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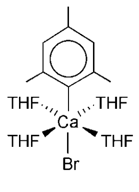
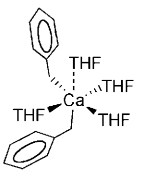
Bis(trimethylsilyl)methyl Derivatives of Calcium, Strontium and Barium: Potentially Useful Dialkyls of the Heavy Alkaline Earth Elements

Mark R. Crimmin,[a] Anthony G. M. Barrett,*[a] Michael S. Hill,*[b]
Dugald J. MacDougall,[b] Mary F. Mahon,[b] and Panayiotis A. Procopiou[c]

Although the first reports of their synthesis were contemporaneous with those of organomagnesium species,[1] organometallic derivatives of the heavier alkaline earths have assumed the role of "Cinderella" compounds over the subsequent 100 years.[2] Despite spectacular recent advancements by Westerhausen and co-workers in the area of arylcalcium analogues of Grignard reagents[3] (e.g., compound **I**)[4] and reports of a variety of triorganosilyl-substituted and donor-stabilised benzyl-, diphenyl- and triphenylmethyl complexes (e.g., **II** and **III**),[5] a well-defined chemistry of comparable alkyl derivatives is still virtually non-existent. Only two alkyl calcium species have been successfully characterised by X-ray diffraction analysis. Eaborn and Smith reported the synthesis of the solvent-free tris(trimethylsilyl)methyl derivative $[Ca\{C(SiMe_3)_3\}_2]$ (**IV**) in 1997,[6] and a 1,4-dioxane complex that contained the less sterically demanding bis(trimethylsilyl)methyl ligand, $[Ca(C_4H_8O_2)_2\{CH(SiMe_3)_2\}_2]$ (**V**), had been described some six years earlier by Lappert.[7] This latter species was prepared under rather specialised metal-vapour synthesis conditions by the co-condensation of calcium atoms with $(Me_3Si)_2CHBr$ and, presumably, subsequent solvent-induced redistribution of the alkylcalcium bromide. In this regard, it is notable that the only heteroleptic species to be unambiguously characterised (NMR spectroscopy and CHN elemental analysis) is Hanusa's mixed cyclopentadienyl alkyl $[Ca\{CH(SiMe_3)_2\}(C_5Me_5)(THF)_3]$.[8]



I



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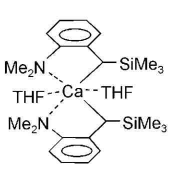

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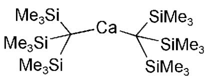
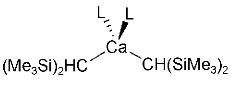
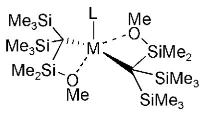


IV



V: L = 1,4-dioxane



VI: M = Sr, L = THF
VII: M = Ba, L = $(DME)_2$

Our interest in this area centers upon calcium compound **V** as an isoelectronic analogue of the easily prepared bis(trimethylsilyl)amides of the heavier alkaline earth elements $[M(L_2)\{N(SiMe_3)_2\}_2]$ (M = Ca, Sr or Ba; L = donor ligand, e.g., THF). These latter compounds have been central in our efforts to develop a distinct catalytic heterofunctionalisation chemistry based upon a protonolysis/insertion strategy.[9] Although this reactivity is broadly comparable to that delineated in d^0 transition-metal and organolanthanide chemistry,[10] extensions to the activation of more challenging substrates with higher pK_a values are limited by the intermediate basicity of the silylamide precatalyst. Previously reported reactions that might reasonably be expected to provide access to a dialkyl similar to **V** by conventional "wet synthetic" methods have produced a variety of products. Subsequent to the description of **V**, Lappert reported that reactions of either $[Ca\{OSO_2C_6H_4\text{-}4\text{-}Me\}_2]$ in THF or CaI_2 in benzene with potassium bis(trimethylsilyl)methanide gave the calciate species $K[Ca\{CH(SiMe_3)_2\}_3]$, irrespective of reaction stoichiometry.[11,12] Westerhausen also demonstrated that reaction of Ca metal and $[Sn\{CH(SiMe_3)_2\}_2]$ in toluene/DME provided the calcium stannanide Ca[Sn{CH-

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[a] Dr. M. R. Crimmin, Prof. A. G. M. Barrett
Department of Chemistry, Imperial College London
Exhibition Road, South Kensington
London, SW7 2AZ (UK)
Fax: (+44) 207-5945805
E-mail: agmb@ic.ac.uk

[b] Dr. M. S. Hill, Dr. D. J. MacDougall, Dr. M. F. Mahon
Department of Chemistry, University of Bath
Claverton Down
Bath, BA2 7AY (UK)
Fax: (+44) 1225-386231
E-mail: msh27@bath.ac.uk

[c] Dr. P. A. Procopiou
GlaxoSmithKline Medicines Research Centre
Gunnels Wood Road, Stevenage
Hertfordshire, SG1 2NY (UK)

$(SiMe_3)_2\}_3]_2$, presumably by insertion of $[Sn\{CH(SiMe_3)_2\}_2]$ into the Ca–C bonds of an initially formed calcium alkyl species.[13] Herein, we demonstrate that the bis-THF-solvate of **V**, compound **1**, may be synthesised straightforwardly and on a preparative scale by using Lappert's previously described $CaI_2/[K\{CH(SiMe_3)_2\}]$ salt metathesis reaction in THF. Perhaps more significantly, this chemistry is readily translated to the syntheses of the analogous strontium and barium alkyl species, **2** and **3**. These latter complexes have also been characterised by X-ray diffraction. Whereas the only previous strontium and barium dialkyls, **VI** and **VII**,[14] were further stabilised by intramolecular O–M coordination, compounds **2** and **3** are the first examples of simple strontium and barium complexes in which alkyl carbon-to-metal bonds are unsupported by additional donor interactions.

Addition of THF at room temperature to a solid mixture of CaI_2 beads and two equivalents of $[K\{CH(SiMe_3)_2\}(THF)]$ gave a pale yellow solution and a heavy colourless precipitate. Evaporation of the solvent and crystallisation from hexane at −30 °C gave colourless crystals of compound **1** in low, but unoptimised, yield (≈35 %). ^1H and ^{13}C NMR spectroscopic analysis of the isolated crystals in C_6D_6 provided data, including a characteristic high-field methine signal observed at $\delta = -1.62$ ppm, similar to that communicated by Lappert for the complex identified as $[Ca\{CH(SiMe_3)_2\}_2(THF)_3]$ en route to compound **V**.[7] Notably, no degradation of the coordinated THF molecules was observed upon extended monitoring of the NMR spectroscopy samples. An X-ray crystallographic diffraction identified compound **1** as a pseudo-tetrahedral complex that contained two molecules of THF (Figure 1). The structure of **1**, in which the calcium is located on a crystallographic two-fold rotational axis, is thus closely related (and effectively isostructural) to that of the bis-dioxane complex **V**.[7] Although the Ca–C bond lengths in **1** (2.4930(18) Å) are identical, within the limits of experimental error, to those reported for the similarly tetracoordinated complex **V** (2.483(5) Å), they are significantly longer than those observed within the solvent-free, and effectively two-coordinate, tris(trimethylsilyl)methyl derivative **IV** (2.459(5) Å).[6] The C1-Ca-C1′ bond angles of **1** and **V** are also comparable (**1** 135.48(9), **V** 133.7(2)°), which indicates that the cyclic ether donors are broadly commensurate with one another in terms of overall steric demands when arrayed around a calcium metal centre with the sterically demanding bis(trimethylsilyl)methyl ligands.

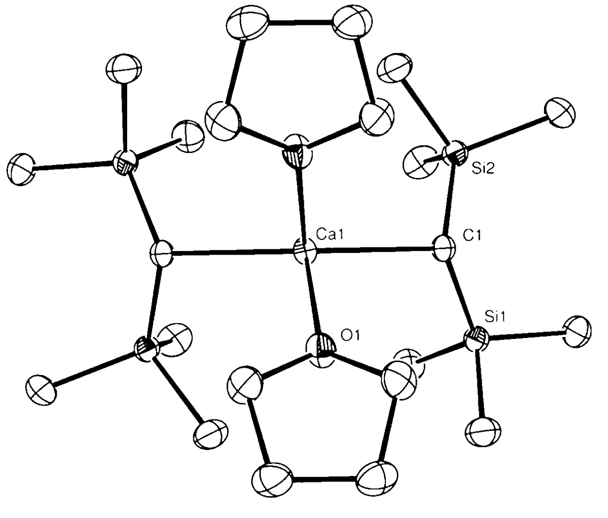

Figure 1. ORTEP plot of **1** (30 % probability ellipsoids); H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ca1–C1 2.4930(18), Ca1–O1 2.3388(14); C1-Ca1-C1′ 135.48(9), O1-Ca1-C1 103.17(5), O1-Ca1-C1′ 110.38(5), O1-Ca1-O1′ 81.00(8).

Encouraged by the successful and straightforward preparation of compound **1**, we sought to extend the synthetic protocol to the synthesis of the analogous organostrontium species. The reaction between SrI_2 and $[K\{CH(SiMe_3)_2\}(THF)]$ under conditions identical to those employed for **1**, again gave a good crop of highly air- and moisture-sensitive crystals, compound **2**. The NMR spectra obtained in C_6D_6 revealed the formation of a compound that contained a single bis(trimethylsilyl)methyl ligand environment. In this case, the ^1H methine C–H resonance of compound **2** occurred at slightly lower field ($\delta = -1.59$ ppm) than that observed in calcium alkyl compound **1** despite the increased electropositivity of the metal dication. Although the alkyl strontiate species, $Li[Sr\{CH(SiMe_3)_2\}(OSO_2C_6H_4\text{-}Me\text{-}4)_2]$ and $K[Sr\{CH(SiMe_3)_2\}_3]$ have been identified spectroscopically,[11] to the best of our knowledge, the only previous complex with a $Sr{-}C_{alkyl}$ σ bond to have been structurally characterised is $[Sr\{C(SiMe_2OMe)(SiMe_3)_2\}_2(THF)]$ (**VI**),[14] which utilised an extremely sterically demanding tris(organosilyl)methyl ligand with an additional *O*-donor functionality within the periphery of the silicon-stabilised carbanion. Although the isolated crystalline compound displayed a tendency to undergo loss of THF, and an integration of the ^1H NMR spectral data indicated a bis-THF-adducted complex similar to that observed within the structure of **1**, a further X-ray analysis revealed that strontium dialkyl **2** crystallises with an additional molecule of donor solvent to form the five-coordinate complex illustrated in Figure 2. The Sr–C bond lengths in **2** (Sr–C1 2.692(3), Sr–C8 2.681(3) Å) are significantly shorter than those observed within **VI** (2.786(3) and 2.849(3) Å) and bear closer comparison to the distances between strontium and the similarly unidentate acetylide ligands in the homoleptic complex $[Sr([18]crown\text{-}6)(Ph_3SiCC)_2]$,[15] most likely a reflection of the comparable charge donation of the bis(trimethylsilyl)methyl ligands to the Sr^{2+} cation. These values are also close to those calculated by employing Hartree–Fock calculations with quasi-relativistic pseudopotentials for both linear (2.673 Å) and bent (2.621 Å) configurations of the, as yet, hypothetical parent dimethylstrontium.[16]

Extension of this simple synthetic methodology to the synthesis of analogous barium complex **3** also proceeded without complications. Although several non-cyclopentadienyl barium organometallic complexes have been reported in recent years,[17] the only previous well-characterised barium alkyl complex is $[Ba(DME)\{(Me_3Si)_2(MeOMe_2Si)C\}_2]$ (**VII**),[14] in which the extremely bulky

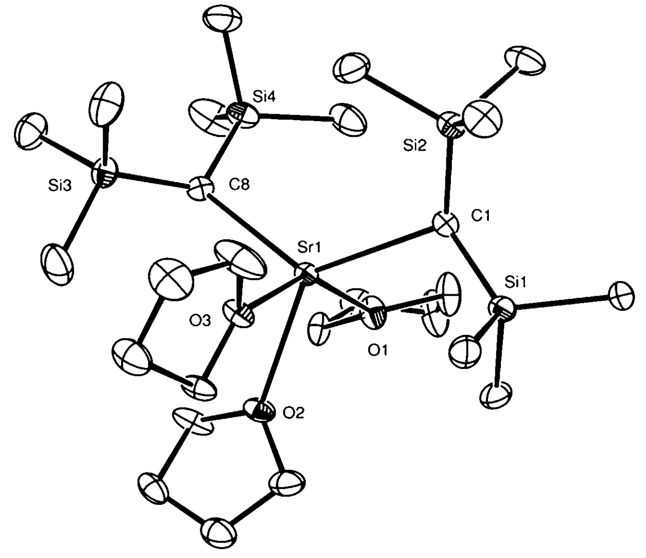

Figure 2. ORTEP plot of **2** (20 % probability ellipsoids); H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sr1−C1 2.692(3), Sr1−C8 2.681(3), Sr1−O1 2.576(2), Sr1−O2 2.579(9), Sr1−O3 2.565(7); C1-Sr1-C8 126.26(9), O1-Sr1-C1 92.72(8), O1-Sr1-C8 95.65(8).

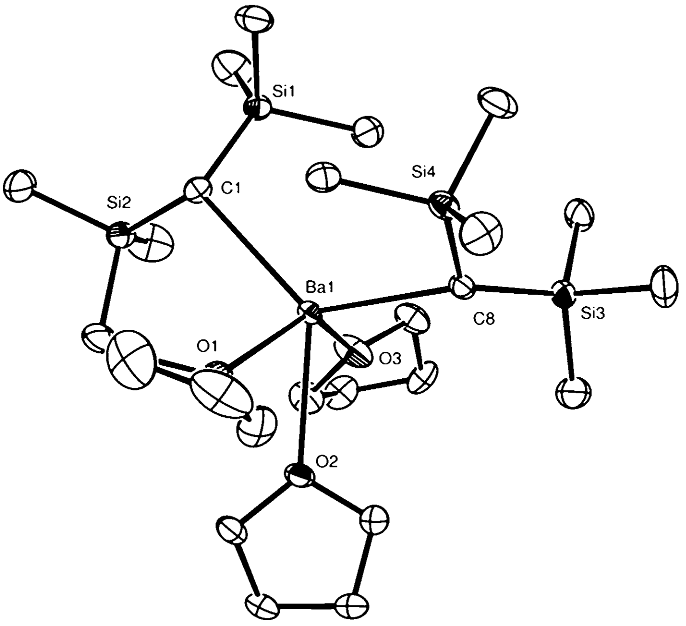

Figure 3. ORTEP plot of **3** (20 % probability ellipsoids); H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ba1−C1 2.879(3), Ba1−C8 2.827(3), Ba1−O1 2.758(2), Ba1−O2 2.751(2), Ba1−O3 2.721(2); C1-Ba1-C8 124.48(10), O1-Ba1-C1 97.70(9), O1-Ba1-C8 95.31(9).

alkyl ligand again provides additional stabilisation through ancillary silyl ether chelation. Compound **3** is, therefore, the first example of an unsupported σ dialkylbarium. Although the extreme solubility of compound **3** in hydrocarbon solvents limited the isolated yield of the crystalline material, the NMR spectra, collected in C_6D_6, were similar to those obtained for **2** and were consistent with a formulation in which all the bis(trimethylsilyl)methyl ligand environments were identical on the NMR timescale. Although the ^{1}H NMR integral values from spectra of the isolated material again indicated the presence of two molecules of coordinated THF, X-ray diffraction analysis revealed that **3** is isostructural to strontium analogue **2**, and exists as a five-coordinate tris-THF adduct in the solid state (Figure 3). Reflecting both the reduced coordination number and lower alkyl ligand denticity, the Ba−C distances (Ba1−C1 2.879(3), Ba1−C8 2.827(3) Å) in **3** are significantly shorter than those reported for six-coordinate complex compound **VII** (3.049(2), 3.0363(18) Å). These measurements are, however, longer than the barium-to-C_{ipso} contacts in a recently reported heteroleptic pentafluorophenyl complex, in which additional kinetic stability was provided by a terphenyl-substituted triazenyl ligand.[14,17b] Although these lengths are again comparable to those in a previously reported unidentate acetylide, $[Ba([18]crown\text{-}6)(Ph_3SiCC)_2]$ (2.852(3), 2.853(3) Å),[15] the isolation of **3** provides the first measurement of a terminal (i.e., non-bridging and unidentate) Ba−C(sp3) distance.

In summary, we have described straightforward syntheses of dialkyl calcium, strontium and barium species. Although the X-ray analyses of **1**–**3** are notable for the identification of typical structural parameters within complexes of this type, of potentially greater significance is the ability of these molecules to operate as readily available reagents for further exploration of the reaction chemistry of both homo- and heteroleptic alkaline earth alkyl derivatives. For example, we have noted in preliminary NMR-scale studies that complex **1** reacts with two equivalents of 1,3-dialkyl carbodiimides to give the anticipated amidinate insertion product in an fashion analogous to previously reported explorations of calcium amide chemistry.[18] We are continuing to explore these possibilities and will describe these experiments in subsequent publications.

Experimental Section

All reactions and manipulations were performed under the rigorous exclusion of water and oxygen, by using either a double manifold vacuum line or an Ar-filled drybox operating at <0.1 ppm O_2. All reagents and solvents were purified by using standard procedures. In common with many previous studies of this nature, compounds **1**–**3** are extremely air and moisture sensitive and lose THF readily upon storage. Melting points are uncorrected and were performed in sealed capillary tubes under an Ar atmosphere. Microanalyses were performed by Mr. S. Boyer of the London Metropolitan University.

Compound 1: CaI_2 (0.81 g, 2.7 mmol) and $[K\{CH(SiMe_3)_2\}(THF)]$ (1.48 g, 5.4 mmol) were combined in a flask, and THF (30 mL) was added with stirring at RT. The resulting mixture was stirred for 14 h to give a pale yellow solution and a colourless precipitate. The solvent was removed in vacuo and the resultant pale yellow solid was extracted with hexane (30 mL). This was filtered and the clear pale yellow solution was concentrated and stored at −30 °C, which resulted in the formation of **1** as extremely air- and moisture-sensitive colourless crystals suitable for X-ray diffraction (0.48 g, 35 % yield). Isolated samples of **1** were prone to partial loss of coordinated THF. The calculated analytical values, therefore, refer to a mono-solvated complex. M.p. softens 90 °C, melts 101–102 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = -1.62$ (s, 2H; C*H*(SiMe)$_2$), 0.36 (s, 36H; SiMe_3), 1.18–1.20 (m, ≈ 8H; THF), 3.45–3.48 ppm (m, ≈8H;THF); ^{13}C{^{1}H} NMR (75.49 MHz, C_6D_6, 25 °C): $\delta = 4.8$ (SiMe, ^1J(Si,C) = 47 Hz), 23.4 (THF), 67.8 ppm (THF); ^{29}Si{^{1}H} NMR (59.62 MHz, C_6D_6, 25 °C): $\delta = -7.8$ ppm; elemental analysis calcd (%) for $C_{18}H_{46}CaOSi_4$: C 50.16, H 10.76; found: C 50.83, H 10.42.

Compound 2: This compound was prepared by the same general method as **1**, with SrI_2 (0.31 g, 0.91 mmol) and [K{CH($SiMe_3$)$_2$}(THF)] (0.50 g, 1.83 mmol) and was isolated as colourless crystals (which darken upon storage, even at −30 °C) suitable for X-ray diffraction (0.22 g, 38% yield). M.p. 94–95 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = -1.59$ (s, 2H; CH(SiMe)$_2$) 0.36 (s, 36H; SiMe), 1.25–1.28 (m, ≈8H; THF), 3.44–3.47ppm (m, ≈8H; THF); ^{13}C{^{1}H} NMR (75.49 MHz, C_6D_6, 25 °C): $\delta = -13.6$ (CH($SiMe_3$)$_2$), 6.3 (SiMe, ^1J(Si,C) = 48 Hz), 23.4 (THF), 67.8 ppm (THF); ^{29}Si{^{1}H} NMR (59.62 MHz, C_6D_6, 25 °C): $\delta = -9.3$ ppm; elemental analysis calcd (%) for $C_{26}H_{62}O_3Si_4Sr$: C 50.15, H 10.04; found: C 50.11, H 9.96

Compound 3: This compound was prepared by the same general method as **1**, with BaI_2 (0.37 g, 0.9 mmol) and [K{CH($SiMe_3$)$_2$}(THF)] (0.51 g, 1.8 mmol) and was isolated as highly air- and moisture-sensitive colourless crystals suitable for X-ray diffraction (0.15 g, 24% yield). M.p. softens 45 °C, melts 70 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = -1.49$ (s, 2H; CH(SiMe)$_2$), 0.35 (s, 36H; SiMe), 1.27–1.30 (m, ≈8H; THF), 3.41–3.45 ppm (m, ≈8H;THF); ^{13}C{^{1}H} NMR (75.49 MHz, C_6D_6, 25 °C): $\delta = 6.0$ (SiMe, ^1J(Si,C) = 46 Hz), 25.2 (THF), 68.4 ppm (THF); ^{29}Si{^{1}H} NMR (59.62 MHz, C_6D_6, 25 °C): $\delta = -11.2$ ppm; elemental analysis calcd for $C_{26}H_{62}BaO_3Si_4$: C 46.44, H 9.29; found: C 46.52, H 9.32.

Crystal structure analysis: Data for the X-ray structural analyses of **1**, **2** and **3** were collected on a Nonius KappaCCD diffractometer [$\lambda(\mathrm{Mo}_{K\alpha}) = 0.71073$ Å], solved by direct methods and refined against all F^2 by using SHELXL-97, with non-hydrogen atoms anisotropic and hydrogen atoms in riding mode.[19] For both **2** and **3**, a semiempirical absorption correction was applied. CCDC-695758 (**1**), -695759 (**2**) and -695760 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

*Crystal data for compound **1***: $C_{22}H_{54}CaO_2Si_4$; $M_w = 503.09$; $T = 173(2)$ K; monoclinic; space group $C2/c$; $a = 18.4180(2)$, $b = 9.8110(2)$, $c = 18.6440(5)$ Å; $\beta = 109.298(1)$°; $V = 3179.66(11)$ Å^3; $Z = 4$; $\rho_{\mathrm{calc}} = 1.051$ mg m^{-3}; $F(000) = 1112$; 29086 reflections, 3619 unique reflections (R(int) = 0.0715), 2661 reflections with $I > 2\sigma(I)$; $R1$, w$R2$ 0.0394, 0.0809 ($I > 2\sigma(I)$) and 0.0676, 0.0920 (all data).

*Crystal data for compound **2***: $C_{26}H_{62}O_3Si_4Sr$; $M_w = 622.74$; $T = 173(2)$ K; monoclinic; space group $P2_1/c$; $a = 18.5860(3)$, $b = 9.614(2)$, $c = 20.0785(4)$ Å; $\beta = 91.633(1)$°; $V = 3678.52(12)$ Å^3; $Z = 4$; $\rho_{\mathrm{calc}} = 1.124$ mg m^{-3}; $F(000) = 1344$; 53370 reflections, 8366 unique reflections (R(int) = 0.0834), 5746 reflections with $I > 2\sigma(I)$; $R1$, w$R2$ 0.0425, 0.0837 ($I > 2\sigma(I)$) and 0.0809, 0.0992 (all data). A moderate amount of disorder was accounted for in the structure of **2**. Specifically, the carbon atoms in the THF ligand based on O1, all atoms in the THF based on O2 and the methyl groups attached to Si1 exhibited 55:45 disorder. In addition, the THF based on O3 was treated for 65:35 disorder. Some similarity restraints were also applied to O–C and C–C distances in the disordered fragments.

*Crystal data for compound **3***: $C_{26}H_{62}BaO_3Si_4$; $M_w = 672.46$; $T = 173(2)$ K; monoclinic; space group $P2_1/c$; $a = 18.6580(2)$, $b = 10.2370(1)$, $c = 19.6180(3)$ Å; $\beta = 90.631(1)$°; $V = 3746.85(8)$ Å^3; $Z = 4$; $\rho_{\mathrm{calc}} = 1.192$ mg m^{-3}; $F(000) = 1416$; 70217 reflections, 8582 unique reflections (R(int) = 0.0916), 5872 reflections with $I > 2\sigma(I)$; $R1$, w$R2$ 0.0386, 0.0702 ($I > 2\sigma(I)$) and 0.0763, 0.0821 (all data). C25 and C26 were disordered over two sites in a 70:30 ratio.

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Keywords: alkaline earth metals · alkyl ligands · barium · calcium · strontium

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