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Synthesis, structure and characterisation of magnesium and calcium β-diketonate complexes $[Ca_3(tmhd)_6]$ and $[Ca_2(tmhd)_4(EtOH)_2]$ (Htmhd = 2,2,6,6-tetramethylheptane-3,5-dione)†

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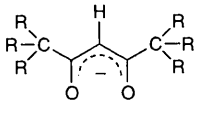
The reaction of the oligomeric Group 2 metal ethoxide complexes $[\{Mg(OEt)_2\}_n]$ and $[\{Ca(OEt)_2(EtOH)_4\}_n]$ with 2 equivalents of 2,2,6,6-tetramethylheptane-3,5-dione (Htmhd) yielded the homoleptic β-diketonate compounds $[\{M(tmhd)_2\}_n]$ (M = Mg **1** or Ca **2**). An intermediate en route to complex **2** is the ethanol-solvated species $[Ca_2(tmhd)_4(EtOH)_2]$ **3**. The reaction of **1** with triglyme (2,5,8,11-tetraoxadodecane, $C_8H_{18}O_4$) yielded the air- and moisture-stable derivative $[\{[Mg(tmhd)_2]_2(C_8H_{18}O_4)\}_n]$ **4**. The calcium complexes **2** and **3** were characterised structurally by X-ray crystallography: **2** is the first structurally characterised homoleptic β-diketonate of calcium and has a novel triangular core, with all the calcium ions six-co-ordinate and held together by tmhd ligands in a wide range of co-ordinating modes; **3** has a dimeric structure with both chelating and bridging tmhd ligands and two terminal ethanol molecules.

The renewed interest in the chemistry of the heavier Group 2 metals can be attributed to their potential use as molecular precursors in the preparation of thin films *via* organometallic chemical vapour deposition (OMCVD), for electroceramics such as superconductors, piezoelectrics and other speciality electronic materials, and also to a fundamental desire for a greater understanding of their co-ordination chemistry.[1] In the latter vein several researchers have recently reported some significant developments in the chemistry of these metals and notable examples include the following. First, the structural chacterisation of a wide range of organomagnesium complexes, *e.g.* the polymeric species $(MgPh_2)_\infty$ and the monomeric tetrahydrofuran adduct $[MgPh_2(thf)_2]$.[2] An unprecedented route to homoallylic alcohols has recently been developed *via* the use of an allylbarium reagent, which shows remarkable α-selectivity and stereospecificity.[3] Finally, other researchers have recently described the facile cleavage of a wide range of organic ligands by the Group 2 metals or their complexes, *i.e.* P–N cleavage of $P(NMe_2)_3O$, C–O cleavage of thf, and C–O bond scission of PhOH and Bu^tOH.[4] These selected examples illustrate some of the remarkable diversity observed in the chemistry of these largely under explored elements in both their co-ordination chemistry and also in their potential applications as organometallic reagents for organic synthesis.



I

tmhd R = Me
hfpd R = F

The chelating β-diketonates 2,2,6,6-tetramethylheptane-3,5-dionate (tmhd) and 1,1,1,5,5,5-hexafluoropentane-2,4-dionate (hfpd) **I** have found extensive application in both main-group and transition-metal chemistry.[1,5] They have been shown to impart appreciable stability and volatility to their metal-complexed products. For example, in aqueous media and/or aerobic conditions the oligomeric complexes $[Ba_5(OH)(tmhd)_9(H_2O)_3]$,[6] $[NHEt_3][Ba_6(O_2)(OH)_2(tmhd)_{10}(H_2O)_4]$[7] and $[Ba_5(tmhd)_9Cl(H_2O)_7]$[8] have been isolated, whilst from methanol a more discrete species $[Ba(tmhd)_2(MeOH)_3]\cdot MeOH$ is obtained.[9] The widely used hydrated Group 2 metal hexafluoropentane-2,4-dionate precursors $[Ca_2(hfpd)_4(H_2O)_4]$ and $[\{Ba(hfpd)_2(H_2O)\}_\infty]$ have also been structurally characterised recently.[10] If, however, more rigorous anaerobic (*i.e.* Schlenk line) conditions are used then it is possible to obtain products of consistently high purity, *e.g.* the Lewis base-adducted dimeric barium complexes, $[Ba_2(tmhd)_4(NH_3)_4]$,[11] $[Ba_2(tmhd)_4(bipy)_2]$[12] (bipy = 2,2′-bipyridine) and $[Ba_2(tmhd)_4(Et_2O)_2]$,[13] and also the fluoro analogues $[H_2en]_{1.5}[Ba(hfpd)_5]$,[6] $[\{Ba_2(hfpd)_4(Et_2O)\}_\infty]$[14] and $[Ba_2(hfpd)_4(EtOH)]$.[15] The stabilisation of such complexes by the addition of either closed or open polyethers, *e.g.* $[Ba(hfpd)_2(18\text{-crown-}6)]$[16] (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) or $[Ba(hfpd)_2(C_{10}H_{22}O_5)]$[17,18] ($C_{10}H_{22}O_5$ = tetraglyme = 2,5,8,11,14-pentaoxapentadecane) has also been reported. With a view to increasing the understanding of this area of chemistry, we and others[19] have investigated the reactions of the Group 2 metals with a range of compounds including alcohols (*e.g.* ethanol). This has provided some important insight into the chemistry of these metals. From the reaction of the metals with ethanol the high-purity, crystalline hydrocarbon-soluble, tetraethanol solvated materials $[\{M(OEt)_2(EtOH)_4\}_n]$ (M = Ca, Sr or Ba) and $[\{Mg(OEt)_2\}_n]$ have recently been obtained.[20] These materials have excellent stability and may be obtained reproducibly in large (> 100 g) batches. For possible commercial exploitation, these factors and others such as potential shelf life (long-term stability), vapour pressure and mass transport need to be carefully evaluated. Herein, we report the use of magnesium ethoxide and tetraethanol solvated calcium ethoxide as starting materials and their *in situ* reaction with the β-diketone 2,2,6,6-tetramethylheptane-3,5-dione.

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† *Non-SI units employed:* Torr ≈ 133 Pa, eV ≈ 1.60×10^{-19} J.

Results and Discussion

There has been considerable interest over the last two years in Group 2 metal β-diketonates. Several notable studies have included the use of barium hydride as a starting material, *e.g.* Gardiner *et al.*,[17] prepared $[Ba(\beta\text{-diket})_2(C_{10}H_{22}O_5)]$ [β-diket = 1,1,1-trifluoropentane-2,4-dionate (tfpd), hfpd or tmhd] using an excess of the polyether as both Lewis base and solvent, metal hydroxide-based routes, *i.e.* $[Ba_5(OH)(tmhd)_9(H_2O)_3]$[6] and $[Ca_2(hfpd)_4(H_2O)_4]$[10] and more recently a barium isopropoxide concentrate route (using the metal dissolved in Pr^iOH as a solubilised source of barium) to $[Ba_2(tmhd)_4(Et_2O)_2]$.[13] More recent work has focused on β-diketoiminate ligands, *e.g.* ref. 21.

We have sought to build on and extend some of these earlier studies, and in particular we wished to use a synthetic strategy that would not only be reproducible on a laboratory scale but also be implicitly simple and cheap. Thus our prime criteria are as follows: (*i*) the starting material should preferably be synthesised in either aqueous or alcoholic media, with no elaborate precautions necessary, to give a material of reproducible stoichiometry; (*ii*) the laboratory synthesis should be such, that if industrial scale-up is desired, then this is achievable at nominal extra cost; (*iii*) finally, and in many ways crucial to our strategy, is that materials such as $[\{M(OEt)_2(EtOH)_x\}_n]$ (M = Mg, x = 0; M = Ca, x = 4) may easily be converted at room temperature *via* simple ethanol–β-diketone ligand-exchange reactions to the desired products.

We have observed that the reaction of the magnesium ethoxide $[\{Mg(OEt)_2\}_n]$ or tetraethanol solvated calcium ethoxide $[\{Ca(OEt)_2(EtOH)_4\}_n]$ (both readily prepared from their respective metal sources and ethanol on the kilogram scale)[20] with Htmhd yields the homoleptic β-diketonate complexes $[\{Mg(tmhd)_2\}_n]$ **1** and $[Ca_3(tmhd)_6]$ **2** in excellent yield [see equation (1) and Scheme 1]. This reaction using

$$[\{M(OEt)_2(EtOH)_x\}_n] + 2n\text{Htmhd} \xrightarrow{\text{hexane, r.t.}} [\{M(tmhd)_2\}_n] + n(2 + x)\text{EtOH} \quad (1)$$

$$M = Mg, x = 0\ \mathbf{1};\ M = Ca, x = 4\ \mathbf{2}$$

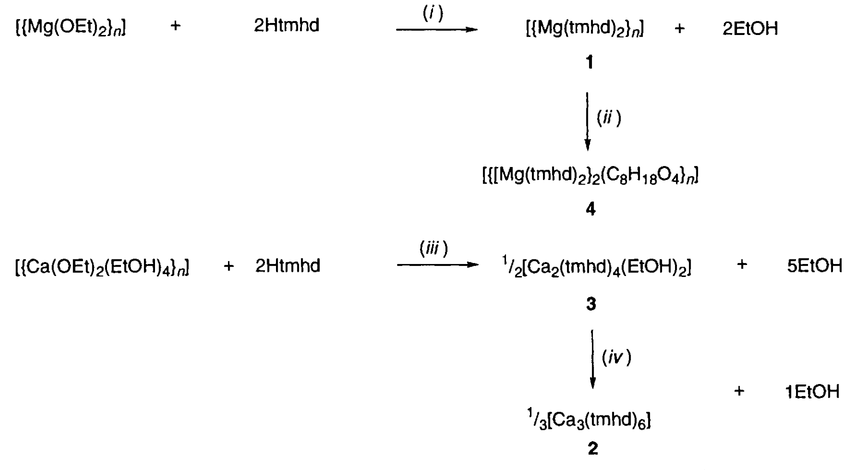
the metal ethoxides as starting materials is exceptionally facile with complete alkoxide–β-diketone ligand exchange occurring within 10 min of addition of the β-diketone Htmhd. The released ethanol from the reaction is readily removed under reduced pressure, and the resultant white solid held under *vacuo* at *ca.* 80 °C for 1 h to remove any last traces of ethanol. The resulting solid materials were then redissolved in hexane to yield colourless crystalline blocks of $[\{Mg(tmhd)_2\}_n]$ **1** or $[Ca_3(tmhd)_6]$ **2** at −25 °C. Both complexes were found to be exceptionally soluble in a wide range of organic solvents, *e.g.* aliphatic, aromatic and co-ordinating.

Spectroscopic data

Infrared spectra of complexes **1** and **2** show several characteristic bands for the co-ordinated tmhd; noteworthy, are the strong absorptions between 1505 and 1591 cm^{-1}. It is not possible to differentiate between the ν(C⋯O) and ν(C⋯C) vibrational modes or individual co-ordination types, due to coupling between the various modes. There is more than one type of C⋯O or C⋯C co-ordination environment in both complexes **1** and **2**. Multinuclear NMR spectroscopy (^1H and ^{13}C) studies in C_6D_6 for **1** reveals three well resolved tmhd environments at room temperature, while for complex **2** only one time-averaged environment was observed, suggesting the tmhd ligands are fluxional in solution at room temperature on the NMR timescale. In contrast, solid-state cross polarisation magic angle spinning (CP MAS) ^{13}C NMR spectra for complexes **1** and **2** revealed several tmhd carbonyl carbon environments (see Fig. 1) and associated signals, indicative of a range of co-ordination modes.

Complex **1** was observed to sublime in a quantitative yield over the range 140–165 °C at 10^{-3} Torr. Similarly, **2** also sublimes intact in excellent yield in the range 170–200 °C at 10^{-3} Torr with minimum decomposition. Thermal gravimetric analysis (Fig. 2) of complex **1** reveals more or less continuous behaviour over the temperature range 60–350 °C, but the first-derivative plot clearly shows at least three reaction processes at (*i*) 60–100, (*ii*) 140–185 and (*iii*) 235–350 °C. The presence of these reactions is also supported by the observation of the corresponding endotherms in the DSC curve. The first two reactions correspond to the loss of Htmhd with a weight loss observed of *ca.* 7.15% (calculated 7.28%). This is followed by a third and final isotherm, which results in sublimation of **1** and 87 ± 1% weight loss, completed by 350 °C, leaving a residue of 5–6%. In contrast, the TGA for compound **2** (Fig. 2) reveals only a single step with a total weight loss of 98 ± 1% over the temperature range 260–360 °C. This demonstrates not only the remarkably high purity of the sample, but also the excellent thermal stability of the Ca_3 trinuclear framework (stable up to 270 °C). Complexes **1** and **2** have $T_{50\%}$ = 281 and 338 °C respectively, which attest to their remarkable thermal stability and good transport behaviour.[22] More importantly and in contrast to the poor thermal stability of $[Ba_4(tmhd)_8]$,[23–25] **1** and **2** have good thermal behaviour and may possibly be useful as potential CVD sources. However, prior to this, vapour-pressure studies and cycled TGA experiments would need to be performed.

Electron-impact (positive-ion) mass spectroscopy for com-



Scheme 1 Synthesis of the magnesium and calcium β-diketonate complexes **1–4**. (*i*) Hexane, 80 °C, 10^{-1} Torr; (*ii*) 0.5 equivalent triglyme (2,5,8,11-tetraoxadodecane, $C_8H_{18}O_4$); (*iii*) hexane, 20 °C, 10^{-1} Torr; (*iv*) 80 °C, 10^{-1} Torr

pound 1 revealed ions corresponding to the $[M_2L_3]^+$ and $[ML_2]^+$ species. While the data for 2 is in accord with a trimeric composition, with clear evidence of the $[M_3L_6]^+$ and $[M_2L_3]^+$ species, other less aggregated ions are also observed, as well as the characteristic tmhd ligand-decomposition pattern.[26] Our mass spectroscopic studies show that these complexes have good volatility in the gas phase in accord with our sublimation and TGA studies.

If the experimental work-up of complex 2 was performed at room temperature an ethanol-adducted intermediate $[Ca_2(tmhd)_4(EtOH)_2]$ 3 is obtained in good yield, whilst the reaction of $[\{Mg(tmhd)_2\}_n]$ 1 with triglyme in hexane yields $[\{Mg(tmhd)_2\}_2(C_8H_{18}O_4)]$ 4 (see Scheme 1).[27] Multinuclear NMR spectroscopy (^1H and ^{13}C) studies in C_6D_6 for 3 reveals signals for both the tmhd ligands and co-ordinated ethanol molecules, whilst 4 displayed only one time-averaged tmhd environment, suggesting the tmhd ligands are fluxional in solution at room temperature on the NMR timescale. Mass spectroscopic studies for 3 and 4 revealed peaks similar to those for 2 and 1 respectively. Interestingly, complexes 3 and 4 sublime intact in excellent yield over the ranges 170–220 and 85–110 °C at 10^{-3} Torr respectively, indicative of strong metal to Lewis base bonds. In contrast, thermal gravimetric analysis study of 3 at atmospheric pressure showed loss of the two ethanol ligands by 150 °C, and above 150 °C the behaviour is nearly identical with that of 2. Similarly, complex 4 exhibits initial glyme loss, followed by sublimation of the remaining solid in 96 ± 1% yield.

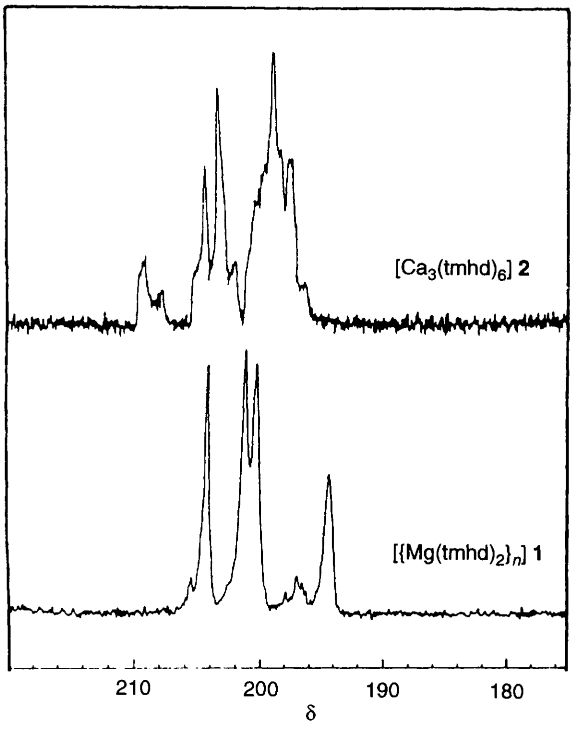


Fig. 1 Solid-state ^{13}C NMR spectra for $[\{Mg(tmhd)_2\}_n]$ 1 and $[Ca_3(tmhd)_6]$ 2

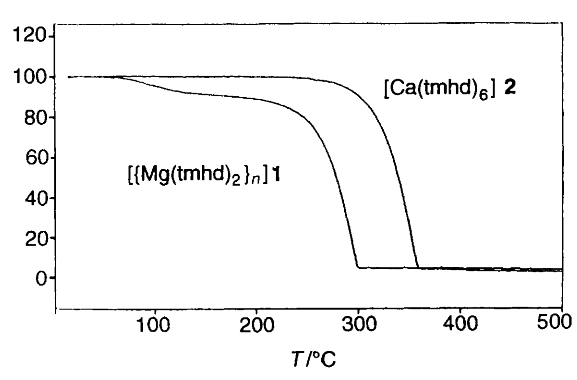


Fig. 2 Thermal gravimetric analysis plots under flowing nitrogen for $[\{Mg(tmhd)_2\}_n]$ 1 and $[Ca_3(tmhd)_6]$ 2

Structures of $[Ca_3(tmhd)_6]$ 2 and $[Ca_2(tmhd)_4(EtOH)_2]$ 3

Complex 2 yielded crystals suitable for a single-crystal X-ray diffraction study from a hexane solution at −25 °C. The molecular structure is illustrated in Fig. 3. An important feature of the present complex is the total absence of any Lewis bases in the structure, *i.e.* ethanol, acetone, water or polyether ligands.[10,28–30] Thus, this is the first example of a homoleptic calcium β-diketonate, and may possibly be a prototypal structural building block in this area of chemistry. To the best of our knowledge, this is also the first example of a trinuclear calcium structural motif.

The Ca···Ca separations in the calcium triangle are 3.348(4), 3.550(4) and 3.709(4) Å, the shortest of which is between the pair [Ca(1) and Ca(2)] bridged by three oxygens; the longer distances involve the pairs of calcium atoms [Ca(1) and Ca(3), Ca(2) and Ca(3)] with only two bridging oxygen atoms between them. All the calcium atoms are six-co-ordinate with highly distorted octahedral geometry and dissimilar ligand environments. Thus, Ca(2) and Ca(3) each bears a chelating tmhd group as well as several bridging tmhds, in contrast with Ca(1) which has only bridging and no chelating tmhd groups.

The tmhd ligands are involved in a variety of co-ordination modes, which is however not very surprising given that complex 2 is molecular and not polymeric. The Ca–O bond lengths (Table 1) fall into three distinct categories which can be correlated with the nature of the oxygen linkage. For example the oxygens forming only one bond to calcium [O(1), O(5), O(6), O(7), O(9), O(11) and O(12)] have very similar and short Ca–O distances [2.224(5)–2.288(5), average 2.247(5) Å], whilst significantly longer bonds are formed by the μ-oxygens [O(2)–O(4) and O(10); 2.311(5)–2.448(5), average 2.376(5) Å]. The unique μ_3-oxygen [O(8)] forms the longest Ca–O bonds [2.456(5)–2.515(6), average 2.493(6) Å]. Thus the Ca–O bond lengths are clearly increased by the increased number of bonds each oxygen makes with the metals. It may also be noted here that the μ_3-oxygen ensures that each metal in the trimer is six-co-ordinate. The capping arrangement does not occur for O(3) which bridges only Ca(1) and Ca(2), most likely due to the distance to Ca(3) being too long [3.135(6) Å] to achieve a bonding contact. Close examination of the Ca–O distances involving each tmhd ligand indicates that whilst one of the purely chelating [that containing O(1) and O(2)] is bonded to

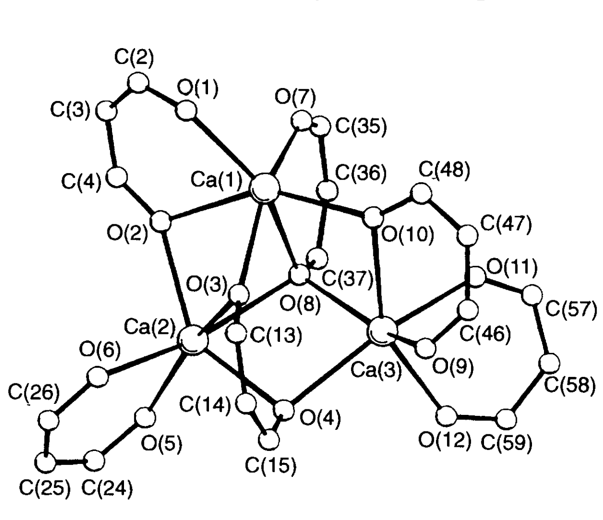


Fig. 3 Molecular structure of $[Ca_3(tmhd)_6]$ 2 showing the atom numbering scheme. Hydrogen atoms and *tert*-butyl groups of the tmhd ligands have been omitted for clarity

Table 1 Selected interatomic distances (Å) and angles (°) for complex **2**

O(1)–Ca(1)	2.238(5)	O(2)–Ca(1)	2.381(5)
O(3)–Ca(1)	2.311(5)	O(7)–Ca(1)	2.224(5)
O(8)–Ca(1)	2.507(6)	O(10)–Ca(1)	2.310(5)
O(2)–Ca(2)	2.354(5)	O(3)–Ca(2)	2.403(5)
O(4)–Ca(2)	2.366(5)	O(5)–Ca(2)	2.241(5)
O(6)–Ca(2)	2.247(5)	O(8)–Ca(2)	2.515(6)
O(4)–Ca(3)	2.436(5)	O(8)–Ca(3)	2.456(5)
O(9)–Ca(3)	2.243(5)	O(10)–Ca(3)	2.448(5)
O(11)–Ca(3)	2.248(5)	O(12)–Ca(3)	2.288(5)
Ca(1) · · · Ca(2)	3.348(4)	Ca(1) · · · Ca(3)	3.550(4)
Ca(2) · · · Ca(3)	3.709(4)		
O(2)–Ca(1)–O(1)	76.4(2)	O(3)–Ca(1)–O(1)	108.1(2)
O(3)–Ca(1)–O(2)	79.5(2)	O(7)–Ca(1)–O(1)	92.1(2)
O(7)–Ca(1)–O(2)	93.2(2)	O(7)–Ca(1)–O(3)	155.9(1)
O(8)–Ca(1)–O(1)	146.5(1)	O(8)–Ca(1)–O(2)	73.0(2)
O(8)–Ca(1)–O(3)	79.4(2)	O(8)–Ca(1)–O(7)	76.6(2)
O(10)–Ca(1)–O(1)	130.7(1)	O(10)–Ca(1)–O(2)	149.9(1)
O(10)–Ca(1)–O(3)	79.1(2)	O(10)–Ca(1)–O(7)	97.8(2)
O(10)–Ca(1)–O(8)	82.5(2)	O(3)–Ca(2)–O(2)	78.3(2)
O(4)–Ca(2)–O(2)	140.9(1)	O(4)–Ca(2)–O(3)	69.6(2)
O(5)–Ca(2)–O(2)	120.1(2)	O(5)–Ca(2)–O(3)	157.5(1)
O(5)–Ca(2)–O(4)	97.0(2)	O(6)–Ca(2)–O(2)	97.1(2)
O(6)–Ca(2)–O(3)	89.0(2)	O(6)–Ca(2)–O(4)	103.8(2)
O(6)–Ca(2)–O(5)	76.5(2)	O(8)–Ca(2)–O(2)	73.3(2)
O(8)–Ca(2)–O(3)	77.5(2)	O(8)–Ca(2)–O(4)	78.4(2)
O(8)–Ca(2)–O(5)	118.6(2)	O(8)–Ca(2)–O(6)	164.7(1)
O(8)–Ca(3)–O(4)	78.3(2)	O(9)–Ca(3)–O(4)	99.3(2)
O(9)–Ca(3)–O(8)	150.7(1)	O(10)–Ca(3)–O(4)	118.9(2)
O(10)–Ca(3)–O(8)	80.8(2)	O(10)–Ca(3)–O(9)	74.8(2)
O(11)–Ca(3)–O(4)	156.4(1)	O(11)–Ca(3)–O(8)	93.4(2)
O(11)–Ca(3)–O(9)	98.5(2)	O(11)–Ca(3)–O(10)	80.8(2)
O(12)–Ca(3)–O(4)	87.8(2)	O(12)–Ca(3)–O(8)	114.0(2)
O(12)–Ca(3)–O(9)	95.0(2)	O(12)–Ca(3)–O(10)	152.4(1)
O(12)–Ca(3)–O(11)	75.4(2)	Ca(2)–O(2)–Ca(1)	90.0(2)
Ca(2)–O(3)–Ca(1)	90.5(2)	Ca(3)–O(4)–Ca(2)	101.1(2)
Ca(2)–O(8)–Ca(1)	83.6(2)	Ca(3)–O(8)–Ca(1)	91.3(2)
Ca(3)–O(8)–Ca(2)	96.5(2)	Ca(3)–O(10)–Ca(1)	96.5(2)

calcium symmetrically with virtually identical bond lengths, the chelate bonds with the other five ligands are quite asymmetric as suggested by variations of 0.037 to 0.183 Å. The largest variation is observed, as expected, in the μ_3-ligand, but surprisingly, the smallest variation is associated with the μ,μ-ligand. The C=O distances (1.247–1.327 Å) show variations which are small but may be correlated with the number of bonds each oxygen makes with calcium. Other aspects worth noting in respect of the tmhd ligands are their planarity, or lack of it, and the folds about the O · · · O axis. Whilst only one of the OCCCO moieties (that containing the μ_3-oxygen) is marginally planar [maximum deviation of atoms from the mean plane 0.013(4) Å], all other ligands are significantly non-planar with atomic deviations ranging from 0.025(5) to 0.074(4) Å, the largest deviation being observed in the μ,μ-ligand. The fold angles about the O · · · O axes fall into three different ranges, 2.3(1)–6.9(1) (involving the μ_3- and purely chelating ligands), 30.7(1)–34.8(1) (the two μ-ligands) and 54.1(1)° (the μ,μ-ligand). Thus the largest distortions in terms of non-planarity and fold angles are observed in the ligand with the μ,μ-bonding modes, which clearly is under greater strain than any other ligand, due to the involvement of both of its oxygens in bridge formation. The least distortions are associated with the two purely chelating, and the μ_3-ligands, which are under less strain. In fact, the tmhd ligands in many other complexes have been found to exhibit different types of linkages with metals, with considerable flexibility and varying degrees of folding about the O · · · O axis.[31–34]

The structure of complex **2** may be contrasted with the few other calcium β-diketonate complexes characterised and reported previously. One such complex is $[Ca_4(dppd)_8(EtOH)_2]$ (dppd = 1,3-diphenylpropane-1,3-dionate) which is tetrameric,[28] and based on a parallelepiped arrangement of oxygen atoms, with the four calcium atoms binding to four of the available faces. The calcium atoms are arranged at the corners of a rhomboid. The complex contains both bridging and chelating dppd ligands with an average Ca–O distance of 2.37 Å. A related complex is the monomeric species $[Ca(pd)_2(H_2O)_2]\cdot H_2O$ (pd = pentane-3,4-dionate),[29] which is octahedral with an average Ca–O distance of 2.33 Å. More recently Bradley *et al.*[10] reported the dimeric species $[Ca_2(hfpd)_4(H_2O)_4]$ in which the calcium atoms are eight-co-ordinate. This high co-ordination number arises from Ca · · · F–C interactions *via* CF_3 groups, and also a chelating hfpd ligand which also bridges the two calcium atoms through one of its oxygens. The average Ca–O distance in this complex was observed to be 2.44 Å, the longer distance primarily being due to the Ca–O bridging hfpd ligands between the metal centres. A further useful comparison may be made with the recently characterised trinuclear barium siloxide, $[Ba_3(OSiPh_3)_6(thf)]$, which has a similar arrangement of μ_3-and μ-oxygen-based ligands.[35]

The trimeric calcium structure completes an interesting series of Group 2 metal β-diketonate complexes. The barium–tmhd compound is a tetramer $[Ba_4(tmhd)_8]$,[23,24] which may be considered to be formally derived from the coupling of two $Ba_2(tmhd)_4$ dimers; the related strontium complex has been shown to consist of a triangular Sr_3 motif $[Sr_3(tmhd)_6(Htmhd)]$ supported by six tmhd ligands in a wide range of co-ordination modes, and also most unusually contains an unmetallated chelating Htmhd ligand.[23] The series of molecules show quite clearly how in each of the complexes the metal centres not only maximise their co-ordination numbers, but also change from a 'formally' open triangle in the calcium trimer to the distorted 'closo' cube observed for $[Ba_4(tmhd)_8]$.[23,24] This subtle difference in molecule architecture more than compensates for the increase in ionic radii (Mg 0.78, Ca 1.06, Sr 1.27, Ba 1.43 Å),[36] and the increased Lewis acidity and polarisation of the dicationic metal centres.

Complex **3** yielded crystals from an hexane solution at −25 °C, which were of rather poor quality. However, a data set was collected from a single crystal and the structure solved. Least-squares refinement resulted in *R* values (0.097) somewhat higher than normally obtained for a 'good' structure, owing to the poor quality of the data, high thermal motion and disorder associated with several *tert*-butyl methyl groups. Nevertheless, the material was characterised unambiguously and the essential structural features and bonding modes were established. The crystal structure contains three discrete dimeric molecules in the unit cell held together by van der Waals forces. One molecule possesses a crystallographic inversion centre (A in Fig. 4); the other (B in Fig. 4) lies in a general position, but it is also nearly centrosymmetric. In both cases, the dimers are based on two tmhd ligands bridging the two $Ca(tmhd)_2(EtOH)$ moieties. The corresponding dimensions in the dinuclear cores are very similar and comparable; the main differences in the two dimeric species are associated with the orientations of the *tert*-butyl groups and to a lesser extent with the co-ordinated ethanol molecules.

The calcium atoms in both dimers are each bonded to a terminal, purely chelating tmhd ligand, one chelating tmhd ligand which also forms a bridge to the second calcium through one of its oxygens, and a terminally co-ordinated ethanol molecule. The calcium atoms are thus six-co-ordinated with highly distorted octahedral geometry. The overall co-ordination geometry of the dinuclear core is distorted, edge-sharing bioctahedral, the common edge being defined by the two bridging oxygens of the two tmhd ligands. The Ca · · · Ca separations [3.642(4) and 3.648(4) Å] are virtually the same in the two dimers.

Interestingly, the unit-cell contents of the analogous barium compound $[Ba(tmhd)_2(MeOH)_3]\cdot MeOH$[9] consist of two units of formula $Ba(tmhd)_2(MeOH)_3$, however dinuclear formation

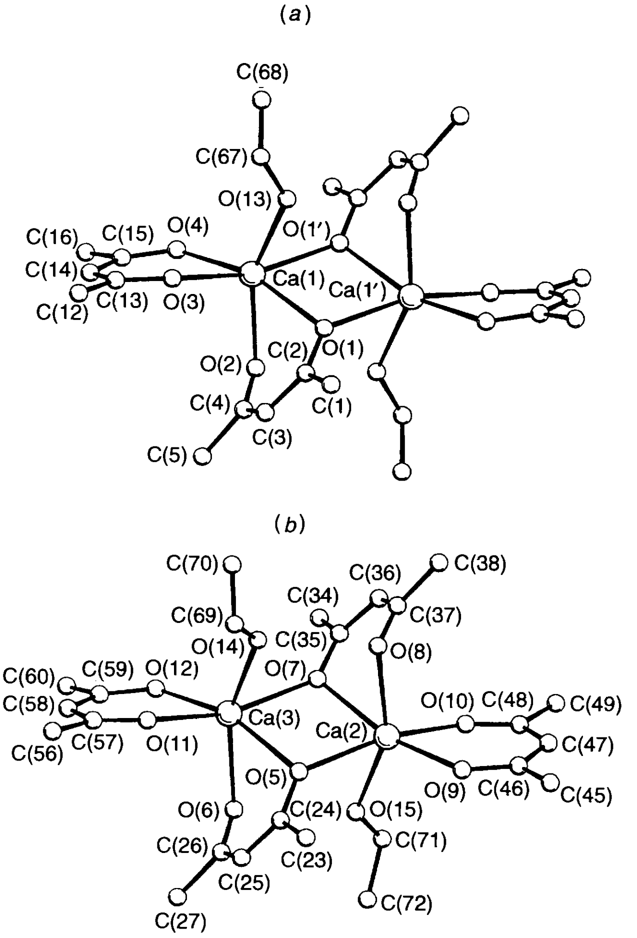


Fig. 4 Structures of the two dimers $[Ca_2(tmhd)_4(EtOH)_2]$ (*a*) and (*b*) in complex **3**. Tertiary butyl groups of the tmhd ligands have been omitted for clarity

Table 2 Selected interatomic distances (Å) and angles (°) for $[Ca_2(tmhd)_4(EtOH)_2]$ **3***

O(1)–Ca(1)	2.400(10)	O(1′)–Ca(1)	2.356(10)
O(2)–Ca(1)	2.326(9)	O(3)–Ca(1)	2.246(11)
O(4)–Ca(1)	2.265(10)	O(13)–Ca(1)	2.351(10)
O(5)–Ca(2)	2.351(9)	O(7)–Ca(2)	2.424(10)
O(8)–Ca(2)	2.327(7)	O(9)–Ca(2)	2.256(10)
O(10)–Ca(2)	2.271(10)	O(15)–Ca(2)	2.378(9)
O(5)–Ca(3)	2.418(9)	O(6)–Ca(3)	2.347(8)
O(7)–Ca(3)	2.363(9)	O(14)–Ca(3)	2.345(9)
O(11)–Ca(3)	2.258(10)	O(12)–Ca(3)	2.267(10)
Ca(1) · · · Ca(1′)	3.642(4)	Ca(2) · · · Ca(3)	3.646(4)
O(2)–Ca(1)–O(1)	71.3(4)	O(3)–Ca(1)–O(1)	102.0(4)
O(3)–Ca(1)–O(2)	101.5(4)	O(4)–Ca(1)–O(1)	163.3(2)
O(4)–Ca(1)–O(2)	92.4(4)	O(4)–Ca(1)–O(3)	77.0(4)
O(13)–Ca(1)–O(1)	81.6(4)	O(13)–Ca(1)–O(2)	152.8(3)
O(13)–Ca(1)–O(3)	87.2(4)	O(13)–Ca(1)–O(4)	114.8(4)
O(1)–Ca(1)–O(1′)	80.1(4)	O(2)–Ca(1)–O(1′)	95.7(4)
O(3)–Ca(1)–O(1′)	162.5(4)	O(4)–Ca(1)–O(1′)	106.0(4)
O(13)–Ca(1)–O(1′)	75.8(4)	O(7)–Ca(2)–O(5)	80.6(3)
O(8)–Ca(2)–O(5)	92.7(3)	O(8)–Ca(2)–O(7)	71.1(3)
O(9)–Ca(2)–O(5)	108.5(4)	O(9)–Ca(2)–O(7)	165.5(2)
O(9)–Ca(2)–O(8)	96.7(3)	O(10)–Ca(2)–O(5)	163.7(2)
O(10)–Ca(2)–O(7)	97.8(4)	O(10)–Ca(2)–O(8)	102.2(3)
O(10)–Ca(2)–O(9)	76.7(4)	O(15)–Ca(2)–O(5)	76.7(3)
O(15)–Ca(2)–O(7)	82.1(4)	O(15)–Ca(2)–O(8)	152.5(3)
O(15)–Ca(2)–O(9)	110.6(4)	O(15)–Ca(2)–O(10)	87.0(4)
O(6)–Ca(3)–O(5)	71.3(3)	O(7)–Ca(3)–O(5)	80.5(4)
O(7)–Ca(3)–O(6)	96.7(3)	O(14)–Ca(3)–O(5)	83.0(3)
O(14)–Ca(3)–O(6)	154.2(3)	O(14)–Ca(3)–O(7)	76.4(4)
O(11)–Ca(3)–O(5)	101.6(4)	O(11)–Ca(3)–O(6)	101.5(4)
O(11)–Ca(3)–O(7)	161.3(2)	O(11)–Ca(3)–O(14)	85.4(4)
O(12)–Ca(3)–O(5)	162.2(2)	O(12)–Ca(3)–O(6)	91.5(4)
O(12)–Ca(3)–O(7)	106.4(4)	O(12)–Ca(3)–O(14)	114.3(3)
O(12)–Ca(3)–O(11)	77.3(4)	Ca(1)–O(1)–Ca(1′)	99.9(4)
Ca(3)–O(5)–Ca(2)	99.7(4)	Ca(3)–O(7)–Ca(2)	99.2(4)

* The primed atoms are generated by the symmetry $-x$, $-y$, $-z$.

is precluded due to the extent of their separation. In contrast, the Ca(tmhd)$_2$(EtOH) units in complex **3** are insufficiently separated, which consequently leads to dimer formation. The dimer of **3** may be contrasted with the analogous dimeric complexes of barium, *e.g.* $[Ba_2(tmhd)_4(NH_3)_4]$,[11] $[Ba_2(tmhd)_4(bipy)_2]$[12] and $[Ba_2(tmhd)_4(Et_2O)_2]$.[13] In complex **3** the chelating bridging tmhd ligands are different to those observed in barium dimers[11–13] where both the oxygen atoms of the tmhd ligand are involved in bridging, resulting in seven- and eight-co-ordinate barium ions.

The Ca–O distances (Table 2) vary from 2.246(10) to 2.424(10) Å and, as in the homoleptic trimer **2**, may be correlated with the modes of linkage. Thus, the shortest Ca–O distances of 2.246(10)–2.267(10) Å (average 2.261 Å) are associated with the terminal, purely chelating tmhd ligands, whilst the longest ones of 2.400(10)–2.424(10) Å, average of 2.414 Å, correspond to the chelating oxygens from the chelating/bridging tmhd ligands. The other bonds (to each calcium) involving the chelating/bridging tmhd ligands have intermediate values [2.326(9)–2.363(9), average 2.345 Å]; the Ca–O bonds with ethanol are also intermediate [2.345(9)–2.378(9), average 2.358 Å]. In both molecules the Ca–O bridge bonds are asymmetric with distance variations of *ca.* 0.057 Å. The Ca–O–Ca angles are very similar and lie in the range 99.2–99.9(4)°. The O–Ca–O chelate angles are 77.0(4), 76.3(4), 77.7(4)° for the terminal and 71.3(4), 71.1(3), 71.3(3)° for the bridging tmhd ligand, the latter being narrowed down from the former by *ca.* 6° due to bridge formation. Again, as a consequence of bridge formation, the bridging tmhd ligands show considerably larger folding about the O · · · O axis (50–56°) compared with those (10–14°) in the terminal ligands. Similar differences in the fold angles in β-diketonate ligands having different modes of bonding with metals have been noted in **2** and also in other cases.[31–34] The remaining bond lengths and angles in tmhd ligands are similar to the expected values. The Ca–O–C and O–C–C angles involving the EtOH ligands are 136.0(7), 130.1(6), 133.7(7)° and 108.4(4), 111.7(6), 110.0(7)° respectively.

Conclusion

We believe that careful design of magnesium and calcium precursors must incorporate not only a multifunctional β-diketonate or alkoxide ligand, but preferably have a Lewis-base moiety either built onto this (as for instance in glycolates or amidoalcohols) or *via* the use of external multidentate Lewis bases.

The metal alkoxide route is not restricted to only ethoxides as starting materials, indeed preliminary investigations have shown that the metal methoxides $[\{Mg(OMe)_2\}_n]$ **1** and $[\{Ca(OMe)_2\}_n]$ **2** also yield high-purity products in good yields. Furthermore, the use of methanol-derived starting materials is decidedly more advantageous from an industrial perspective. An important point to note is the total absence of any oxide or hydroxide ligands in the final products, the incorporation such having hampered previous research. This suggests that our starting materials and synthetic strategies are highly effective in producing high-purity products reproducibly.

Complexes **1**, **2** and **4** exhibited good volatilities and thermal stabilities and as such may find application as potential OMCVD precursors. Indeed, their excellent solubilities and well defined compositions may also find use in sol–gel processes. This approach is currently being explored and the materials evaluated, by both classical chemical techniques and where appropriate, vapour-pressure and mass-transport studies.

Experimental

General methods

All manipulations were carried out under an atmosphere of dry (molecular sieves) nitrogen using standard glove-box (Miller-Howe FF 160 with double recirculator system) and Schlenk techniques. All hydrocarbon solvents were rigorously pre-dried and then distilled first over calcium oxide, and then redistilled over sodium metal by standard techniques. Elemental analyses were performed by the microanalytical department of Imperial College. The melting points were measured under argon in sealed capillaries and are uncorrected.

Physical techniques

Infrared spectra were recorded on a Perkin-Elmer FTIR 1720 spectrometer as either Nujol or hexachlorobutadiene mulls between 25 × 4 mm CsI plates. The Nujol and hexachlorobutadiene were both pre-dried with 4 Å molecular sieves prior to use (and stored in the glove-box), and the samples were protected from the atmosphere by an O-ring sealed Presslok holder (available from Aldrich chemicals). The NMR spectra were recorded on a JEOL GS 270 MHz spectrometer, using the protio impurities of the deuteriated solvent as reference for ^1H spectra and the ^{13}C resonance of the solvent for ^{13}C spectra. Chemical shifts were also independently referenced to tetramethylsilane (*ca.* 1%) added by volume. All chemical shifts are reported positive to high frequency of the standard. Solid-state CP MAS ^{13}C-{^1H) NMR spectra were recorded on a Bruker MSL 300 MHz spectrometer by the University of London Solid State NMR Service. The samples were handled under an inert atmosphere. Mass spectrometric studies were performed on a Kratos MS 30 (University of London Mass Spectrometry Service at the Royal School of Pharmacy) or a VG Autospec-Q (Imperial College Mass Spectrometry Service) instrument operating in electron-impact (positive) mode (70 eV) using a direct insertion probe and the temperature range 50–200 °C. The samples were prepared in micro sure-seal bottles. Controlled thermal analysis of the complexes was investigated using a Polymer Laboratories STA 1500H simultaneous thermal analyser, controlled by a Omni Pro 486DX-33 personal computer. The masses of the samples investigated were between 12 and 22 mg. The measurements were carried out in alumina crucibles under an atmosphere of flowing (25 cm^3 min^{-1}) nitrogen gas, using heating rates of 5 °C min^{-1}.

Syntheses

All reactions were performed with dry oxygen-free solvents, stored over 4 Å molecular sieves. 2,2,6,6-Tetramethylheptane-3,5-dione (Htmhd) was obtained from Inorgtech of Mildenhall, Suffolk. Magnesium ethoxide [{$Mg(OEt)_2$}$_n$] and tetraethanol-solvated calcium ethoxide [{$Ca(OEt)_2(EtOH)_4$}$_n$] were prepared according to literature procedures.[20]

[{$Mg(tmhd)_2$}$_n$] 1. To a white suspension of [{$Mg(OEt)_2$}$_n$] (1.71 g, 15 mmol) in hexane (25 cm^3) was added Htmhd (6.26 cm^3, 30 mmol), resulting in a clear solution after stirring for 10 min. The solvent and liberated ethanol were then removed under reduced pressure to yield a white solid, which was held under *vacuo* at 80 °C for *ca.* 1 h. This product was then redissolved in hot hexane (8 cm^3), and left to crystallise at 0 °C. Yield 4.21 g (72% based on magnesium ethoxide), m.p. 255–265 °C, sublimes 140–165 °C at 10^{-3} Torr (Found: C, 66.9; H, 9.3. $C_{22}H_{38}MgO_4$ requires C, 67.7; H, 9.7%). IR: (Nujol) 1609s, 1597s, 1587s, 1547m, 1537s, 1505s, 1418s, 1279m, 1260m, 1249m, 1226m, 1182m, 1147m, 1128m, 1095w, 1023w, 965w, 956w, 932w, 872s, 798m, 764m, 733m, 616w, 585w, 506m, 481w and 368w; (hexachlorobutadiene) 2964s, 2905m, 2869m, 1597s, 1586s, 1536m, 1505s, 1393m and 1361m cm^{-1}. NMR: ^1H (C_6D_6, 270 MHz), δ 1.18–1.27 (36 H, m, CH_3) and 5.86–5.91 (2 H, m, CH); ^{13}C-{^1H} (C_6D_6, 65.94 MHz), δ 28.54 (s, CH_3), 28.79 (s, CH_3), 29.22 (s, CH_3), 40.94 [s, *C*$(CH_3)_3$], 41.28 [s, *C*$(CH_3)_3$], 90.71 (s, CH), 92.03 (s, CH), 94.74 (s, CH), 201.15 (s, CO) and 202.02 (s, CO); ^{13}C-{^1H} (CP MAS solid state, 75.67 MHz), δ 27.76 (s, CH_3), 28.60 (s, CH_3), 29.42 (s, CH_3), 40.02 [s, *C*$(CH_3)_3$], 40.69 [s, *C*$(CH_3)_3$], 41.82 [s, *C*$(CH_3)_3$], 91.07 (br s, CH), 92.00 (br s, CH), 93.14 (br s, CH), 93.40 (br s, CH), 194.26 (s, CO), 196.84 (s, CO), 200.09 (s, CO), 200.99 (s, CO), 203.98 (s, CO) and 205.31 (s, CO). Mass spectrum (positive-ion EI): *m*/*z* 597 [$Mg_2(tmhd)_3$, 10], 391 [$HMg(tmhd)_2$, 15], 376 [$HMg(tmhd)_2$ − Me, 10], 334 [$HMg(tmhd)_2$ − Bu^t, 100] and 207 [Mg(tmhd), 25%].

[$Ca_3(tmhd)_6$] 2. To a suspension of [{$Ca(OEt)_2(EtOH)_4$}$_n$] (6.28 g, 20 mmol) in hexane (25 cm^3) was added Htmhd (8.34 cm^3, 40 mmol). The reaction conditions and work-up were as for complex **1**. Yield 6.90 g (85% based on calcium ethoxide), m.p. 238–241 °C, sublimes 170–220 °C at 10^{-2} Torr (Found: C, 63.9; H, 8.7. $C_{66}H_{114}Ca_3O_{12}$ requires C, 65.0; H, 9.4%). IR: (Nujol) 1592s, 1580s, 1559s, 1539s, 1505s, 1407s, 1277m, 1245m, 1225m, 1179m, 1132m, 1115m, 1022w, 956w, 941w, 868m, 805m, 795m, 775w, 765w, 757w, 734m, 602w, 505w, 482m, 407m and 313m; (hexachlorobutadiene) 2963s, 2905m, 2890m, 2868m, 1591s, 1579s, 1558s, 1540s, 1506s, 1453s, 1421s, 1392m and 1359m cm^{-1}. NMR: ^1H (C_6D_6, 270 MHz), δ 1.26 (36 H, m, CH_3) and 5.90 (2 H, m, CH); ^{13}C-{^1H} (C_6D_6, 65.94 MHz), δ 28.77 (s, CH_3), 41.41 [s, *C*$(CH_3)_3$], 92.40 (s, CH), 201.71 (s, CO) and 201.85 (s, CO); ^{13}C-{^1H} (CP MAS solid state, 75.67 MHz), δ 28.48 (s, CH_3), 28.71 (s, CH_3), 29.00 (s, CH_3), 29.17 (s, CH_3), 29.50 (s, CH_3), 29.87 (s, CH_3), 30.36 (s, CH_3), 31.37 (s, CH_3), 41.16 [s, *C*$(CH_3)_3$], 41.41 [s, *C*$(CH_3)_3$], 41.60 [s, *C*$(CH_3)_3$], 42.16 [s, *C*$(CH_3)_3$], 42.44 [s, *C*$(CH_3)_3$], 42.56 [s, *C*$(CH_3)_3$], 42.75 [s, *C*$(CH_3)_3$], 88.43 (br s, CH), 88.76 (br s, CH), 89.76 (br s, CH), 90.91 (br s, CH), 91.30 (br s, CH), 91.72 (br s, CH), 92.91 (br s, CH), 97.01 (br s, CH), 97.63 (br s, CH), 98.11 (br s, CH), 197.61 (s, CO), 198.84 (s, CO), 200.11 (s, CO), 201.96 (s, CO), 203.36 (s, CO), 204.46 (s, CO), 207.70 (s, CO) and 209.09 (s, CO). Mass spectrum (positive-ion EI): *m*/*z* 1118 [$Ca_3(tmhd)_6$ − $C_6H_{12}O$, 10], 629 [$Ca_2(tmhd)_3$, 10], 407 [$HCa(tmhd)_2$, 10] and 223 [Ca(tmhd), 55%].

[$Ca_2(tmhd)_4(EtOH)_2$] 3. To a suspension of [{$Ca(OEt)_2$-$(EtOH)_4$}$_n$] (5.34 g, 17 mmol) in hexane (25 cm^3) was added Htmhd (7.10 cm^3, 34 mmol) resulting in a clear solution on stirring for 10 min. The solvent and liberated ethanol were then removed under reduced pressure at 50 °C to yield a white solid, which was redissolved in hot hexane (10 cm^3) and left to crystallise at −25 °C. Yield 6.00 g (78% based on calcium ethoxide), m.p. desolvates 112–115, 235–238 °C, sublimes 170–220 °C at 10^{-3} Torr to yield **3** (Found: C, 63.1; H, 8.5. $C_{48}H_{88}Ca_2O_{10}$ requires C, 63.7; H, 9.7%). IR: (Nujol) 3331m, 1591s, 1579s, 1543m, 1504m, 1413m, 1280m, 1245m, 1225m, 1184m, 1135m, 1085m, 1052m, 1026m, 956w, 934w, 885w, 867m, 804m, 792w, 756w, 733m, 601w, 473m and 408w; (hexachlorobutadiene), 3334w, 2963s, 2905m, 2887m, 2868m, 1591s, 1579s, 1540m, 1506s, 1452m, 1410s, 1390m and 1358m cm^{-1}. NMR: ^1H (C_6D_6, 270 MHz), δ 1.04 (3 H, t, CH_3, EtOH), 1.26 (36 H, s, CH_3, tmhd), 2.96 (1 H, s, OH, EtOH), 3.86 (2 H, q, CH_2, EtOH) and 5.88 (2 H, s, CH); ^{13}C-{^1H} (C_6D_6, 65.94 MHz), δ 18.28 (s, CH_3, EtOH), 28.77 (s, CH_3, tmhd), 41.30 [s, *C*$(CH_3)_3$], 58.59 (s, CH_2, EtOH), 91.56 (s, CH) and 201.39 (s, CO). Mass spectrum (positive-ion EI): *m*/*z* 629 [$Ca_2(tmhd)_3$, 10], 407 [$HCa(tmhd)_2$, 15] and 223 [Ca(tmhd), 5%].

[{$[Mg(tmhd)_2]_2(C_8H_{18}O_4)$}$_n$] 4. To a suspension of [{Mg-$(OEt)_2$}$_n$] (1.50 g, 13.16 mmol) in hexane (25 cm^3) was added Htmhd (4.80 cm^3, 26 mmol) resulting in a clear solution on

Table 3 Crystal data and details of data collection and refinement for $[Ca_3(tmhd)_6]$ **2** and $[Ca_2(tmhd)_4(EtOH)_2]$ **3**[a]

	Complex **2**	Complex **3**
Formula	$C_{66}H_{114}Ca_3O_{12}$	$C_{48}H_{88}Ca_2O_{10}$
M	1219.86	905.38
Crystal system	Orthorhombic	Triclinic
a/Å	20.023(4)	13.556(6)
b/Å	19.638(6)	14.138(6)
c/Å	18.906(5)	23.266(9)
α/°		74.07(2)
β/°		73.96(2)
γ/°		80.25(3)
U/Å^3	7434.06	4099.72
Space group	$Pca2_1$ (no. 29)	$P\bar{1}$ (no. 2)
Z	4	3
D_c/g cm^{-3}	1.09	1.100
F(000)	2664	1488
μ(Mo-Kα)/cm^{-1}	2.6	2.5
Crystal size/mm	0.45 × 0.20 × 0.15	0.50 × 0.35 × 0.25
θ range for data/°	2.1–29.7	2.0–29.8
hkl Ranges	−18 to 27, −25 to 23, −25 to 25	−17 to 13, −18 to 18, −21 to 30
Total data measured	51 504	19 919
Total unique	17 322	17 540
R_{int}	0.052	0.058
Total observed $[F_o > 3\sigma(F_o)]$	8590	7078
No. of parameters	810	809
ρ_{min}, ρ_{max}/e Å^{-3}	−0.53, +0.54	−0.92, +1.01
$(\Delta/\sigma)_{max}$	0.55	0.40
R	0.042[b]	0.097
R'	0.049[b]	0.115

[a] $R = \Sigma(\Delta F)/\Sigma(F_o)$; $R' = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, unit weights. [b] The R (R') values for the inverted structure are 0.0440 (0.0514).

stirring for 10 min. Triglyme (1.19 cm^3, 6.58 mmol) was added and reaction conditions and work-up were as for complex **3**. Yield 5.38 g (72% based on magnesium ethoxide), m.p. 120–123 °C (Found: C, 64.7; H, 9.2. $C_{26}H_{47}MgO_6$ requires C, 65.1; H, 9.8%). IR: (Nujol) 1594s, 1578s, 1541s, 1508s, 1410s, 1288m, 1261m, 1249m, 1227m, 1206m, 1179s, 1137m, 1106s, 1085s, 1023s, 960w, 933w, 915m, 867s, 823m, 793s, 755m, 735m, 615m, 547w, 496w, 474m, 426w and 351m; (hexachlorobutadiene) 3010w, 2950s, 2903m, 2881s, 2862m, 1592s, 1580s, 1548m, 1509s, 1490m, 1453m, 1435m, 1387m and 1356m cm^{-1}. NMR: ^1H (C_6D_6, 270 MHz), δ 1.25 (36 H, s, CH_3, tmhd), 3.24 (3 H, s, CH_3, triglyme), 3.31 (2 H, br m, CH_2, triglyme), 3.81 (2 H, br m, CH_2, triglyme), 4.04 (2 H, s, CH_2, triglyme) and 5.79 (2 H, s, CH); $^{13}C-\{^1H\}$ (C_6D_6, 65.94 MHz), δ 28.74 (s, CH_3, tmhd), 40.98 [s, $C(CH_3)_3$], 59.21 (s, CH_3, triglyme), 69.78 (s, CH_2, triglyme), 70.64 (s, CH_2, triglyme), 70.95 (s, CH_2, triglyme), 88.68 (s, CH) and 200.65 (s, CO). Mass spectrum (positive-ion FAB): m/z 597 $[Mg_2(tmhd)_3$, 45], 391 $[HMg(tmhd)_2$, 65], 376 $[HMg(tmhd)_2$ − Me, 15], 334 $[HMg(tmhd)_2$ − Bu^t, 75] and 207 [Mg(tmhd), 100%].

Crystallography

Crystals of $[Ca_3(tmhd)_6]$ **2** and $[Ca_2(tmhd)_4(EtOH)_2]$ **3** suitable for X-ray work were grown from hexane. Those of **3** were of poor quality, with relatively large mosaicity (≈ 1.2). The unit-cell dimensions and intensity data for both compounds were measured at 150 K using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator and using Mo-Kα radiation (λ = 0.710 69 Å), following procedures described elsewhere.[37] The data were corrected for Lorentz-polarisation factors but not for absorption. The structures were solved by direct methods (SHELXS 86)[38] and refined on F by full-matrix least squares (SHELX 80)[39] to final R and R' values of 0.0415 and 0.0490 respectively for 8590 observed $[F_o > 3\sigma(F_o)]$ data and 810 parameters for **2**, and 0.097 and 0.115 respectively for 7078 observed data and 809 parameters for **3**. In both structures, several of the *tert*-butyl groups were orientationally disordered, those in **3** very severely; all of these were refined with partial site occupancies. In **2** the trimeric species lie in general positions but in **3** there were three dimeric molecules in the unit cell, one possessing a crystallographic inversion centre and one lying in a general position. All non-hydrogen atoms in **2** and most of those in **3** were refined successfully with anisotropic displacement coefficients but several *tert*-butyl carbons in **3** became non-positive definite, which were treated isotropically. The hydrogen atoms in **2** were included in calculated positions [a common U_{iso} refined to 0.108(2) Å^2] but those in **3** were all ignored. Although the refinement of **3** resulted in relatively high R values (due to poor crystal quality, disorder, and non-inclusion of the hydrogen atoms), the essential structural features and modes of bonding were clearly established. Owing to the flexibility of structural types observed in metal complexes of tmhd and related complexes, and also because the structures may have important relevance to the physicochemical properties, we present and discuss the crystallographic results of **3** together with **2** in the present work. The calculations were performed on a 486DX2/66 personal computer. Sources of scattering factors as in ref. 39. The crystal data and details of data collection and structure refinement for both compounds are presented in Table 3.

Atomic coordinates, thermal parameters and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/48.

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