight coordinate Ba metal atom.

Introduction

The synthesis of heavy alkaline earth organometallics, organoamides and aryloxides is attracting increasing attention due to the potential use of these species as catalysts in polymerisation and organic transformations,[1–6] and as molecular precursors in MOCVD and sol–gel processes.[7–12] Although the chemistry of the heavy alkaline earth elements is often comparable with that of the divalent rare earth elements due to similarities in size to charge ratios of elements,[13] the metal–organic chemistry of the heavy alkaline earth elements is still in its infancy.[14,15] Typical synthetic routes to heavy alkaline earth complexes are metathesis using anhydrous halides, and protolysis of alkaline earth precursors, such as the bis(trimethylsilylamides).[15,16] Both of these synthetic pathways have drawbacks, including the low solubility of heavy alkaline earth halides in organic solvents, and the necessity to synthesise or purchase air and moisture sensitive alkaline earth precursors. The preferred more soluble anhydrous alkaline earth iodides are very expensive in highly pure form. Metal based synthetic routes are a viable and cost-effective alternative to metathesis and protolysis reactions in the synthesis of rare earth complexes;[17–21] the highly electropositive alkaline earth metals are now finding increasing use as precursors in the synthesis of heavier alkaline earth complexes.[15,16] Activation of alkaline earth metals with anhydrous liquid ammonia has proved to be particularly fruitful, affording a range of alkaline earth complexes, including calcium Grignard reagents.[22,23] Treatment of alkaline earth metals with pyrazoles and bulky phenols (2,6-diphenylphenol and 2,6-dibenzylphenol) at elevated temperature afforded homoleptic alkaline earth pyrazolate[24–26] and phenolate complexes.[27,28] Redox transmetallation ligand exchange reactions involving an alkaline earth metal, a diarylmercurial and a protic ligand in thf or dme (1,2-dimethoxyethane) (eqn (1)) have afforded alkaline earth pyrazolate[24,25] and formamidinate complexes,[29,30] and we have recently reported the application of this synthetic route to the synthesis of alkaline earth complexes containing the moderately bulky 2,4,6-trimethylphenolate (Omes) ligand.[31] This success with Ca, Sr and Ba contributes to the wider applicability of the redox transmetallation ligand exchange synthetic method.

$$\begin{aligned} &\mathrm{Ae} + \mathrm{HgR_2} + 2\mathrm{HL} \xrightarrow{\text{solvent}} [\mathrm{AeL_2(solvent)}_x] + \mathrm{Hg} + 2\mathrm{RH} \\ &\mathrm{R} = \mathrm{C_6F_5, C_6H_5} \\ &\mathrm{L} = \text{pyrazolate, formamidinate} \\ &\text{solvent} = \text{thf, dme} \qquad (1) \end{aligned}$$

Aryloxide chemistry of the heavier alkaline earth metals has mainly focussed on very bulky ligands, such as 2,6-di-*tert*-butyl-4-R-phenolates (R = H, Me, ^{t}Bu), using predominantly metathesis and protolysis reactions.[32–38] The moderately bulky 2,6-di-iso-propylphenolate (Odipp) ligand has not been extensively studied in alkaline earth chemistry; the only structurally characterised examples are {2[Ca(Odipp)$_2$(thf)$_3$]·[Ca(Odipp)$_2$(thf)$_4$]}·thf and [Ca(μ-Odipp)(Odipp)(thf)$_2$]$_2$;[38] the heavier alkaline earth congeners are not reported. We report a study of the synthesis and structures of the heavy alkaline earth 2,6-di-iso-propylphenolates, prepared using redox transmetallation ligand exchange reactions in 1,2-dimethoxyethane (dme), to provide an understanding of the change in ionic radius on structures when a moderately bulky aryloxide ligand is used.

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Results and discussion

Synthesis and characterisation

Treatment of freshly filed calcium, strontium and barium metal with two equivalents of 2,6-di-iso-propylphenol (HOdipp) in dme at room temperature, in the presence of one equivalent of bis(pentafluorophenyl)mercury, affords monomeric alkaline earth 2,6-di-iso-propylphenolate complexes (Scheme 1). The structural influence of the increasing ionic radius of the heavy alkaline earth metals from Ca^{2+} to Ba^{2+} was evident, as employing Ca metal in the reaction afforded $[Ca(Odipp)_2(dme)_2]$ **1**, Sr metal yielded $\{3[Sr(Odipp)_2(dme)_2]\cdot[Sr(Odipp)_2(dme)_3]\}$ **2** and Ba metal afforded $[Ba(Odipp)_2(dme)_3]$ **3**.

The IR spectra of **1–3** display typical absorptions for phenolate ligands, and the absence of an O–H band at ~3300 cm^{-1} indicates complete consumption of the phenol during the reaction. The ^1H NMR spectrum of **1** performed in $[D_6]$benzene displays two aryloxide and two dme environments, while the ^1H NMR spectrum of **1** performed in $[D_8]$thf displays single aryloxide and dme environments, suggesting that **1** exists as a dimer in non-coordinating solvents. The ability of the Odipp ligand to support both monomeric and dimeric alkaline earth species has been previously exemplified by the isolation of both monomeric $\{2[Ca(Odipp)_2(thf)_3]\cdot[Ca(Odipp)_2(thf)_4]\}\cdot thf$ and dimeric $[Ca(\mu\text{-}Odipp)(Odipp)(thf)_2]_2$ complexes, by employing slight changes in the reaction conditions.[38] In the present case, in the absence of a donor medium, the dissociation (eqn 2(a)):

$$2[Ca(Odipp)_2(dme)_2] \xrightarrow{C_6D_6} [Ca(Odipp)(\mu\text{-}Odipp) \times (dme)]_2 + 2dme \quad (2a)$$

$$2[Ca(Odipp)_2(dme)_2] \xrightarrow{C_6D_6} [Ca(Odipp)(\mu\text{-}Odipp) \times (\eta^2\text{-}dme)(\eta^1\text{-}dme)]_2 \quad (2b)$$

may occur. It involves a reduction in coordination number from six to five, and a slight reduction in crowding.[39] Five coordination is observed in the $[Ca(Odipp)_2(thf)_3]$ component of $\{2[Ca(Odipp)_2(thf)_3]\cdot[Ca(Odipp)_2(thf)_4]$.[38] Alternatively, a rearrangement involving partial conversion to unidentate dme (eqn 2(b)), as observed in **2**, would also account for the ^1H NMR observations and would maintain the coordination number.

The ^1H NMR spectra of **2** (dissolved in $[D_6]$benzene) and **3** (dissolved in $[D_5]$pyridine) display single aryloxide and dme environments. Given that **2** contains two complexes with different coordination number and two different dme coordination modes, rapid exchange owing to the larger size of Sr must occur. In $[D_5]$-pyridine, used owing to solubility problems, displacement of dme by the solvent is likely. Elemental analyses and crystallographic studies unequivocally establish the identity of the complexes.

X-Ray crystallographic studies

X-Ray quality crystals of **1–3** were grown from dme at −20 °C. Relevant data collection and refinement parameters for all compounds are summarised in the Experimental section. Selected bond lengths (Å) and angles (°) are given in Tables 1 (**1** and **3**) and 2 (**2**), and structures are depicted in Fig. 1–4.

$[Ca(Odipp)_2(dme)_2]$ **1** (Fig. 1) crystallises in the monoclinic space group $P2_1/n$. The Ca metal atom is surrounded by two aryloxide ligands and two chelating dme ligands, giving a coordination number of six, and distorted octahedral

Table 1 Bond lengths (Å) and angles (°) for compounds **1** and **3**

	1 Ae = Ca	**3** Ae = Ba
Bond distances		
Ae(1)–O(1)	2.133(1)	2.506(1)
Ae(1)–O(2)	2.174(1)	2.515(1)
Ae(1)–O(3)	2.416(1)	2.790(1)
Ae(1)–O(4)	2.461(1)	2.938(1)
Ae(1)–O(5)	2.397(1)	2.874(1)
Ae(1)–O(6)	2.455(1)	2.878(1)
Ae(1)–O(7)		2.943(1)
Ae(1)–O(8)		2.844(1)
Bond angles		
O(1)–Ae(1)–O(2)	115.45(5)	125.99(4)
O(1)–Ae(1)–O(3)	89.89(5)	77.67(3)
O(1)–Ae(1)–O(4)	150.51(5)	130.72(3)
O(1)–Ae(1)–O(5)	96.73(5)	135.39(4)
O(1)–Ae(1)–O(6)	92.07(5)	94.93(4)
O(2)–Ae(1)–O(3)	100.99(5)	87.79(4)
O(2)–Ae(1)–O(4)	87.04(5)	74.81(3)
O(2)–Ae(1)–O(5)	89.93(5)	93.87(4)
O(2)–Ae(1)–O(6)	146.45(5)	136.17(4)
O(3)–Ae(1)–O(4)	66.14(5)	57.30(3)
O(3)–Ae(1)–O(5)	163.38(5)	128.44(4)
O(3)–Ae(1)–O(6)	97.66(5)	86.42(4)
O(4)–Ae(1)–O(5)	102.38(5)	73.49(3)
O(4)–Ae(1)–O(6)	75.36(5)	65.64(3)
O(5)–Ae(1)–O(6)	66.98(5)	58.02(5)
O(1)–Ae(1)–O(7)		73.19(4)
O(2)–Ae(1)–O(7)		127.16(4)
O(3)–Ae(1)–O(7)		143.59(4)
O(4)–Ae(1)–O(7)		134.19(3)
O(5)–Ae(1)–O(7)		66.12(4)
O(6)–Ae(1)–O(7)		74.96(4)
O(8)–Ae(1)–O(7)		57.07(4)
O(1)–Ae(1)–O(8)		86.80(4)
O(2)–Ae(1)–O(8)		74.03(4)
O(3)–Ae(1)–O(8)		142.46(4)
O(4)–Ae(1)–O(8)		141.19(3)
O(5)–Ae(1)–O(8)		86.13(4)
O(6)–Ae(1)–O(8)		129.27(4)

$$\begin{tikzcd}
{[Ca(Odipp)_2(dme)_2]} & Ae + Hg(C_6F_5)_2 + 2\,HOdipp \arrow[l, "dme", "Ae = Ca"'] \arrow[r, "dme", "Ae = Ba"'] \arrow[dd, "dme\ Ae = Sr"] & {[Ba(Odipp)_2(dme)_3]} \\
\mathbf{1} & & \mathbf{3} \\
& \{3[Sr(Odipp)_2(dme)_2]\cdot[Sr(Odipp)_2(dme)_3]\} & \\
& \mathbf{2} &
\end{tikzcd}$$

Scheme 1

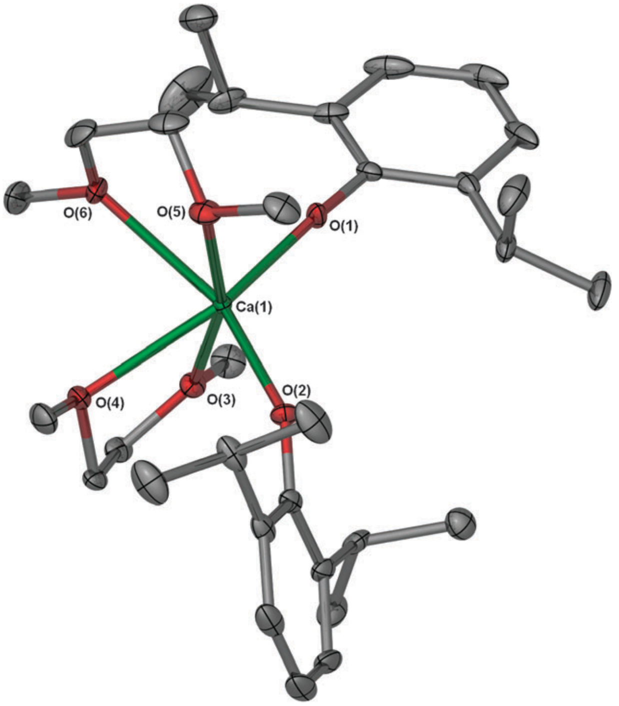

Fig. 1 Structure of [Ca(Odipp)$_2$(dme)$_2$], **1**. Hydrogen atoms are omitted for clarity.

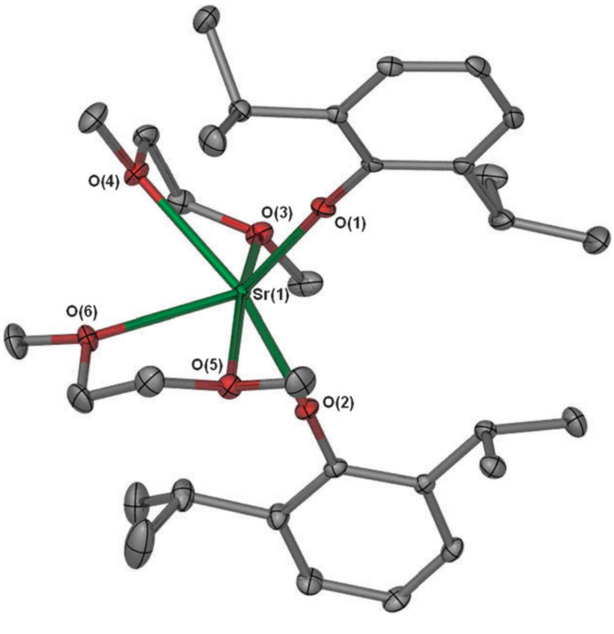

Fig. 2 Structure of [Sr(1)(Odipp)$_2$(dme)$_2$] in {3[Sr(Odipp)$_2$(dme)$_2$]·[Sr(Odipp)$_2$(dme)$_3$]}, **2**. Hydrogen atoms are omitted for clarity.

coordination geometry. The aryloxide ligands adopt a cisoid geometry around the Ca atom, demonstrated by the O–Ca–O (aryloxide) angle of 115.45(5)° (Table 1). The structural framework of **1** is quite similar to that of [Ca(Odmp)$_2$(dme)$_2$] (Odmp = 2,6-dimethylphenolate),[40] but is different from the dinuclear structural motif of [Ca$_2$(Omes)$_4$(dme)$_4$] (Omes = 2,4,6-trimethylphenolate),[31] indicating that small changes in the steric bulk of phenolate ligands (steric CN of Odipp 1.70; Odmp 1.59)[39] can lead to discernible structural differences.

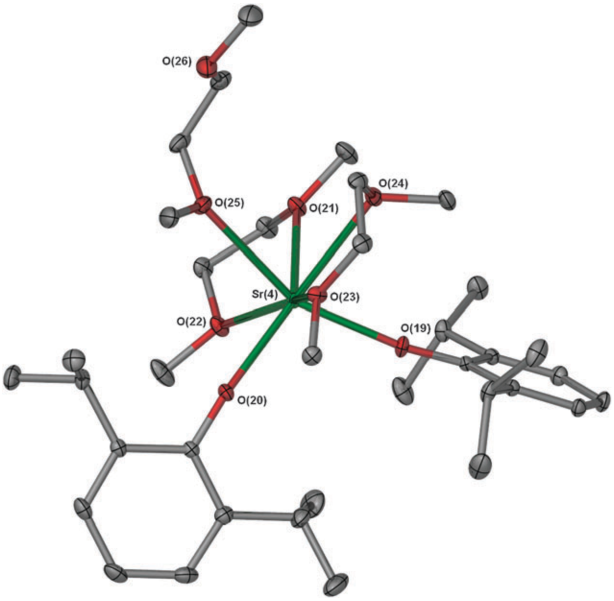

Fig. 3 Structure of [Sr(4)(Odipp)$_2$(dme)$_3$] in {3[Sr(Odipp)$_2$(dme)$_2$]·[Sr(Odipp)$_2$(dme)$_3$]}, **2**, depicting the unidentate dme ligand. Hydrogen atoms are omitted for clarity.

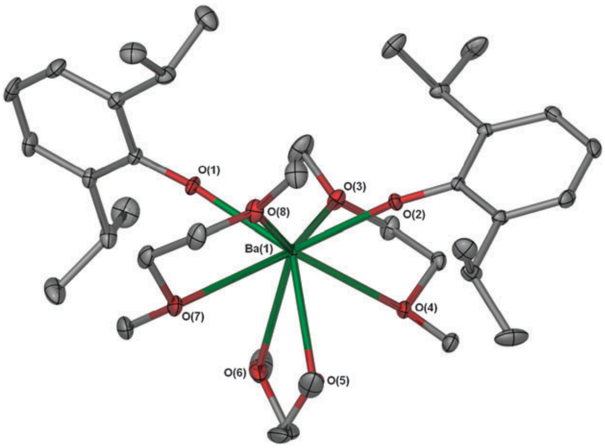

Fig. 4 Structure of [Ba(Odipp)$_2$(dme)$_3$], **3**. Hydrogen atoms are omitted for clarity.

In contrast to **1**, {3[Sr(Odipp)$_2$(dme)$_2$]·[Sr(Odipp)$_2$(dme)$_3$]} **2** crystallises in the triclinic space group $P\bar{1}$, and consists of three similar but crystallographically distinct [Sr(Odipp)$_2$(dme)$_2$] molecules and a [Sr(Odipp)$_2$(dme)$_3$] molecule. For brevity only [Sr(1)(Odipp)$_2$(dme)$_2$] (Fig. 2), and [Sr(4)(Odipp)$_2$(dme)$_3$] (Fig. 3) are discussed, and selected bond lengths and angles for **2** are listed in Table 2. The structure of six coordinate [Sr(1)(Odipp)$_2$(dme)$_2$] consists of two cisoidal aryloxide ligands and two chelating dme ligands; the O–Sr(1)–O (aryloxide) angle of 117.87(5)° (Table 2) is comparable to the analogous O–Ca–O angle (115.45(5)°) in **1**. However, in [Sr(1)(Odipp)$_2$(dme)$_2$] the coordination geometry displayed by the Sr atom is distorted trigonal antiprismatic, due to a different arrangement of dme ligands compared with **1**. The capping positions of the antiprism are: (a) O(1) from an aryloxide ligand, and O(5) and O(6) from a chelating dme ligand, and (b) O(2) from an aryloxide ligand and O(3) and O(4) from a chelating dme ligand.

Table 2 Bond lengths (Å) and angles (°) for compound **2**

Bond distances							
Sr(1)–O(1)	2.294(1)	Sr(2)–O(7)	2.310(1)	Sr(3)–O(13)	2.287(2)	Sr(4)–O(19)	2.317(1)
Sr(1)–O(2)	2.298(1)	Sr(2)–O(8)	2.287(2)	Sr(3)–O(14)	2.299(2)	Sr(4)–O(20)	2.356(1)
Sr(1)–O(3)	2.668(2)	Sr(2)–O(9)	2.642(2)	Sr(3)–O(15)	2.601(2)	Sr(4)–O(21)	2.704(1)
Sr(1)–O(4)	2.604(2)	Sr(2)–O(10)	2.618(2)	Sr(3)–O(16)	2.632(2)	Sr(4)–O(22)	2.654(1)
Sr(1)–O(5)	2.622(2)	Sr(2)–O(11)	2.608(2)	Sr(3)–O(17)	2.572(2)	Sr(4)–O(23)	2.638(1)
Sr(1)–O(6)	2.621(2)	Sr(2)–O(12)	2.606(1)	Sr(3)–O(18)	2.591(2)	Sr(4)–O(24)	2.691(1)
						Sr(4)–O(25)	2.658(2)
Bond angles							
O(1)–Sr(1)–O(2)	117.87(5)	O(7)–Sr(2)–O(8)	110.57(6)	O(13)–Sr(3)–O(14)	103.68(6)	O(19)–Sr(4)–O(20)	106.16(5)
O(1)–Sr(1)–O(3)	108.05(5)	O(7)–Sr(2)–O(9)	93.00(5)	O(13)–Sr(3)–O(15)	87.06(6)	O(19)–Sr(4)–O(21)	95.76(5)
O(1)–Sr(1)–O(4)	97.17(5)	O(7)–Sr(2)–O(10)	119.11(7)	O(13)–Sr(3)–O(16)	149.01(6)	O(19)–Sr(4)–O(22)	105.64(5)
O(1)–Sr(1)–O(5)	82.00(5)	O(7)–Sr(2)–O(11)	142.14(5)	O(13)–Sr(3)–O(17)	128.14(7)	O(19)–Sr(4)–O(23)	92.53(5)
O(1)–Sr(1)–O(6)	118.76(5)	O(7)–Sr(2)–O(12)	84.67(5)	O(13)–Sr(3)–O(18)	86.61(6)	O(19)–Sr(4)–O(24)	80.18(5)
O(2)–Sr(1)–O(3)	79.77(5)	O(8)–Sr(2)–O(9)	143.50(6)	O(14)–Sr(3)–O(15)	131.02(6)	O(20)–Sr(4)–O(21)	140.79(5)
O(2)–Sr(1)–O(4)	135.04(5)	O(8)–Sr(2)–O(10)	84.64(7)	O(14)–Sr(3)–O(16)	96.04(6)	O(20)–Sr(4)–O(22)	80.66(5)
O(2)–Sr(1)–O(5)	87.04(5)	O(8)–Sr(2)–O(11)	99.91(6)	O(14)–Sr(3)–O(17)	84.34(6)	O(20)–Sr(4)–O(23)	77.63(5)
O(2)–Sr(1)–O(6)	108.63(5)	O(8)–Sr(2)–O(12)	112.13(6)	O(14)–Sr(3)–O(18)	145.31(7)	O(20)–Sr(4)–O(24)	139.82(5)
O(3)–Sr(1)–O(4)	62.23(5)	O(9)–Sr(2)–O(10)	59.23(7)	O(15)–Sr(3)–O(16)	62.02(5)	O(21)–Sr(4)–O(22)	62.06(4)
O(3)–Sr(1)–O(5)	166.08(5)	O(9)–Sr(2)–O(11)	73.69(6)	O(15)–Sr(3)–O(17)	125.85(6)	O(21)–Sr(4)–O(23)	134.31(4)
O(3)–Sr(1)–O(6)	117.80(5)	O(9)–Sr(2)–O(12)	97.01(5)	O(15)–Sr(3)–O(18)	81.81(7)	O(21)–Sr(4)–O(24)	74.99(4)
O(4)–Sr(1)–O(5)	127.32(5)	O(10)–Sr(2)–O(11)	84.77(7)	O(16)–Sr(3)–O(17)	76.92(6)	O(22)–Sr(4)–O(23)	154.86(5)
O(4)–Sr(1)–O(6)	73.02(5)	O(10)–Sr(2)–O(12)	145.05(7)	O(16)–Sr(3)–O(18)	90.63(6)	O(22)–Sr(4)–O(24)	136.96(5)
O(5)–Sr(1)–O(6)	62.35(5)	O(11)–Sr(2)–O(12)	62.81(5)	O(17)–Sr(3)–O(18)	64.07(7)	O(23)–Sr(4)–O(24)	62.34(5)
						O(19)–Sr(4)–O(25)	156.98(5)
						O(20)–Sr(4)–O(25)	93.09(5)
						O(21)–Sr(4)–O(25)	75.94(5)
						O(22)–Sr(4)–O(25)	89.59(5)
						O(23)–Sr(4)–O(25)	79.14(5)
						O(24)–Sr(4)–O(25)	76.94(5)

The [Sr(4)(Odipp)$_2$(dme)$_3$] molecule in **2** (Fig. 3) consists of two aryloxide ligands, two chelating dme ligands and a unidentate dme ligand bound to a Sr atom, giving a coordination number of seven. The coordination geometry around the Sr atom is pentagonal bipyramidal, with the equatorial positions occupied by four O atoms of the chelating dme ligands, and O(20) from an aryloxide ligand. The second aryloxide ligand (O(19)), and O(25) from the unidentate dme ligand reside in the axial positions (O(19)–Sr–O(25) 156.98(5)°). The two aryloxide ligands are thus in a cisoid orientation with a O(19)–Sr(4)–O(20) angle of 106.16(5)° (Table 2). A unidentate dme ligand is extremely rare in alkaline earth chemistry. There are only four such structurally characterised examples reported. In addition to two dinuclear aryloxo complexes [Ae$_2$(Omes)$_4$(dme)$_4$] (Ae = Ca, Sr),[31] the complex *rac*-[Ca(1,2-di-*tert*-butyl-1,2-bis-(η^5-cyclopentadienyl)ethane)(dme)$_2$][41] contains both a unidentate and a chelating dme ligand and the heterometallic siloxide complex [KBa$_2$(OSiPh$_3$)$_5$(dme)$_2$][42] contains a unidentate dme ligand bound to one Ba atom and a chelating dme ligand bound to the second Ba atom. The structure of **2** is also noteworthy in that it contains both six coordinate [Sr(Odipp)$_2$(dme)$_2$] and seven coordinate [Sr(Odipp)$_2$(dme)$_3$] species. In a similar vein, the structure of {2[Ca(Odipp)$_2$(thf)$_3$]·[Ca(Odipp)$_2$(thf)$_4$]}·thf contains Ca atoms with three and four thf ligands coordinated giving molecules with five and six coordination respectively.[38] This indicates that the moderately bulky Odipp ligand does not sufficiently shield the alkaline earth atom; hence coordinating solvents play a pivotal role in stabilising a mononuclear structural motif.

Mononuclear [Ba(Odipp)$_2$(dme)$_3$] **3** (Fig. 4) crystallises in the triclinic space group $P\bar{1}$, and consists of an eight coordinate Ba atom bound to two aryloxide ligands and three chelating dme ligands, giving irregular coordination geometry around the Ba atom. Despite the additional chelating dme ligand, the aryloxide ligands in **3** adopt a cisoid orientation, demonstrated by the O(1)–Ba(1)–O(2) angle of 125.99(4)° (Table 1), though this becomes increasingly large in the sequence Ca < Sr < Ba. The average Ae–O (aryloxide) bond lengths are 2.15 Å (**1**), 2.30 Å (**2** (Sr(1))), 2.34 Å (**2** (Sr(4))), and 2.51 Å (**3**). Subtracting the relevant ionic radius of the alkaline earth metal,[43] and adjusting for differences in coordination number gives 1.15 Å (**1**), 1.12 Å (**2** (Sr(1))), 1.13 Å (**2** (Sr(4))), and 1.09 Å (**3**). The larger value for **1** reflects enhanced congestion with the smaller Ae^{2+} ion, whilst the smaller value for **3** indicates reduced steric repulsion with the large Ba^{2+} despite the increase in coordination number. The average Ca–O (aryloxide) bond length in **1** is comparable with the average Ca–O (aryloxide) bond length in [Ca(Odmp)$_2$(dme)$_2$] (2.15 Å),[40] while the average Sr–O (aryloxide) bond length in **2** (Sr(1)) is comparable with that in five coordinate [Sr(OAr)$_2$(thf)$_3$]·0.5thf (OAr = 2,4,6-tri-*tert*-butylphenolate) (2.31 Å),[37] despite the lower coordination number and transoid arrangement of the bulky aryloxide ligands in the reported structure. The average Ba–O (aryloxide) bond length in **3** is longer than the average value in five coordinate [Ba(OAr)$_2$(thf)$_3$]·thf (OAr = 2,6-di-*tert*-butyl-4-methylphenolate) (2.40 Å);[32] however this difference is likely to arise partly from the variation in the Ba coordination number between the two complexes. The Ae–O (dme) bond lengths in **1** range from 2.397(1)–2.461(1) Å (Table 1), similar to the range in **2** (Sr(1) 2.604(1)–2.668(1); Sr(4) 2.638(1)–2.704(1) Å). The Sr(4)–η^1O(25) distance is 2.658(1) Å, indicating that the unidentate dme ligand is midway in this range. In **3**, the Ba–O (dme) bond lengths fall over a large range, from 2.790(1)–2.943(1) Å (Table 1), due to asymmetric chelation of the dme ligands.

Conclusion

Redox transmetallation ligand exchange reactions of the heavy alkaline earth metals with bis(pentafluorophenyl)-mercury and HOdipp in dme afforded mononuclear alkaline earth aryloxides. Inspired by the success of this method in synthesising alkaline earth metal–organics, we have recently had success in its utilisation in the synthesis of aluminium organoamido compounds demonstrating wider applicability to other main group elements.[44] The influence of the increasing ionic radius of the alkaline earth metals down the group on the resulting solid state structures was evident; differences in the numbers and binding modes of the dme ligands were observed. The results of the study demonstrate that metal based reactions are a facile route to heavy alkaline earth aryloxides containing moderately bulky phenolate ligands, and are a competitive alternative to metathesis and protolysis reactions. The ability of moderately bulky ligands to support mononuclear heavy alkaline earth species is noteworthy given the current interest in heavy alkaline earth complexes as catalysts and molecular precursors for MOCVD and sol–gel processes.

Experimental

Methods and materials

The compounds prepared herein are extremely air and moisture sensitive; consequently all reactions and manipulations were performed using standard Schlenk line and dry box techniques under an atmosphere of purified nitrogen. 1,2-Dimethoxyethane (dme) was dried and de-oxygenated by refluxing over, and distillation from, sodium benzophenone ketyl. 2,6-Di-iso-propylphenol (HOdipp) was obtained from Aldrich and was de-gassed and subsequently dried over molecular sieves prior to use. Bis(pentafluorophenyl)mercury was prepared using a literature method.[45] Alkaline earth metals were obtained from Aldrich as chunks or turnings which were freshly filed under nitrogen prior to use. Infrared spectra were recorded as Nujol mulls sandwiched between NaCl plates on a Perkin-Elmer 1600 Fourier transform infrared spectrometer. ^{1}H NMR spectra were obtained with Bruker DPX 300 MHz or Bruker AC 200 MHz spectrometers, using dried, de-gassed deuterated solvents. Chemical shifts were referenced to the residual ^{1}H resonances of the solvent. Microanalyses were performed in duplicate by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

Syntheses

Caution! Hg compounds are toxic requiring well-ventilated or fully contained handling methods. Residues should be consigned to heavy metal waste or Hg metal recycled.

[Ca(Odipp)$_2$(dme)$_2$] (1). A Schlenk flask was charged with Ca metal (0.12 g, 3.0 mmol), HOdipp (0.74 cm^3, 4.0 mmol), Hg(C$_6$F$_5$)$_2$ (1.07 g, 2.0 mmol) and dme (50 cm^3). The reaction mixture was stirred at room temperature for 5 days, giving a pale yellow solution. The reaction mixture was filtered, and the solution volume reduced to *ca.* 20 cm^3 *in vacuo*. Colourless crystals of **1** deposited overnight after cooling the solution to −20 °C. Yield: 0.81 g, (70%); found: C, 66.61; H, 9.28%. $C_{32}H_{54}Ca_1O_6$ requires C, 66.86; H, 9.47%; IR (Nujol): $\tilde{\nu}$ = 1939 w, 1863 w, 1821 w, 1782 w, 1585 s, 1557 w, 1430 s, 1348 s, 1280 s, 1263 m, 1244 m, 1210 w, 1193 m, 1150 m, 1138 m, 1117 s, 1107 s, 1072 s, 1040 m, 1028 m, 1016 m, 949 w, 932 m, 885 m, 864 s, 802 w, 749 s, 686 m cm^{-1}; ^{1}H NMR (200 MHz, [D$_6$]benzene, 25 °C): δ = 7.35–7.23 (m, 3H; ArH), 7.09–6.80 (m, 3H; ArH), 3.70 (sept., $^3J_{HH}$ = 6.7 Hz, 2H; C*H*(CH$_3$)$_2$), 3.49 (sept., $^3J_{HH}$ = 6.8 Hz, 2H; C*H*(CH$_3$)$_2$), 3.22 (s, 4H; dme-C*H*$_2$), 3.10 (s, 6H; dme-C*H*$_3$), 2.78 (s, 4H; dme-C*H*$_2$), 2.64 (s, 6H; dme-C*H*$_3$), 1.42 (d, $^3J_{HH}$ = 6.9 Hz, 3H; CH(C*H*$_3$)$_2$), 1.32–1.23 (overlapping d, 21H; CH(C*H*$_3$)$_2$); ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 6.86 (m, 4H; ArH), 6.33 (m, 2H; ArH), 3.63 (overlapping sept., $^3J_{HH}$ = 6.8 Hz, 4H; C*H*(CH$_3$)$_2$), 3.58 (overlapping s, 8H; dme-C*H*$_2$), 3.42 (s, 12H; dme-C*H*$_3$), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$).

{3[Sr(Odipp)$_2$(dme)$_2$]·[Sr(Odipp)$_2$(dme)$_3$]} (2). Sr metal (0.26 g, 3.0 mmol), HOdipp (0.74 cm^3, 4.0 mmol) and Hg(C$_6$F$_5$)$_2$ (1.07 g, 2.0 mmol) were stirred in dme (50 cm^3) at ambient temperature for 5 days. The resulting dark yellow solution was filtered and concentrated to *ca.* 20 cm^3 *in vacuo*. The solution was stored at −20 °C, and colourless crystals of **2** were obtained after several days. Yield: 0.79 g, (61%); found: C, 61.29; H, 8.68%. $C_{132}H_{226}O_{26}Sr_4$ requires C, 61.46; H, 8.83%; IR (Nujol): $\tilde{\nu}$ = 1926 w, 1867 w, 1827 w, 1790 w, 1585 s, 1557 m, 1426 s, 1345 s, 1283 s, 1264 s, 1244 m, 1208 m, 1192 m, 1153 m, 1138 m, 1110 s, 1067 s, 1041 m, 1019 m, 980 m, 934 m, 885 m, 852 s, 802 w, 752 s, 684 m cm^{-1}; ^{1}H NMR (200 MHz, [D$_6$]benzene, 25 °C): δ = 7.19–6.77 (m, 24H; ArH), 3.55 (sept., $^3J_{HH}$ = 6.8 Hz, 16H; C*H*(CH$_3$)$_2$), 3.03 (s, 36H; dme-C*H*$_2$), 2.93 (s, 54H; dme-C*H*$_3$), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 96H; CH(C*H*$_3$)$_2$).

[Ba(Odipp)$_2$(dme)$_3$] (3). Ba metal (0.41 g, 3.0 mmol), HOdipp (0.74 cm^3, 4.0 mmol), Hg(C$_6$F$_5$)$_2$ (1.07 g, 2.0 mmol), and dme (50 cm^3) were loaded into a Schlenk flask, and the reaction mixture was stirred at room temperature for 5 days. The dark yellow solution was filtered and the volume reduced to *ca.* 20 cm^3 *in vacuo*. Cooling to −20 °C afforded colourless crystals of **3** after several days. Yield: 0.95 g, (63%); found: C, 56.52; H, 8.20%. $C_{36}H_{64}Ba_1O_8$ requires C, 56.73; H, 8.46%; IR (Nujol): $\tilde{\nu}$ = 1857 w, 1818 w, 1585 m, 1552 w, 1424 s, 1349 s, 1279 s, 1262 m, 1248 m, 1225 w, 1210 m, 1192 m, 1152 m, 1136 m, 1124 s, 1106 s, 1075 s, 1038 m, 1020 m, 980 m, 932 w, 882 m, 843 s, 798 w, 760 m, 748 s, 682 m, 668 w cm^{-1}; ^{1}H NMR (200 MHz, [D$_5$]pyridine, 25 °C): δ = 7.26–7.22 (m, 4H; ArH), 6.77–6.69 (m, 2H; ArH), 3.96 (sept., $^3J_{HH}$ = 6.9 Hz, 4H; C*H*(CH$_3$)$_2$), 3.48 (s, 12H; dme-C*H*$_2$), 3.25 (s, 18H; dme-C*H*$_3$), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 24H; CH(C*H*$_3$)$_2$).

X-Ray structure determinations. Intensity data were collected using a Bruker X8 Apex II CCD at 123 K with Mo-Kα radiation (λ = 0.7170 Å). Suitable crystals were immersed in viscous hydrocarbon oil and mounted on a glass fibre which was mounted on the diffractometer. Using ψ and ω scans N_t (total) reflections were measured, which were reduced to N_o unique reflections, with $F_o > 2\sigma(F_o)$ being considered observed. Data were initially processed and corrected for absorption using the Bruker Apex II program suite.[46] The structures were solved using direct methods, and observed reflections were used in least squares refinement on F^2, with anisotropic thermal parameters refined for non-hydrogen atoms. Hydrogen atoms were constrained in calculated positions and refined with a riding model. Structure solutions and refinements were performed using the programs SHELXS-97 and SHELXL-97[47] through the graphical interface X-Seed,[48] which was also used to generate the figures. Crystal data for **1**: $C_{32}H_{54}CaO_6$, M = 574.83, monoclinic, $P2_1/n$ (No. 14), a = 17.3295(4), b = 11.5394(3), c = 18.6004(4) Å, β = 114.0310(10)°, V = 3397.17(14) Å^3, Z = 4, D_c = 1.124 g cm^{-3}, F_{000} = 1256, μ = 0.222 mm^{-1}, $2\theta_{max}$ = 55.0°, 51359 reflections collected, 7796 unique (R_{int} = 0.0279). Final GooF = 1.257, R_1 = 0.0566, wR_2 = 0.1185, R indices based on 7584 reflections with $I > 2\sigma(I)$ (refinement on F^2), 364 parameters, 0 restraints. Crystal data for **2**: $C_{132}H_{226}O_{26}Sr_4$, M = 2579.61, triclinic, $P\bar{1}$ (No. 2), a = 20.0029(3), b = 20.0434(3), c = 22.7191(4) Å, α = 64.4540(10)°, β = 72.6090(10)°, γ = 61.0870(10)°, V = 7146.6(2) Å^3, Z = 2, D_c = 1.199 g cm^{-3}, F_{000} = 2756, μ = 1.548 mm^{-1}, $2\theta_{max}$ = 55.0°, 88650 reflections collected, 32786 unique (R_{int} = 0.0298). Final GooF = 1.018, R_1 = 0.0351, wR_2 = 0.0823, R indices based on 25542 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1542 parameters, 0 restraints. Crystal data for **3**: $C_{36}H_{64}BaO_8$, M = 762.21, triclinic, $P\bar{1}$ (No. 2), a = 10.8104(2), b = 12.7872(2), c = 15.1158(3) Å, α = 86.8780(10)°, β = 75.0680(10)°, γ = 82.6430(10)°, V = 2001.85(6) Å^3, Z = 2, D_c = 1.265 g cm^{-3}, F_{000} = 800, μ = 1.035 mm^{-1}, $2\theta_{max}$ = 55.0°, 21091 reflections collected, 8996 unique (R_{int} = 0.0143). Final GooF = 1.060, R_1 = 0.0196, wR_2 = 0.0482, R indices based on 8507 reflections with $I > 2\sigma(I)$ (refinement on F^2), 420 parameters, 0 restraints. CCDC 766089–766091 (**1–3**).‡

Variata. For compound **2**, atoms C(58), C(59), C(60) and O(10) of a dme ligand bound to Sr(2) were disordered over two positions. The disorder was successfully modelled with 35 : 65 occupancy levels.

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References

1 T. M. A. Al-Shboul, G. Volland, H. Görls and M. Westerhausen, *Z. Anorg. Allg. Chem.*, 2009, **635**, 1568.
2 A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock and P. A. Procopiou, *Dalton Trans.*, 2008, 4474.
3 F. Feil and S. Harder, *Eur. J. Inorg. Chem.*, 2003, 3401.
4 M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2004, **43**, 6717.
5 F. Feil and S. Harder, *Eur. J. Inorg. Chem.*, 2005, 4438.
6 D. F-J. Piesik, K. Häbe and S. Harder, *Eur. J. Inorg. Chem.*, 2007, 5652.
7 K. M. Fromm, *Dalton Trans.*, 2006, 5103.
8 D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317.
9 J. S. Matthews and W. S. Rees Jr., *Adv. Inorg. Chem.*, 2000, **50**, 173.
10 L. G. Hubert-Pfalzgraf, *J. Mater. Chem.*, 2004, **14**, 3113.
11 K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.
12 K. M. Fromm and E. D. Gueneau, *Polyhedron*, 2004, **23**, 1479.
13 G. B. Deacon, P. C. Junk, G. J. Moxey, K. Ruhlandt-Senge, C. St. Prix and M. F. Zuniga, *Chem.–Eur. J.*, 2009, **15**, 5503; S. Harder, *Angew. Chem., Int. Ed.*, 2004, **43**, 2714.
14 T. P. Hanusa, *Coord. Chem. Rev.*, 2000, **210**, 329.
15 J. S. Alexander and K. Ruhlandt-Senge, *Eur. J. Inorg. Chem.*, 2002, 2761.
16 T. P. Hanusa, *Chem. Rev.*, 1993, **93**, 1023.
17 G. Meyer, *Z. Anorg. Allg. Chem.*, 2008, **634**, 201; G. B. Deacon and C. M. Forsyth, in *Inorganic Chemistry Highlights*, ed. G. Meyer, D. Naumann and L. Wesemann, Wiley-VCH, Cambridge, 2002, ch. 7, p. 139.
18 G. B. Deacon, C. M. Forsyth and S. Nickel, *J. Organomet. Chem.*, 2002, **647**, 50.
19 M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. Konstas and J. Wang, *Chem.–Eur. J.*, 2007, **13**, 8092.
20 G. B. Deacon, C. M. Forsyth, P. C. Junk, B. W. Skelton and A. H. White, *Chem.–Eur. J.*, 1999, **5**, 1452.
21 G. B. Deacon, P. C. Junk and G. J. Moxey, *Chem.–Asian J.*, 2009, **4**, 1717.
22 M. Westerhausen, M. Gärtner, R. Fischer, J. Langer, L. Yu and M. Reiher, *Chem.–Eur. J.*, 2007, **13**, 6292.
23 R. Fischer, M. Gärtner, H. Görls and M. Westerhausen, *Organometallics*, 2006, **25**, 3496.
24 J. Hitzbleck, A. Y. O'Brien, C. M. Forsyth, G. B. Deacon and K. Ruhlandt-Senge, *Chem.–Eur. J.*, 2004, **10**, 3315.
25 J. Hitzbleck, G. B. Deacon and K. Ruhlandt-Senge, *Eur. J. Inorg. Chem.*, 2007, 592.
26 J. Hitzbleck, G. B. Deacon and K. Ruhlandt-Senge, *Angew. Chem., Int. Ed.*, 2004, **43**, 5218.
27 G. B. Deacon, C. M. Forsyth and P. C. Junk, *J. Organomet. Chem.*, 2000, **607**, 112.
28 M. L. Cole, G. B. Deacon, C. M. Forsyth, P. C. Junk, K. M. Proctor, J. L. Scott and C. R. Strauss, *Polyhedron*, 2007, **26**, 244.
29 M. L. Cole and P. C. Junk, *New J. Chem.*, 2005, **29**, 135.
30 M. L. Cole, G. B. Deacon, C. M. Forsyth, K. Konstas and P. C. Junk, *Dalton Trans.*, 2006, 3360.
31 G. B. Deacon, P. C. Junk, G. J. Moxey, M. Guino-o and K. Ruhlandt-Senge, *Dalton Trans.*, 2009, 4878.
32 K. F. Tesh, T. P. Hanusa, J. C. Huffman and C. J. Huffman, *Inorg. Chem.*, 1992, **31**, 5572.
33 K. F. Tesh, D. J. Burkey and T. P. Hanusa, *J. Am. Chem. Soc.*, 1994, **116**, 2409.
34 P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, *J. Chem. Soc., Chem. Commun.*, 1990, 1141.
35 F. G. N. Cloke, P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, *J. Chem. Soc., Chem. Commun.*, 1991, 724.
36 J. P. Dunne, M. Tacke, C. Selinka and D. Stalke, *Eur. J. Inorg. Chem.*, 2003, 1416.
37 S. R. Drake, D. J. Otway, M. B. Hursthouse and K. M. A. Malik, *Polyhedron*, 1992, **11**, 1995.
38 T. J. Boyle, B. A. Hernandez-Sanchez, C. M. Baros, L. N. Brewer and M. A. Rodriguez, *Chem. Mater.*, 2007, **19**, 2016.
39 J. Marcalo and A. Pires De Matos, *Polyhedron*, 1989, **8**, 2431.
40 W. J. Evans, W. G. McClelland, M. A. Greci and J. W. Ziller, *Eur. J. Solid State Inorg. Chem.*, 1996, **33**, 145.
41 P.-J. Sinnema, B. Höhn, R. L. Hubbard, P. J. Shapiro, B. Twamley, A. Blumenfeld and A. Vij, *Organometallics*, 2002, **21**, 182.
42 P. S. Coan, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1991, **30**, 5019.
43 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Cryst.*, 1976, **32**, 751.
44 G. O. Lloyd, J. M. Bakker, L. J. Barbour, G. B. Deacon, J. W. Steed and P. C. Junk, unpublished results.
45 G. B. Deacon, J. E. Cosgriff, E. T. Lawrenz, C. M. Forsyth and D. L. Wilkinson, in *Synthetic Methods of Organometallic and Inorganic Chemistry*, ed. F. T. Edelmann, G. Thieme, Verlag, Stuttgart, 1997, vol. 6, p. 48.
46 Apex II Version 2.1, Bruker AXS Ltd., Madison, Wisconsin.
47 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.
48 L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.