DALTON

Facile synthesis of alkaline-earth-metal β-diketonates and the structure of the loose dimer [{$Ca(hfpd)_2$}$_2$(heptaglyme)] [hfpd = $F_3CCOCHCOCF_3$ and heptaglyme = $Me(OCH_2CH_2)_7OMe$)]

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The reaction of the Group 2 metal hydroxides, oxides or carbonates in 95% ethanol in the presence of a suitable glyme ligand L−L [*i.e.* $Me(OCH_2CH_2)_nOMe$, $n = 3$, 4 or 7] and a β-diketone, has yielded either [M(β-diket)$_2$(L−L)] or [{M(β-diket)$_2$}$_2$(L−L)] [M = Mg–Ba; β-diket = Htmhd (2,2,6,6-tetramethylheptane-3,5-dione), Hhfpd (1,1,1,5,5,5-hexafluoropentane-2,4-dione), Hdppd (1,3-diphenylpropane-1,3-dione) or Hfod (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione, L−L = tri-, tetra- or hepta-glyme)]. The crystal structure of the complex [{$Ca(hfpd)_2$}$_2$(heptaglyme)] has been determined, revealing it to contain two $Ca(hfpd)_2$ units linked by a glyme ligand in an unusual symmetrical bridging/chelating mode.

Materials technology over the last twenty years has emphasised the importance of combining ceramic properties with the desirable optical, ionic and electronic conductivity and superconductivity physical properties. Advanced ceramic materials have been usually synthesized by classical 'heat and bake' techniques, ball milling and high-temperature isostatic pressing to form high-density solids.[1] Alternative techniques, including sputtering and chemical vapour deposition (CVD), have also been developed for applications in the preparation of electroceramic oxide films, *e.g.* $YBa_2Cu_3O_{7-x}$, $SrTiO_3$, Cd_2SnO_4, $LiNbO_3$ and $Y_3Fe_5O_{12}$.[2] Chemical vapour deposition offers considerable control of the film growth parameters, generally milder processing conditions and most importantly a considerable degree of control over the film stoichiometry and microstructure compared with those obtained from other deposition processes.[3] For successful CVD films an important consideration is the design, synthesis and evaluation of the molecular precursors.

For the Group 2 metals the β-diketonate complexes have found widespread application as CVD precursors, *e.g.* the oligomeric materials [$Ca_3(tmhd)_6$],[4] [$Sr_3(tmhd)_6$(Htmhd)] and [$Ba_4(tmhd)_8$] (Htmhd = 2,2,6,6-tetramethylheptane-3,5-dione).[5] For metal cations as large as Sr^{2+} or Ba^{2+} (radii 1.27 and 1.36 Å respectively), tailoring of the co-ordination sphere generally requires a subtle choice of the ligand set. Previous workers have shown that there is a pronounced tendency for these metals to form a range of aggregates, often stabilised by either oxo-,[6] hydroxo- or water impurities, rather than monomers.[7,8] Given the inherent difficulties involved, we and others have sought to control the degree of oligomerisation of such materials by the use of open or closed polyethers either as independent ligands,[8,9] or 'anchored' to a β-diketonate unit.[10]

We have recently developed a synthetic strategy using Group 2 metal ethoxides as precursors for metal β-diketonate glyme complexes, [M(RCOCHCOR)$_2$(L−L)],[5c,11] (R = Bu^t, CF_3, C_3F_7, Ph or Me; L−L = a multidentate glyme ligand). Although this process is facile, it has several inherent limitations, notably the use of air/moisture-sensitive metal ethoxides, the need for anaerobic/anhydrous atmosphere techniques and complex apparatus. For such precursors to be useful metal–organic (MO)CVD sources they should preferably be prepared using as inexpensive and plentiful sources of the metal as possible, *e.g.* a mineral source (metal oxide, hydroxide or carbonate) and the synthetic set-up should be minimal. Furthermore the experimental apparatus should allow scale-up at minimum effort, and also the precursors should have a good balance between atmospheric stability and volatility.

In this paper oxide, carbonate and hydroxide sources have been used for the effective synthesis of a range of Group 2 β-diketonate complexes supported by multidentate glyme ligands. The single-crystal structure of a calcium complex, [{$Ca(hfpd)_2$}$_2$(heptaglyme)] is also described [Hhfpd = 1,1,1,5,5,5-hexafluoropentane-2,4-dione, heptaglyme = Me-(OCH_2CH_2)$_7$OMe].

Results and Discussion

The oxides, carbonates or hydroxides of the Group 2 metals (Mg–Ba) were either suspended or dissolved in 95% aqueous ethanol at 75 °C; to this was added a multidentate glyme L−L, and 2.2 equivalents of the β-diketones as specified in Table 1 and the Experimental section. The reaction mixtures were refluxed until all the solids had dissolved. Recrystallisation from hexane or toluene gave either [M(β-diket)$_2$(L−L)] or [{M(β-diket)$_2$}$_2$(L−L)], the nature of the product being dependent on the glyme ligand used. The complexes **1**–**6** formed by this procedure are summarised in Table 1 and include examples with Mg, Ca, Sr and Ba with the β-diketonates Htmhd, Hhfpd, Hdppd (1.3-diphenylpropane-1,3-dione) or Hfod (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione), and tri-, tetra- and hepta-glyme supporting ligands $Me(OCH_2CH_2)_nOMe$ ($n = 3$, 4 or 7).

The present synthetic route draws on previous experience of the synthesis of metal β-diketonates, which involved either the use of hydroxides or chlorides as the metal sources. The disadvantage of these routes was that they yielded hydrated products of poorly defined stoichimetry.[12] Indeed, a recent study by Sievers and co-workers[13] has revealed one of these materials to be the pentameric barium-based aggregate [$Ba_5O(OH)_3(tmhd)_5$-(Htmhd)$_4$]. The strategy reported in this paper utilizes a 95%

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Table 1 Products obtained, yields, melting points and microanalysis data for compounds **1**–**6**[a]

				Analysis (%)[b]		
Reagents	Product	Yield (%)	M.p./°C	C	H	Ref.
MgO, Hfod, triglyme	**1** $[\{Mg(fod)_2\}_2(triglyme)]$	72	49–52	39.5 (40.9)	3.8 (4.1)	This work
$Mg(OH)_2$, Hhfpd, heptaglyme	**2** $[\{Mg(hfpd)_2\}_2(heptaglyme)]$	78	Liquid at r.t.	35.1 (35.1)	2.8 (3.1)	This work
$CaCO_3$, Hhfpd, heptaglyme	**3** $[\{Ca(hfpd)_2\}_2(heptaglyme)]$	74	112–116	34.4 (34.2)	2.7 (3.0)	This work
$Sr(OH)_2$, Hdppd, tetraglyme	**4** $[Sr(dppd)_2(tetraglyme)]$	80	104–106	63.8 (63.5)	6.1 (5.8)	11
$Ba(OH)_2$, Htmhd, triglyme	**5** $[Ba(tmhd)_2(triglyme)]$	83	77–79	53.0 (53.1)	7.9 (8.0)	This work
$BaCO_3$, Hhfpd, heptaglyme	**6** $[\{Ba(hfpd)_2\}_2(heptaglyme)]$	58	109–112	30.0 (29.7)	2.7 (2.6)	This work

[a] The general procedure is the same for all complexes: The metal oxide, hydroxide or carbonate was either dissolved or suspended in 95% ethanol to which was added the multidentate ligand and the solution was heated to *ca.* 75 °C. Addition of the β-diketone and refluxing for 2–4 h yields a near colourless solution with dissolution of >95% of the solid. Removal of the solvent *in vacuo* and dissolution in an appropriate hydrocarbon solvent (*e.g.* hexane or toluene) yields a large crop of crystalline solid on standing at 0 °C. [b] Calculated values in parentheses.

alcohol solution and is primarily based on either the solubility of the hydroxides in this media or the solubilisation of the metal oxides in the presence of the ligands, see equation (1).[14]

$$MO + 2.2\ RCOCH_2COR + L{-}L \xrightarrow[\text{heat}]{\text{95\% EtOH}} [M(RCOCHCOR)_2(L{-}L)] \qquad (1)$$

The solubility of these starting materials increases markedly on descending the group and thereby reduces the required reaction time.

The metal carbonates presumably react *via* a similar route, albeit with the evolution of carbon dioxide. To ensure that these reactions go to completion compounds with a $pK_a > 20$ have been used, *e.g.* hfpd or fod, with some of the weakly basic materials [*e.g.* $Mg(OH)_2$ or MgO].

Our studies suggest that the reactions might be proceeding *via* either alcohol- or water-solvated intermediates.[15] Indeed, the reaction need not be restricted to ethanol, it works equally well in other alcohols such as MeOH or Pr^iOH. Surprisingly, the reactions also proceed in non-polar solvents, such as hexane or toluene, albeit in significantly lower yields (*ca.* 50%). A chelate-induced effect was noted with regard to the size of the multidentate ligand used; when the number of oxygens present in the glyme was less than three, either mixed hydrated glyme complexes were obtained or the glymes did not co-ordinate.

Spectroscopic characterisation

The IR spectra of complexes **1**–**6** were studied as both hexachlorobutadiene and Nujol mulls between CsI windows. Selected frequencies are listed in the Experimental section. The bands are assigned on the basis of data for previously characterised transition-metal β-diketonates.[3] In the region 1500–1650 cm^{-1}, bands at about 1650, 1590, 1560 and 1540 cm^{-1} are assigned to the $\nu(C{\cdots}O)$ stretching modes and those at about 1570 and 1500 cm^{-1} to the $\nu(C{\cdots}C)$ stretching modes. The bands assigned as $\nu(C{-}O{-}C)$ for the glyme ligands occur at slightly lower frequencies than the same peaks for the free glymes (either tri-, tetra- or hepta-glyme), 1350–1360, 1270, 1220 and also at 1110–1120 cm^{-1}. The shifts from the free glyme are *ca.* 20 cm^{-1} which is indicative of co-ordinated glyme, with relatively weak M–O interactions.

Multinuclear NMR spectroscopy (^1H and ^{13}C) for complexes **1**–**6** in C_6D_6, $C_6D_5CD_3$ or $(CD_3)_2SO$ shows only one time-averaged β-diketonate and glyme environment which suggests that these molecules are fluxional in solution at room temperature on the NMR time-scale. The ^{13}C-{^1H} NMR spectrum of **1** in $C_6D_5CD_3$ shows some notable features; the $CF_3CF_2CF_2$ group of the fod ligands produces a well defined peak pattern between δ 125 and 105, from which the coupling constants may be clearly derived. The CF_3 resonance is centred at δ 118.42 and consists of a quartet of triplets, with $^1J = 290$ and $^2J = 34$ Hz. The $\mathit{C}F_2CO$ resonance is a triplet of triplets observed at δ 110.76 ($^1J = 262$ and $^2J = 30$ Hz) and similarly the $CF_3\mathit{C}F_2$-CF_2CO peak is a triplet of quartets (albeit not as well resolved as the other two resonances) centred at δ 109.24 with $^1J = 268$ and $^2J = 38$ Hz. The hfpd–heptaglyme complexes **2**, **3** and **6** give a similar set of coupling constants for their CF_3 resonances.

The positive-ion electron-impact (EI) mass spectrometry data for the complexes are of variable quality. For the monomers **1**, **4** and **5** only the homoleptic species $[ML]^+$, $[ML_2]^+$ and $[M_2L_3]^+$ were observed, indicating loss of their respective glyme ligands in the mass spectrometer. This observation is corroborated by sublimation data for these compounds where only the homoleptic species are seen to sublime onto the cold-finger of the sublimation vessel. However, for compounds **2**, **3** and **6**, the parent ions observed are of the type $[M(hfpd)_x(heptaglyme)]^+$ ($x = 1$ or 2) illustrating that the heptaglyme ligands in these dinuclear complexes are held more tightly than the smaller tri- and tetra-glyme ligands on the monomers. (This behaviour has also been noted for the nuclear lanthanide compounds $[\{Ln(tmhd)_3\}_2(triglyme)]$ (Ln = Eu, Y, Tb, *etc.*) and the corresponding monomeric compound $[La(tmhd)_3(tetraglyme)]$, where the latter dissociates in the mass spectrometer or on sublimation to give $[\{La(tmhd)_3\}_2]$ and the dinuclear compounds sublime/fly in the mass spectrometer intact with their associated glyme ligand.)[16]

Physical properties

The fluorinated β-diketone complexes sublime intact in excellent yield.[8,9,17] Thermogravimetric analyses on the non-fluorinated complexes show strong evidence for clean loss of the glyme ligand at *ca.* 200 °C, and above this essentially 96 ± 2% sublimation of the homoleptic compounds occurs by 500 °C while the fluorinated compounds show evidence of improved thermal stability and mass transport; coupled with this is their improved moisture stability, suggesting that these materials may be suitable alternative molecular precursors for CVD of Group 2 metal fluorides (see Fig. 1).

Crystal structure of $[\{Ca(hfpd)_2\}_2(heptaglyme)]$ 3

The structure of $[\{Ca(hfpd)_2\}_2(heptaglyme)]$ **3** derived from a single-crystal X-ray determination is shown in Fig. 2 and important bond lengths and angles are presented in Table 2. The molecule is centrosymmetric and consists of two $Ca(hfpd)_2$

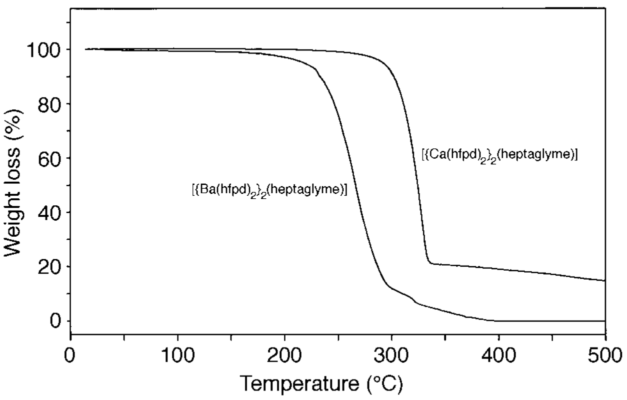

Fig. 1 The TGA plots for [{Ca(hfpd)$_2$}$_2$(heptaglyme)] **3** and [{Ba(hfpd)$_2$}$_2$(heptaglyme)] **6**

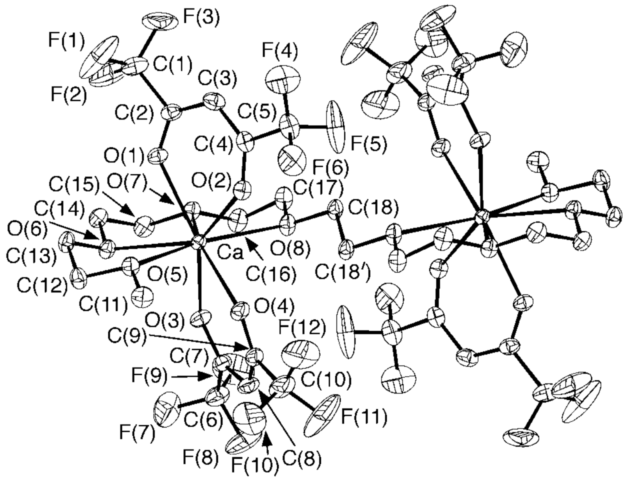

Fig. 2 Structure of the centrosymmetric molecule [{Ca(hfpd)$_2$}$_2$(heptaglyme)] **3** showing the atom numbering scheme. Only one orientation (major occupancy) of the disordered CF$_3$ groups is shown. Thermal ellipsoids are drawn at the 40% probability level. The hydrogen atoms are omitted for clarity

moieties linked by a heptaglyme involving an unusual co-ordination mode. The glyme utilises all its eight oxygens in bonding with the two metal centres, thus forming the centrosymmetric 'dimer'. Each calcium atom is eight-co-ordinate and the co-ordination polyhedron approximates to a distorted square antiprism. This high co-ordination number is a common feature of Group 2 metal β-diketonates, *e.g.* [Ba(tmhd)$_2$(tetraglyme)].[9,11] One of the most interesting features of this complex is that the heptaglyme is functioning simultaneously as a bridging ligand {*via* the central ethylene bridge [C(18) and C(18′)]} and as a tetradentate chelate to each metal ion. To the best of our knowledge this co-ordination mode of a glyme ligand to a Group 2 metal is unique; such ligands are normally found either chelating or acting as terminally bound monodentate. It is noted, however, that the recently characterised lanthanide β-diketonate compounds, *i.e.* [{Ln(tmhd)$_3$}$_2$(triglyme)] (Ln = Eu, Y, Tb, *etc.*),[16] also contain a glyme ligand which is both chelating and bridging.

The Ca–O bond lengths [2.464(2)–2.542(2) Å] of the glyme binding to the metal centres are an interesting example of the subtle steric factors involved in this interesting structural motif. The Ca–O(6) bond length of 2.478(2) Å is *ca.* 0.02 Å shorter than that of Ca–O(5) 2.502(2) Å and this is most likely due to O(5) carrying the pendant methyl group which prevents it bonding strongly to the metal centre. In contrast, O(6) can bend back and snap into place to create the chelate ring, with a fairly acute angle O(5)–Ca–O(6) of 66.03(5)°. Similar asymmetry in the Ca–O(7) and Ca–O(8) bonds, 2.464(2) and 2.542(2) Å respectively, may also be explained in terms of the larger steric requirements of O(8) which carries the bridging (CH$_2$)$_2$ group. The bonding observed at the other end of the glyme to the symmetry-related Ca is exactly the same.

Table 2 Selected bond lengths (Å) and angles (°) for [{Ca(hfpd)$_2$}$_2$(heptaglyme)] **3**

Ca–O(1)	2.413(2)	Ca–O(2)	2.398(2)
Ca–O(3)	2.396(2)	Ca–O(4)	2.354(2)
Ca–O(5)	2.502(2)	Ca–O(6)	2.478(2)
Ca–O(7)	2.464(2)	Ca–O(8)	2.542(2)
O(1)–C(2)	1.236(3)	O(2)–C(4)	1.249(3)
O(3)–C(7)	1.242(3)	O(4)–C(9)	1.243(3)
O(5)–C(11)	1.430(3)	O(5)–C(12)	1.428(3)
O(6)–C(13)	1.423(3)	O(6)–C(14)	1.428(3)
O(7)–C(15)	1.428(3)	O(7)–C(16)	1.431(3)
O(8)–C(17)	1.438(3)	O(8)–C(18)	1.438(3)
O(4)–Ca–O(3)	72.01(6)	O(4)–Ca–O(2)	81.36(6)
O(3)–Ca–O(2)	147.66(6)	O(4)–Ca–O(1)	146.41(6)
O(3)–Ca–O(1)	140.05(6)	O(2)–Ca–O(1)	70.56(6)
O(4)–Ca–O(7)	138.20(6)	O(3)–Ca–O(7)	72.66(6)
O(2)–Ca–O(7)	121.07(6)	O(1)–Ca–O(7)	74.20(6)
O(4)–Ca–O(6)	122.76(6)	O(3)–Ca–O(6)	75.18(6)
O(2)–Ca–O(6)	136.29(6)	O(1)–Ca–O(6)	71.82(6)
O(7)–Ca–O(6)	67.23(5)	O(4)–Ca–O(5)	77.06(6)
O(3)–Ca–O(5)	102.57(6)	O(2)–Ca–O(5)	88.62(6)
O(1)–Ca–O(5)	84.04(6)	O(7)–Ca–O(5)	132.55(5)
O(6)–Ca–O(5)	66.03(5)	O(4)–Ca–O(8)	87.24(5)
O(3)–Ca–O(8)	82.51(6)	O(2)–Ca–O(8)	78.11(5)
O(1)–Ca–O(8)	104.06(6)	O(7)–Ca–O(8)	66.60(5)
O(6)–Ca–O(8)	132.83(5)	O(5)–Ca–O(8)	160.85(5)
C(2)–O(1)–Ca	134.6(2)	C(4)–O(2)–Ca	134.4(2)
C(7)–O(3)–Ca	134.2(2)	C(9)–O(4)–Ca	135.3(2)
C(12)–O(5)–C(11)	110.7(2)	C(12)–O(5)–Ca	116.37(13)
C(11)–O(5)–Ca	123.49(14)	C(13)–O(6)–C(14)	112.2(2)
C(13)–O(6)–Ca	114.11(13)	C(14)–O(6)–Ca	113.61(12)
C(15)–O(7)–C(16)	112.3(2)	C(15)–O(7)–Ca	114.74(13)
C(16)–O(7)–Ca	113.97(13)	C(17)–O(8)–C(18)	109.9(2)
C(17)–O(8)–Ca	113.80(12)	C(18)–O(8)–Ca	126.40(12)

The hfpd ligands are both bonded to Ca in a classical chelating manner with Ca–O(1), Ca–O(2), Ca–O(3) and Ca–O(4) distances of 2.413(2), 2.398(2), 2.396(2) and 2.354(2) Å respectively. These values indicate that one hfpd ligand is symmetrically bonded to Ca, whilst the other is asymmetric. The two Ca–hfpd chelates are also somewhat folded about the O···O axis as indicated by the dihedral angles between the CaO$_2$ and O$_2$C$_3$ moieties of 5.2(2) and 14.3(2)°. The Ca–O (hfpd) distances are, as expected, shorter than the Ca–O (glyme) distances and similar to those observed in other related complexes *e.g.* [Ca$_3$(tmhd)$_6$] 2.35(5) Å,[4] [Ca$_4$(dppd)$_8$(EtOH)$_2$] 2.37 Å,[18] [Ca(pd)$_2$(H$_2$O)$_2$]·H$_2$O 2.33 Å (Hpd = pentane-2,4-dione),[19] and also [Ca$_2$(hfpd)$_4$(H$_2$O)$_4$] 2.44 Å.[20] The dihedral angle between the planes of the hfpd ligands and their disposition with respect to the heptaglyme was found to be 80.2(2) and 100.0(2)°. The molecule shows considerable puckering of the heptaglyme ring and significant deviation from planarity. There is retention of essentially *gauche* geometry about the C–C bonds within the polyether ligand, although there are notable departures from conventional *anti* geometries about some of the C–O linkages.

Conclusion

The total absence of any oxide or hydroxide ligands in the final products is particularly noteworthy. This suggests that the reported synthetic strategy is effective in producing molecular species with multifunctional ligands which are relatively volatile because the hydrogen bonding present in the parent hydrated compounds has been removed, thus reducing the degree of oligomerisation observed. Despite the fact that the compounds appear to be somewhat involatile (mass spectrometry), similar

Group 2 β-diketonate and carboxylate compounds have found utility as CVD precursors for both MO and MF_2 thin films.[9,10]

Experimental

General procedures

All manipulations were carried out on the bench in round-bottom flasks, using solvents from Aldrich. Elemental analyses were performed by the microanalytical department of Imperial College. The melting points were measured in sealed capillaries and are uncorrected. Sublimation studies were carried out at 5×10^{-3} Torr (*ca.* 0.67 Pa) over the temperature range 20–250 °C.

Instrumentation

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 predried with 4 Å molecular sieves prior to use (and stored in a glove-box). The NMR spectra were recorded on a JEOL GS 270 MHz spectrometer, using the protio impurities of the deuteriated solvent as reference for ^1H and the ^{13}C resonance of the solvent as a reference for ^{13}C. 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. Mass spectra (EI positive-ion mode) were run on a Kratos MS30 instrument at the Royal School of Pharmacy Mass Spectrometry service, University of London and on a VG Autospec at the Mass Spectrometry service, Imperial College.

Controlled thermal analysis of the complexes was investigated using a Polymer Laboratories 1500H simultaneous thermal analyser, controlled by a Omni Pro 486DX-30 personal computer. The weight of the samples investigated was between 11 and 16 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}.

Starting materials

Nujol, hexachlorobutadiene, tri-, tetra- and hepta-glyme were obtained from Aldrich chemicals and dried over 4 Å molecular sieves prior to use. The compounds Htmhd, Hhfpd, Hdppd and Hfod were obtained from Inorgtech and used without further purification.

Syntheses

$[\{Mg(fod)_2\}_2(triglyme)]$ 1. Magnesium oxide (0.40 g, 10 mmol) was suspended in hot 95% ethanol (30 cm^3) at 75 °C and to this was added triglyme (1.80 cm^3, 10 mmol) and 2.2 equivalents of Hfod (5.11 cm^3, 22 mmol). The reaction mixture was refluxed until all the solid material had dissolved. Then the solvent was removed under reduced pressure and the resultant solid redissolved in hot toluene. Crystallisation of complex **1** occurred on cooling this solution at 0 °C. Infrared (Nujol): $\tilde{\nu}/cm^{-1}$ 1645s, 1626s, 1578w, 1515s, 1496s, 1396w, 1347s, 1287m, 1230vs, 1184s, 1160s, 1122s, 1106s, 1072s, 1044w, 1023w, 964w, 942vw, 912m, 877vw, 836w, 789m, 756w, 744m, 692w, 627vw, 596w and 543vw. NMR ($C_6D_5CD_3$, 20 °C): ^1H (270 MHz), δ 1.03 (s, CH_3), 3.12 (s, OCH_3), 3.26 (s, OCH_2 a), 3.78 (s, OCH_2 b), 3.90 (s, OCH_2 c) and 6.05 (s, CH); ^{13}C-{^1H} (67.94 MHz), δ 26.94 (s, CH_3), 41.33 [s, $C(CH_3)_3$], 58.51 (s, OCH_3), 69.38 (s, OCH_2), 69.88 (s, OCH_2), 70.55 (s, OCH_2), 91.57 (s br, CH), 109.24 (t of q, $CF_3CF_2CF_2$, $^1J = 268$, $^2J = 38$), 110.76 (t of t, CF_2CO, $^1J = 262$, $^2J = 30$), 118.42 (q of t, CF_3, $^1J = 290$, $^2J = 34$), 172.90 (s, CF_2CO, $^2J = 24$ Hz) and 195.63 (s, Bu^tCO). EI positive-ion mass spectrum: *m*/*z* 789 {$[Mg(fod)_2(triglyme)]^+$, 1}, 615 {$[Mg(fod)_2]^+$, 10}, 558 ($[Mg(fod)\{CF_3CF_2CF_2COCHCO(H)\}]^+$, 100) and 445 $[Mg(fod)\{Me_3CCOCHCO(H)\}]^+$, 6%).

$[\{Mg(hfpd)_2\}_2(heptaglyme)]$ 2. Magnesium hydroxide (0.58 g, 10 mmol) was suspended in hot 95% ethanol at 75 °C and to this was added heptaglyme (3.54 cm^3, 10 mmol) and 2.2 equivalents of Hhfpd (3.10 cm^3, 22 mmol). The reaction conditions and work-up were as for compound **1**, except that **2** is a liquid. Infrared (neat): $\tilde{\nu}/cm^{-1}$ 2891m, 1732vw, 1658vs, 1618vw, 1605vw, 1556m, 1532vs, 1517vs, 1474m, 1351w, 1325vw, 1256vs, 1205vs, 1146vs, 1104s, 1065m, 1030w, 952w, 858vw, 798s, 766vw, 733m, 697w, 666vs, 586m and 529vw. NMR (C_6D_6, 20 °C): ^1H (270 MHz), δ 3.01 (6 H, s, OCH_3), 3.07 (8 H, s, OCH_2 b, d), 3.37 (8 H, s, OCH_2, a, c), 3.40 (4 H, s, OCH_2 e), 3.43 (4 H, s, OCH_2 f), 3.45 (4 H, s, OCH_2 g) and 6.62 (4 H, s, CH); ^{13}C-{^1H} (67.94 MHz), δ 58.85 (s, OCH_3), 70.08 (s, OCH_2 b), 70.35 (s, OCH_2 d), 70.57 (s, OCH_2 a, c, e), 71.02 (s, OCH_2 f), 71.11 (s, OCH_2 g), 90.33 (s, CH), 118.18 (q, CF_3, $^1J = 286$) and 179.62 (q, CO, $^2J = 34$ Hz). EI positive-ion mass spectrum: *m*/*z* 1023 {$[Mg_2(hfpd)_3(heptaglyme)]^+$, 0.25}, 791 {$[Mg(hfpd)_2(heptaglyme)]^+$, 0.2}, 669 {$[Mg_2(hfpd)_3]^+$, 2}, 437 {$[Mg(hfpd)_2]^+$, 32} and 230 {$[Mg(hfpd)]^+$, 18%}.

$[\{Ca(hfpd)_2\}_2(heptaglyme)]$ 3. Calcium carbonate (1 g, 10 mmol) was suspended in hot 95% ethanol at 75 °C and to this was added heptaglyme (3.54 cm^3, 10 mmol) and 2.2 equivalents of Hhfpd (3.10 cm^3, 22 mmol). The reaction conditions and work-up were as for compound **1**. Infrared: $\tilde{\nu}/cm^{-1}$ (Nujol) 1661s, 1590s, 1526s, 1356m, 1260s, 1195m, 1143m, 1085m, 1066m, 1032m, 1021m, 957s, 872s, 856m, 795s, 738m, 722w, 661m and 580w; (hexachlorobutadiene) 2947s, 2869s, 1660s, 1611w, 1589m, 1526s, 1487s, 1447m, 1455m, 1368m, 1355m, 1338m, 1316m, 1261s, 1187m, 1143m, 1085m, 1066m, 1033m, 1022m, 872w, 763m, 739m and 581m. NMR [$(CD_3)_2SO$, 20 °C]: ^1H (90 MHz), δ 3.19 (6 H, s, OCH_3), 3.21 (4 H, s, OCH_2 b), 3.39 (4 H, s, OCH_2 a), 3.41 (4 H, s, OCH_2 d), 3.43 (4 H, s, OCH_2 e), 3.46 (12 H, s, OCH_2 c, f, g) and 5.52 (4 H, s, CH); ^{13}C-{^1H} (22.61 MHz), δ 57.44 (s, OCH_3), 69.03 (s, OCH_2 b), 69.22 (s, OCH_2 a, g, d, e, f), 70.74 (s, OCH_2 c), 84.11 (s, CH), 118.25 (q, CF_3, $^1J = 296$) and 171.57 (q, CO, $^2J = 28$ Hz). EI positive-ion mass spectrum: *m*/*z* 701 {$[Ca_2(hfpd)_3]^+$, 20}, 601 {$[Ca(hfpd)(heptaglyme)]^+$, 100}, 557 {$[Ca(hfpd)(hexaglyme)]^+$, 25}, 513 {$[Ca(hfpd)_2(CH_2CH_2O_2)]^+$, 5}, 454 {$[Ca(hfpd)_2]^+$, 5}, 325 {$[Ca(hfpd)(CH_2CH_2O_3)]^+$, 5} and 247 {$[Ca(hfpd)]^+$, 7%}.

$[Sr(dppd)_2(tetraglyme)]$ 4. Strontium hydroxide (1.22 g, 10 mmol) was suspended in hot 95% ethanol at 75 °C and to this was added tetraglyme (2.20 cm^3, 10 mmol) and 2.2 equivalents of Hdppd (4.93 g, 22 mmol). The reaction conditions and work-up were as for compound **1**. Infared: $\tilde{\nu}/cm^{-1}$ (Nujol) 1620s, 1582s, 1513s, 1324s, 1222m, 1108s, 935s, 870s, 733m, 580w and 513w; (hexachlorobutadiene) 2918s, 1471w, 1425s, 1299m, 1224s, 1113s, 1026m, 748m, 731m, 690w and 579m. NMR (C_6D_6, 20 °C): ^1H (270 MHz), δ 3.23 (6 H, s, OCH_3), 3.41 (4 H, s, OCH_2 b), 3.42 (4 H, s, OCH_2 a), 3.48 (4 H, s, OCH_2 c), 3.51 (4 H, s, OCH_2 d), 6.57 (2 H, s, CH), 7.40 and 7.98 (20 H, m, Ph); ^{13}C-{^1H} (67.94 MHz), δ 58.72 (s, OCH_3), 70.28 (s, OCH_2 b), 70.48 (s, OCH_2 a), 71.97 (s, OCH_2 c), 72.87 (s, OCH_2 d), 92.36 (s, CH), 128.87 (m, Ph) and 182.52 (s, CO). The positive-ion EI mass spectrum showed only ligand decomposition.

$[Ba(tmhd)_2(triglyme)]$ 5. Barium hydroxide (1.73 g, 10 mmol) was suspended in hot 95% ethanol at 75 °C and to this was added triglyme (1.78 cm^3, 10 mmol) and 2.2 equivalents of Htmhd (4.58 cm^3, 22 mmol). The reaction conditions and work-up were as for compound **1**. Infrared: $\tilde{\nu}/cm^{-1}$ (Nujol) 2362w, 1965w, 1587s, 1532s, 1504s, 1269m, 1224m, 1185s, 1099s, 1031s, 950s, 865s, 832m, 788m, 748s, 731m, 590w and 553w; (hexachlorobutadiene) 2949s, 1965w, 1425s, 1356m, 1224s, 1100s, 1023m, 748m, 731m and 591w. NMR (C_6D_6, 20 °C): ^1H (270 MHz), δ 1.32 (36 H, s, CH_3), 3.13 (6 H, s, OCH_3), 3.15 (4 H, s, OCH_2 b), 3.20 (4 H, s, OCH_2 a), 3.31 (4 H, s, OCH_2 c) and

5.79 (2 H, s, CH); ^{13}C-{^{1}H} (67.94 MHz), δ 28.26 (s, CH_3), 40.66 (s, CMe_3), 58.24 (s, OCH_3), 69.09 (s, OCH_2 b), 69.13 (s, OCH_2 a), 70.58 (s, OCH_2 c), 87.20 (s, CH) and 196.78 (s, CO). EI positive-ion mass spectrum: *m*/*z* 825 {$[Ba_2(tmhd)_3]^+$, 35}, 504 {$[Ba(tmhd)_2]^+$, 5} and 321 {$[Ba(tmhd)]^+$, 100%}.

[{Ba(hfpd)$_2$}$_2$(heptaglyme)] 6. Barium carbonate (1.97 g, 10 mmol) was suspended in hot 95% ethanol at 75 °C and to this was added heptaglyme (3.54 cm^3, 10 mmol) and 2.2 equivalents of Hhfpd (3.1 cm^3, 22 mmol). The reaction conditions and work-up were as for compound **1**. Infrared: $\tilde{\nu}$/cm^{-1} (Nujol) 3423m, 1670m, 1604w, 1529m, 1306w, 1253m, 1195w, 1142m, 1096w, 952w, 846w, 801w, 791m, 725w and 659m; (hexachlorobutadiene) 3425w, 2925s, 1668s, 1611m, 1528m, 1468w, 1351w, 1253m, 1196m, 1144m, 1097m, 1044w, 1025m, 893w, 737w, 735w and 577m. NMR [$(CD_3)_2SO$, 20 °C]: ^{1}H (250 MHz), δ 3.19 (s, 6 H, CH_3), 3.46 (m, 28 H, CH_2) and 5.48 (s, 4 H, CH); ^{13}C-{^{1}H} (125.76 MHz), δ 57.62 (s, CH_3), 69.21 (s, CH_2), 69.40 (s, CH_2), 70.92 (s, CH_2), 83.92 (s, CH), 114.0 (q, CF_3) and 171.1 (q, CO). EI positive-ion mass spectrum: *m*/*z* 905 {$[Ba(hfpd)_2(heptaglyme)]^+$}, 875 {$[Ba(hfpd)_2(heptaglyme) - OMe]^+$}, 861 {$[Ba(hfpd)_2(heptaglyme) - OMeCH_2]^+$}, 699 {$[Ba(hfpd)(heptaglyme)]^+$}, 655 {$[Ba(hfpd)(heptaglyme) - MeOCO]^+$}, 345 {$[Ba(hfpd)]^+$} and 246 {$[Ba(CF_3COCH)]^+$}.

X-Ray crystallography

Crystals of complex **3** were grown from toluene at 0 °C, then mounted using silicone oil and transferred to the goniostat. The oil acted both as a coating and an adhesive.

Crystal data. $C_{36}H_{38}Ca_2F_{24}O_{16}$, $M_r = 1262.82$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.288(2)$, $b = 24.335(5)$, $c = 11.011(2)$ Å, $\beta = 109.660(12)°$, $U = 2596.0(9)$ Å^3 (by least-squares refinement of diffractometer angles for 250 reflections within $2.26 \leqslant \theta \leqslant 29.92°$, $\lambda = 0.710\ 69$ Å), $Z = 2$, $D_c = 1.616$ g cm^{-3}, $F(000) = 1276$, $\mu = 0.368$ mm^{-1}, $T = 150$ K, colourless prism, crystal size 0.20 × 0.13 × 0.13 mm.

Data collection and processing.[21] Delft instruments FAST TV-area detector diffractometer positioned at the window of a rotating-anode generator, Mo-Kα radiation, 13154 reflections measured ($2.26 \leqslant \theta \leqslant 29.92°$; index ranges $-12 \leqslant h \leqslant 14$, $-27 \leqslant k \leqslant 32$, $-10 \leqslant l \leqslant 14$), 6533 unique [merging $R = 0.0783$ after absorption correction[22] (maximum and minimum correction factors = 0.846, 1.006)].

Structure analysis and refinement. The structure was solved by direct methods[23] and refined[24] by full-matrix least-squares on F^2 using all 6533 unique data and 403 parameters (non-hydrogen atoms anisotropic, hydrogens in idealised positions with U_{iso} free to refine) to $wR2$ (on F^2) = 0.1411 and $R1$ (on F) = 0.0723. The corresponding $wR2$ and $R1$ values for 3707 data with $I > 2\sigma(I)$ were 0.1155 and 0.0464 respectively. Three of the four unique CF_3 groups were orientationally disordered; the F atoms of these groups were refined with partial occupancies. The weighting scheme used was $w = 1/\sigma^2(F_o)^2$, which gave satisfactory agreement analysis. An extinction coefficient refined to a final value of 0.015(1). Minimum and maximum residual electron density = −0.37 and 0.14 e Å^{-3}. The diagram was drawn by the program SNOOPI.[25] Atom scattering factors as in SHELXL 93.[24] All calculations were done on a 486DX2/66 personal computer.

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.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/416.

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