Group 2 β-diketonate complexes stabilized by O and N donor ligands; crystal structure of [Ca(PhCOCHCOPh)₂(pmdeta)] (pmdeta = $N,N,N',N'N''$-pentamethyldiethylenetriamine)

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Abstract—The calcium(II) β-diketonate complexes [Ca(dppd)₂(EtOH)₀.₅]ₙ · C₇H₈ (**1**) and [Ca(dppd)₂(H-dppd)] (**2**) have been synthesized from the reactions of [Ca(OEt)₂(EtOH)₄]ₙ with 2 and 3 molar equiv. of H-dppd (H-dppd = 1,3-diphenylpropane-1,3-dione), respectively. The reaction of the tetra-ethanol solvated calcium ethoxide with 2 and 1 molar equiv. of H-dppd and pmdeta [Me₂NCH₂CH₂N(Me)CH₂CH₂NMe₂], respectively, gave [Ca(dppd)₂(pmdeta)] (**3**). A single crystal X-ray structural study of complex **3** has shown it be monomeric. The reaction of [Sr(OEt)₂(EtOH)₄]ₙ with 3 molar equiv. of H-tmhd (H-tmhd = 2,2,6,6-tetramethylheptane-3,5-dione) also yielded [Sr(tmhd)₂(H-tmhd)] (**4**). © 1997 Published by Elsevier Science Ltd

Keywords: calcium; strontium; β-diketone; pmdeta; crystal structure.

Metal organic chemical vapour deposition (MOCVD) and sol–gel processing have found extensive application for the preparation of either thin or thick multimetallic electroceramic oxide films, e.g. PbLaZrTiO₃ (PLZT), LiNbO₃ and BaTiO₃ [1]. Chemical vapour deposition (CVD) offers considerable control over the film growth parameters, generally milder processing conditions and, most importantly, a considerable degree of control over film stoichiometry and microstructure [2]. For CVD, one of the most critical parameters is that of the synthesis and evaluation of suitable molecular precursors.

For the heavier alkaline earth metals, the metal β-diketonates have found considerable applications, e.g. the oligomeric complexes [Ca₃(tmhd)₆] (H-tmhd = 2,2,6,6-tetramethylheptane-3,5-dione) [3], [Sr₃(tmhd)₆ (H-tmhd)] and [Ba₄(tmhd)₈] [4]. For metals as large as Ba²⁺ (1.45 Å) and Sr²⁺ (1.28 Å), tailoring of the coordination spheres of these metals which generally prefer to have high coordination numbers requires subtle and judicious choice of the ligand set, which should be suitably matched to these hard Lewis acidic metals. Previous workers have already shown the propensity for barium and strontium to form a wide range of large aggregates [5,6]. Given these difficulties, we and others have sought to reduce the degree of oligomerization by the use of suitable multidentate open and closed polyethers [6–9].
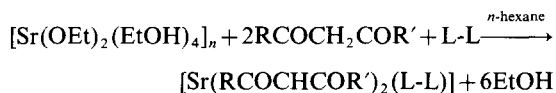
We have previously shown that tetra-ethanol solvated adducts, [M(OEt)₂(EtOH)₄]ₙ(M = Ba, Sr, Ca), may be prepared and used as crystalline hydrocarbon

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soluble sources of these metals of known stoichiometry [6,10]. We also reported a synthetic strategy using such materials as molecular precursors for stabilised metal β-diketonates *via* the route outlined below (where R and R' = C_3F_7, Ph, Bu^t, CF_3, CH_3 and L-L = a multidentate glyme ligand [11].

$$[Sr(OEt)_2(EtOH)_4]_n + 2RCOCH_2COR' + L\text{-}L \xrightarrow{n\text{-hexane}}$$

$$[Sr(RCOCHCOR')_2(L\text{-}L)] + 6EtOH$$

The known ability of the group 2 β-diketonates to form adducts in both solution and the solid state has also been exploited in the vapour phase. A range of additives such as H-tmhd, H-hfpd (H-hfpd = 1,1,1,5,5,5-hexafluoropentane-2,4-dione), tetrahydrofuran (thf) and amines (e.g. NEt_3 and NH_3) have been added to the carrier gas stream to improve the mass transport, volatility and thermal stability of both $[Ba_4(tmhd)_8]$ [4] and $[Ba(hfpd)_2]_n$ [12]. Until recently, the precise nature of the role of the diketone additives has been unknown, although it has been speculated that it has a significant effect on the degree of oligomerization of these materials. Herein, we describe the synthesis and spectroscopic characterization of some group 2 β-diketonate complexes, which have been stabilized by either O (in the form of EtOH or the parent diketone) or N (pmdeta) donor ligands, and the single-crystal X-ray structure of one of these complexes.

EXPERIMENTAL

General procedures

The manipulations of all reactants and products were carried out under nitrogen (Schlenk line), argon (glove-box) or *in vacuo*, with rigorous exclusion of moisture and air. The solvents were dried, then distilled prior to use and stored over 4 Å molecular sieves under nitrogen in a glass storage vessel fitted with a Young's high vacuum PTFE stopcock.

Physical techniques

IR spectra were recorded on a Perkin–Elmer FTIR 1720 spectrometer as Nujol or hexachlorobutadiene mulls between 25×4 mm^2 KBr plates. The Nujol and hexachlorobutadiene were both pre-dried with 4 Å molecular sieves prior to use and the samples were protected from the atmosphere by an O-ring sealed Presslock™ holder (Aldrich Chemicals). The NMR spectra were recorded on a Jeol GS 270 spectrometer in dry and oxygen-free dimethyl-d_6 sulfoxide (dmso-d_6) or C_6D_6, using the protio impurities of the deuterated solvent as reference for ^1H NMR and the ^{13}C NMR resonances of the solvent as a reference for ^{13}C NMR.

Elemental analyses were performed by the Micro-

analytical Department of Imperial College. The melting points were measured in capillaries and are uncorrected. Mass spectra were obtained using a VG Autospec. instrument at the Mass Spectrometry Department at Imperial College. Controlled thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) measurements of the complexes were done using a Polymer Laboratories 1500H simultaneous thermal analyser, controlled by an Omni Pro 486DX-33 PC. The weight of the samples investigated was between 19 and 28 mg. The measurements were carried out in alumina crucibles under an atmosphere of flowing nitrogen gas (25 cm^3 min^{-1}), using heating rates of $15°C$ min^{-1}.

Starting materials

H-dppd (1,3-diphenylpropane-1,3-dione), H-tmhd (H-tmhd = 2,2,6,6-tetramethylheptane-3,5-dione) and pmdeta [$Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$] were obtained from Aldrich. The metal ethoxides $[Ca(OEt)_2(EtOH)_4]_n$ and $[Sr(OEt)_2(EtOH)_4]_n$ were prepared according to procedures described elsewhere [6,10].

Synthesis of $[Ca(dppd)_2(EtOH)_{0.5}]_n \cdot C_7H_8$ (1)

To a stirred suspension of $[Ca(OEt)_2(EtOH)_4]_n$ (1.50 g, 4.86 mmol) in chloroform (25.0 cm^3) was added H-dppd (2.17 g, 9.72 mmol), resulting in dissolution of the ethoxide after 10 min. The yellow solution was reduced to dryness *in vacuo* and the resultant yellow paste kept under reduced pressure at $80°C$ for 1 h to yield a yellow solid. This was partially solubilized in toluene (30.0 cm^3), filtered to remove any insoluble solid, then layered with n-hexane (25.0 cm^3) and left for a few days at $-20°C$. The compound was obtained as a crystalline orange solid (yield 2.43 g, 83%). Melting point = $258–262°C$ (decomposes). Found: C, 75.6; H, 5.4. $C_{38}H_{33}CaO_{4.5}$ requires: C, 75.9; H, 5.5%. IR (Nujol): 3408 (m), 1607 (s), 1598 (s), 1583 (s), 1546 (s), 1516 (s), 1496 (s), 1483 (s), 1426 (m), 1414 (m), 1308 (m), 1277 (w), 1221 (m), 1184 (s), 1158 (m), 1068 (s), 1041 (m), 1023 (w), 999 (m), 941 (m), 812 (w), 783 (m), 746 (m), 727 (s), 694 (w), 610 (w) cm^{-1}. IR (hexachlorobutadiene): 3400 (m), 3056 (m), 2920 (m), 1606 (s), 1518 (s), 1496 (m), 1481 (s), 1462 (m), 1407 (m), 1306 (s), 1223 (m), 1184 (s), 1158 (m), 1068 (s), 1041 (m), 1022 (m), 747 (w), 729 (s), 695 (w), 609 (w), 522 (s) cm^{-1}. ^1H NMR (dmso-d_6, 270 MHz, $20°C$): δ 1.07 (1.5H, s, CH_3 of EtOH), 2.29 (3H, s, CH_3 toluene), 3.44–3.48 (1H, q, CH_2 of EtOH), 4.39 (0.5H, t, OH of EtOH), 6.67 (2H, s, CH), 7.10–7.99 (25H, m, toluene/dppd phenyls). ^{13}C NMR (dmso-d_6, 67.94 MHz, $20°C$): δ 18.6 (s, CH_3 of EtOH), 21.0 (s, CH_3 toluene), 56.0 (CH_2 of EtOH), 92.5 (s, CH), 125.3 (s, *p*-toluene Ph), 126.9 (s, *p*-dppd Ph), 128.0 (s, *m*-toluene Ph), 128.2 (s, *m*-dppd Ph), 128.9 (s, *o*-toluene Ph), 129.9 (s, *o*-dppd Ph), 137.2 (s,

i-toluene Ph), 141.8 (s, *i*-dppd Ph), 183.8 (s, CO). Mass spectrum (EI⁺, m/z^+ ; major ions) : shows only ligand decomposition.

Synthesis of [Ca(dppd)₂(H-dppd)] (2)

To a stirred suspension of [Ca(OEt)₂(EtOH)₄]ₙ (1.4 g, 4.54 mmol) in chloroform (25.0 cm³) was introduced H-dppd (3.05 g, 13.6 mmol), producing a pale yellow solution. The solution was reduced to dryness *in vacuo* to yield a yellow solid and kept at 80°C for 1 h. This was partially solubilized in refluxing toluene (30.0 cm³), filtered to remove any insoluble solid and left to cool slowly overnight yielding orange crystals (yield 1.34 g, 42%). Melting point = 68–72°C. Found : C, 75.3 ; H, 4.8. CaC₄₅O₆H₃₃ requires : C, 76.1 ; H, 4.6%. IR (Nujol) : 1732 (w), 1598 (m), 1557 (m), 1309 (w), 1261 (m), 1228 (w), 1094 (m), 1024 (m), 802 (m), 756 (m), 723 (m), 700 (w), 682 (m), 609 (m) cm⁻¹. IR (hexachlorobutadiene) : 2958 (s), 2926 (m), 2855 (m), 1730 (w), 1611 (m), 1523 (s), 1481 (s), 1455 (m), 1403 (m), 1305 (m), 1261 (m), 1225 (m), 1171 (m), 1135 (m), 1071 (m), 1024 (m), 754 (w), 726 (m), 655 (w), 609 (w), 548 (w) cm⁻¹. ¹H NMR (dmso-d_6, 270 MHz, 20°C) : δ 4.88 (s, 1H, CH₂), 7.34 (s, 3H, CH/CH₂), 7.53–8.18 (m, 30H, Ph). ¹H NMR (C₆D₆, 270 MHz, 20°C) : δ 6.56 (s, 4H, CH/CH₂), 7.01–7.85 (m, 30H, dppd Ph). ¹³C NMR (dmso-d_6, 67.94 MHz, 20°C) : δ 49.2 (s, CH₂), 93.3 (s, CH), 127.5 (s, *p*-dppd Ph), 128.9 (s, *m*-dppd Ph), 133.1 (s, *o*-dppd Ph), 134.7 (s, *i*-dppd Ph), 185.4 (s, CO). Mass spectrum (EI⁺, m/z^+ ; major ions) : 748 [Ca₂(dppd)₃]⁺, 711 [Ca(dppd)(H-dppd)₂]⁺.

Synthesis of [Ca(dppd)₂(pmdeta)] (3)

To a stirred suspension of [Ca(OEt)₂(EtOH)₄]ₙ (1.92 g, 6.16 mmol) in chloroform (25.0 cm³) was introduced H-dppd (2.73 g, 12.32 mmol), producing a yellow coloured solution. Pmdeta (3.0 cm³, 14.0 mmol) was added and the solution stirred at room temperature for 1 h. The solution was reduced to dryness *in vacuo* to yield a yellow solid. This was redissolved in refluxing toluene (25.0 cm³) and left to cool at 0°C, yielding orange crystals (yield 2.78 g, 68.5%). Melting point = 143–145°C. Found : C, 71.3 ; H, 6.9 ; N, 6.2. CaC₃₉O₄H₄₅N₃ requires : C, 71.0 ; H, 6.8 ; N, 6.4%. IR (Nujol) : 1610 (w), 1601 (m), 1555 (m), 1511 (m), 1412 (s), 1302 (w), 1261 (s), 1219 (w), 1134 (m), 1068 (m), 1022 (s), 964 (w), 938 (m), 898 (m), 797 (m), 780 (m), 750 (w), 723 (m), 693 (m), 619 (w) cm⁻¹. ¹H NMR (dmso-d_6, 270 MHz, 20°C) : δ 2.26 (s, 12H, NMe₂), 2.29 (s, 3H, NMe), 2.4 (m, 4H, NCH₂), 2.52 (s, 4H, NCH₂), 6.8 (s, 2H, CH), 7.55–8.12 (m, 20H, dppd Ph). ¹³C NMR (dmso-d_6, 67.94 MHz, 20°C) : δ 43.3 (s, NMe), 46.3 (s, NMe₂), 56.3 (s, NCH₂), 57.8 (s, NCH₂), 93.2 (s, CH), 128.3 (s, *p*-dppd Ph), 129.3 (s, *m*-dppd Ph), 133.3 (s, *o*-dppd Ph), 143.1 (s, *i*-dppd Ph), 184.4 (s, CO). Mass spectrum

(EI⁺, m/z ; major ions) : 749 (6) [Ca₂(dppd)₃]⁺, 709 (2) [Ca(dppd)₃]⁺, 263 (100%) [Ca(dppd)]⁺.

Synthesis of [Sr(tmhd)₂(H-tmhd)] (4)

To a stirred suspension of [Sr(OEt)₂(EtOH)₄]ₙ (4.71 g, 14.2 mmol) in *n*-hexane (25.0 cm³) was introduced H-tmhd (10.0 cm³, 45.0 mmol), producing a colourless solution. The solution was reduced to dryness *in vacuo* to yield a colourless liquid which was kept *in vacuo* at 80°C for 1 h. This was redissolved in hexane (8.0 cm³) and left to cool slowly overnight (0 °C), yielding colourless crystals (yield 6.21 g, 69%). Melting point = 76–81°C. Found : C, 62.0 ; H, 8.7. SrC₃₃O₆H₅₈ requires : C, 62.1 ; H, 9.1%. IR (Nujol) : 1725 (w), 1592 (s), 1579 (m), 1561 (m), 1537 (m), 1505 (s), 1425 (m), 1361 (m), 1276 (m), 1245 (m), 1222 (m), 1185 (m), 1132 (m), 1024 (m), 956 (w), 867 (m), 793 (m), 758 (w), 736 (m), 596 (w), 564 (m), 476 (m), 386 (w) cm⁻¹. IR (hexachlorobutadiene) : 2962 (s), 2868 (m), 1722 (w), 1592 (s), 1578 (s), 1538 (m), 1505 (s), 1416 (m), 1390 (m), 1359 (m), 1261 (m), 1245 (m), 1222 (m), 1185 (m), 1133 (m), 1061 (m), 1022 (m), 758 (w), 736 (w), 655 (w), 595 (w) cm⁻¹. ¹H NMR (dmso-d_6, 90 MHz, 20°C) : δ 0.99 (s, 54H, CH₃), 3.80 (s, 2H, CH₂), 5.35 (s, H, CH). 6.21 (s, H, CH). ¹H NMR (C₆D₆, 270 MHz, 20°C) : δ 1.15 (s, 54H, CH₃), 5.78 (br, 4H, CH/CH₂). ¹³C NMR (dmso-d_6, 67.94 MHz, 20°C) : δ 28.7 (s, CH₃), 46.2 (s, br, C{CH₃}₃/CH₂). 86.7 (s, CH), 87.0 (s, CH), 210.60 (s, CO). Mass spectrum (EI⁺, m/z^+ ; major ions) : 726 (52) [Sr₂(tmhd)₃]⁺, 454 (16) [Sr(tmhd)₂]⁺, 271 (52) [Sr(tmhd)]⁺, 185 (100%) [H-tmhd]⁺.

Crystallographic data collection and structure refinement

All crystallographic measurements for [Ca(dppd)₂(pmdeta)] (3) were made at 120(2) K on a Delft instruments FAST TV area detector diffractometer positioned at the window of a rotating anode generator using Mo-K_α radiation (λ = 0.71069 Å) by following procedures described elsewhere [13].

Crystal data. C₃₉H₄₅CaN₃O₄, f.wt = 659.86, monoclinic, space group C2/c, a = 50.531(12), b = 17.625(5), c = 12.230(3) Å, β = 101.840(10)°, V = 10660(5) Å³, D_c = 1.233 Mg m⁻³, μ(Mo-K_α) = 0.220 mm⁻¹, F(000) = 4224, crystal size 0.35 × 0.25 × 0.20 mm, colourless blocks.

Intensities of 13,398 reflections were measured (2.03 ≤ θ ≤ 24.01° ; −56 ≤ h ≤ 56 ; −9 ≤ k ≤ 19 ; −10 ≤ l ≤ 13) and processed to yield 6934 unique data with intensities > 0 (R_{int} = 0.0298). The structure was solved by direct methods (SHELXS86) [14] and difference synthesis, and refined on F^2 by full-matrix least-squares (SHELXL93) [15] using all unique data corrected for Lorentz and polarization factors. Absorption effects were ignored.

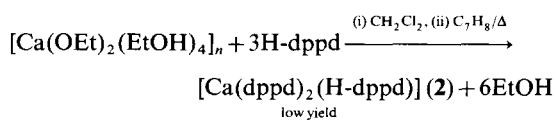The structure analysis indicated that one [Ca(C₁₅

$H_{11}O_2)_2(Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2)]$ molecule was in a general position and another on a crystallographic two-fold axis. In both molecules, the central —$CH_2N(Me)CH_2$— moiety of the pmdeta ligands were orientationally disordered; for the molecule in the general position, the disordered carbon sites were 60:40 occupied, whilst for the molecule in the special position the disorder was 50:50. The geometry of the central nitrogen remained, as expected, close to tetrahedral. During refinement, the N—C and C—C distances involving the disordered atoms were constrained at 1.50(1) and 1.52(1) Å, respectively. All non-hydrogen atoms were anisotropic. The hydrogen atoms of the disordered carbons were ignored; others included in calculated positions (riding model) with U_{iso} tied to the U_{eq} of the parent atoms. The structure finally refined to $R[= \Sigma\{(F_o)-(F_c)\}/\Sigma(F_o)] = 0.0584$ and wR $(= [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}) = 0.1419$ for 683 parameters and all 6934 data. The corresponding R values for 5041 observed data $[I > 2\sigma(I)]$ were 0.0457 and 0.1274, respectively. The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$, which gave satisfactory agreement analyses. The largest peak and hole in the final difference map were 0.400 and -0.385 e Å^{-3}, respectively. Sources of scattering factors as in ref. [15]. The diagrams were drawn with SNOOPI [16]. The calculations were performed on a pentium P5-90 personal computer.

Selected bond lengths and angles are given in Table 1. The atomic coordinates, thermal parameters, full lists of bond lengths and angles, and structure factor tables have been deposited with the Editor as supplementary material.

RESULTS AND DISCUSSION

Synthesis and characterization

The crystalline tetra-ethanol solvated ethoxide $[Ca(OEt)_2(EtOH)_4]_n$ was dissolved in chloroform and allowed to react with 2 and 3 equiv. of H-dppd (H-dppd = 1,3-diphenylpropane-1,3-dione), respectively. Both the reactions were instantaneous with complete dissolution of all the material, however, the mixtures were allowed to stir for ca 1 h. Crystallization from hot toluene solutions produced yellow crystals of $[Ca(dppd)_2(EtOH)_{0.5}]_n \cdot C_7H_8$ (1) and pale orange crystals of $[Ca(dppd)_2(H-dppd)]$ (2), respectively (shown below for compound 2).

$$[Ca(OEt)_2(EtOH)_4]_n + 3H\text{-}dppd \xrightarrow{\text{(i) }CH_2Cl_2, \text{ (ii) }C_7H_8/\Delta}$$

$$[Ca(dppd)_2(H\text{-}dppd)] (2) + 6EtOH$$
low yield

Reaction of the tetra-ethanol solvated calcium ethoxide complex with 2 molar equiv. of H-dppd and 1 molar equiv. of pmdeta in chloroform yielded the monomeric complex $[Ca(dppd)_2(pmdeta)]$ (3) after

recrystallization from toluene. In order to study the generality of this approach, we have also studied the reaction of the strontium ethoxide [Sr(O-Et)_2(EtOH)_4]_n with 3 equiv. of H-tmhd in *n*-hexane to yield $[Sr(tmhd)_2(H\text{-}tmhd)]$ (4). Complexes 3 and 4 can be compared with the neutral lanthanide *tris*-chelate complex $[Er(tmhd)_3]$, which has been characterized by a single crystal diffraction study and shown to be monomeric [17]. Comparison of the ionic radii of calcium(II) (0.99 Å) and erbium(III) (1.0 Å) suggests the calcium compound 2 is likely to be monomeric, however, a structure determination could not be undertaken due to the lack of good quality crystals.

Complexes 1–3 showed good solubilities in a range of organic solvents including thf, chloroform, dmso and hot toluene, and showed poor solubilities in *n*-hexane. In contrast, compound 4 showed excellent solubilities in both coordinating solvents and *n*-hexane.

The spectroscopic data for complexes 1–4 are found to be in accord with the formulae given. IR spectra of complexes 1–4 clearly exhibit vibrational absorption bands characteristic of β-diketonate ligands. The $v(C\text{---}O)$ and $v(C\text{---}C)$ stretching modes of the β-diketonate complexes are observed in the frequency range 1611–1496 cm^{-1} and have been tentatively assigned elsewhere [18]. Furthermore, the IR spectra (Nujol) for complexes 2 and 4 show bands at 1732 and 1725 cm^{-1}, respectively, which correlate well with the $v(C\text{=}O)$ stretch for the parent diketone ligands H-dppd and H-tmhd, respectively ($\sim$1700 cm^{-1} for the free diketones). A similar $v(C\text{=}O)$ stretch was previously observed at 1723 cm^{-1} in the IR spectrum for $[Sr_3(tmhd)_6(H\text{-}tmhd)]$ [4]. Additionally for complex 1, a $v(O\text{---}H)$ stretch due to the coordinated ethanol was observed at ca 3400 cm^{-1}.

Most importantly, the ^1H NMR spectrum in dmso-d_6 for compound 2 reveals both a methylene (CH$_2$) signal at δ 4.88 and the methyne (CH) peak (at δ 7.34) of the diketone and β-diketone ligands, respectively. The relative intensities of the CH$_2$ and CH signals did not yield the expected 1:1 ratio. Presumably, this occurs as a result of rapid fluxional exchange processes (compared with the ^1H NMR timescale) between deuterated dmso, dppd and H-dppd. The corresponding ^{13}C NMR solution spectrum for complex 2 (dmso-d_6) clearly discriminates between the diketone and β-diketone ligands, with single sharp peaks being observed at δ 49.2 and 93.3 for the CH$_2$ and CH carbon signals, respectively.

The ^1H NMR solution spectrum (dmso-d_6) for complex 4 shows two discrete methyne (CH) signals (δ 5.35 and δ 6.21) as well as a methylene (CH$_2$) signal (at δ 3.80). The peak integrals for these signals were observed in the expected ratio of 2:1:1, respectively. The corresponding ^{13}C NMR solution spectrum for complex 4 also reveals two distinct CH environments (at δ 86.7 and δ 87.0) and possibly a CH$_2$ signal which is superimposed under the broad tertiary butyl carbon $[\underline{C}(CH_3)_3]$ signal. As a result of the larger cationic

Table 1. Selected bond lengths (Å) and angles (°) for [Ca(dppd)₂(pmdeta)]

Ca(1)—O(2)	2.309(2)	Ca(1)—O(3)	2.314(2)
Ca(1)—O(1)	2.319(2)	Ca(1)—O(4)	2.326(2)
Ca(1)—N(2)	2.582(3)	Ca(1)—N(1)	2.649(3)
Ca(1)—N(3)	2.678(3)		
Ca(2)—O(5)	2.298(2)	Ca(2)—O(6)	2.327(2)
Ca(2)—N(5)	2.604(4)	Ca(2)—N(4)	2.654(3)
O(2)—Ca(1)—O(3)	98.36(8)	O(2)—Ca(1)—O(1)	76.13(7)
O(3)—Ca(1)—O(1)	75.26(8)	O(2)—Ca(1)—O(4)	173.38(8)
O(3)—Ca(1)—O(4)	76.38(7)	O(1)—Ca(1)—O(4)	98.45(7)
O(2)—Ca(1)—N(2)	96.16(7)	O(3)—Ca(1)—N(2)	142.52(8)
O(1)—Ca(1)—N(2)	142.02(8)	O(4)—Ca(1)—N(2)	90.45(7)
O(2)—Ca(1)—N(1)	92.45(8)	O(3)—Ca(1)—N(1)	76.27(8)
O(1)—Ca(1)—N(1)	147.27(8)	O(4)—Ca(1)—N(1)	90.20(8)
N(2)—Ca(1)—N(1)	68.73(8)	O(2)—Ca(1)—N(3)	91.84(8)
O(3)—Ca(1)—N(3)	144.35(8)	O(1)—Ca(1)—N(3)	74.23(8)
O(4)—Ca(1)—N(3)	90.28(8)	N(2)—Ca(1)—N(3)	68.84(8)
N(1)—Ca(1)—N(3)	137.58(9)	C(7)—O(1)—Ca(1)	133.4(2)
C(9)—O(2)—Ca(1)	132.6(2)	C(22)—O(3)—Ca(1)	127.1(2)
C(24)—O(4)—Ca(1)	129.1(2)		
O(5)—Ca(2)—O(5′)*	168.57(11)	O(5)—Ca(2)—O(6′)	93.80(7)
O(5)—Ca(2)—O(6)	77.04(7)	O(6)—Ca(2)—O(6′)	74.92(11)
O(5)—Ca(2)—N(5)	95.71(5)	O(6)—Ca(2)—N(5)	142.54(5)
O(5)—Ca(2)—N(4′)	91.97(8)	O(6)—Ca(2)—N(4′)	147.16(8)
O(5)—Ca(2)—N(4)	92.22(8)	O(6)—Ca(2)—N(4)	75.06(8)
N(5)—Ca(2)—N(4)	68.48(6)	N(4)—Ca(2)—N(4′)	136.96(12)
C(46)—O(5)—Ca(2)	130.2(2)	C(48)—O(6)—Ca(2)	128.4(2)

The primed atoms in this table and Fig. 1 belong to one and the same molecule and generated by the symmetry $-x, y, 0.5-z$.

radius of strontium (in compound 4) compared with calcium (in complex 2), the deuterated dmso solvent is possibly able to coordinate more readily to compound 4 and hinder rapid fluxional exchange processes between the diketone and β-diketonate ligands.

In less polar solvents such as C_6D_6, only one time averaged CH_2/CH signal was observed in the ^1H NMR spectra for complexes 2 and 4. Evidently, deuterated benzene acts as an innocent solvent and it fails to coordinate sufficiently to the metal centres as to significantly hinder rapid exchange processes.

The mass spectral data reveal that compounds 2–4 can oligomerize in the gas phase to give $[M_2L_3]^+$ species as well as the monomer $[ML_3]^+$ (for compounds 2 and 3 only). However, no nitrogen containing species (pmdeta) are observed in the mass spectrum for compound 3, suggesting that the pmdeta ligand is fairly labile under these conditions compared to dppd.

Thermal analyses

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were made for complexes 2–4. TGA measurements can give vital insights into the thermal behaviour of materials at elevated temperatures, whilst DSC allows the study of the enthalpy change occurring during the thermolysis and the nature of the reaction (i.e. phase

change, melting point or chemical change such as a decomposition reaction).

The TGA plot for 2 shows two distinct regions of weight loss which are observed between ca 229–275 (80.4%) and 344–411°C (14.9%), to give a residue of 2.60% at 500°C (metal oxide CaO₂ would be expected to give a residue of 7.9%). The DSC plot for this compound reveals only two isotherms centred at 79.2 (due to melting) and 265.9°C (due to sublimation). The data are consistent with sublimation of H-dppd and possibly some Ca(dppd)₂ at lower temperatures, with decomposition of the Ca(dppd)₂ above 340°C. In summary, the compound does not sublime intact at higher temperatures.

The TGA plot for compound 3 shows four regions of weight loss between ca 129–279 (37.6% loss), 426–467 (14.7%), 522–571 (25.9%) and 704–785°C (8.4%), to give a residue of 10.8% at 800°C (metal oxide CaO₂ would be expected to give a residue of 8.5%). The DSC plot for this compound reveals at least five isotherms centred at ca 122.2, 213.6, 455.6, 566.7 and 766.7°C, of which the first peak corresponds to melting of the compound. The data suggest that a series of decomposition reactions occur to give the metal oxide, which is probably slightly carbonaceous.

In stark contrast to the TGA plots for the aforementioned compounds, the corresponding curve for compound 4 clearly suggests loss of the diketone (H-

tmhd) below 200°C (loss *ca* 24%; expected 28.5%), followed by sublimation of the remaining [Sr(tmhd)₂]ₙ between *ca* 270 and 390°C (74.6%) to give a minimal residue of 3.4% by 415°C. The DSC curve reveals an isotherm due to melting of the compound at 70.8°C and a second isotherm (due to the sublimation) centred at 384.2°C. A comparison of the thermogravimetric analysis plots for complex 4 and the previously reported compound [Sr₃(tmhd)₆(H-tmhd)] reveals that the latter complex also loses a molecule of H-tmhd at lower temperatures and shows almost identical sublimation behaviour to that observed for compound 4 thereafter [4,18]. Coupled with the improved thermal stability and improved mass transport of compound 4 is its improved air and moisture stability (compared with the homoleptic), suggesting that this material may possibly be a suitable low cost precursor towards the CVD deposition of strontium oxide.

Crystal structure of [Ca(dppd)₂(pmdeta)] (3)

A single crystal X-ray study was undertaken for [Ca(dppd)₂(pmdeta)] (3) to unambiguously establish the bonding modes of the pmdeta and dppd ligands. It was found that there are 12 molecules of [Ca(C₁₅H₁₁O₂)₂(Me₂NCH₂CH₂N(Me)CH₂CH₂NMe₂)] in the unit cell, with one set of eight molecules in general positions and another set of four on two-fold special positions. The structure of the two molecules together with the numbering scheme are shown in Fig. 1. The central —CH₂N(Me)CH₂— moiety of the tridentate pmdeta ligands was disordered in both molecules (see experimental) with expected tetrahedral geometry around the nitrogen atoms. From Fig. 1, it is apparent

that both molecules have very similar structures, although the equivalent two-fold axis in the molecule in the general position [passing through the Ca(1)—N(2) bond] is less exact. The conformational disorder associated with the NCH₂CH₂N bridges are also similar.

The calcium atoms in both molecules are seven-coordinate with a distorted pentagonal bipyramidal geometry. In molecule A, the pentagonal girdle is formed by the three nitrogen atoms [N(1), N(2) and N(3)] from the amine and two oxygen atoms [O(1), O(3)] from the two β-diketonate ligands, with the axial positions being occupied by the other two β-diketonate oxygens [O(2), O(4)]. Similarly in molecule B, the pentagonal girdle is formed by the atoms N(4), N(5), N(4′), O(6), O(6′), with O(5), O(5′) occupying the axial sites. The distortions from ideal geometry are reflected in the variations in the angles involving the *trans* (axial) ligands, 173.38(8) for Ca(1) and 168.57(11)° for Ca(2), and also in the pentagonal angles ranging from 68.73(8) to 76.27(8)° for Ca(1) (sum 363.33°) and 68.48(6) to 75.06(8)° for Ca(2) (sum 362.00°).

The Ca—O distances lie in the range 2.298(2)–2.327(2) Å and the average value (2.315 Å) is comparable with those previously reported for other calcium complexes with oxygen donor ligands, e.g. 2.30 Å in [Ca₂(OSiPh₃)₄(NH₃)₄]·0.5(toluene) [13], 2.35 Å in [Ca₃(tmhd)₆] [3], 2.33 Å in [Ca₂(tmhd)₄(EtOH)₂] [3], 2.33 Å in [Ca(pd)₂(H₂O)₂]·H₂O (H-pd = pentane-2,4-dione) [19], 2.44 Å in [Ca₂(hfpd)₄(H₂O)₄] (H-hfpd = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) [20], 2.28 Å in [Ca₄(tmhd)₄(OArₙ)₄ (EtOH)₂](HOArₙ = 2,6-N,N-dimethylaminomethyl-4-methylphenol) [21], 2.28 Å in [Ca₄(tmhd)₄

(A)   (B)
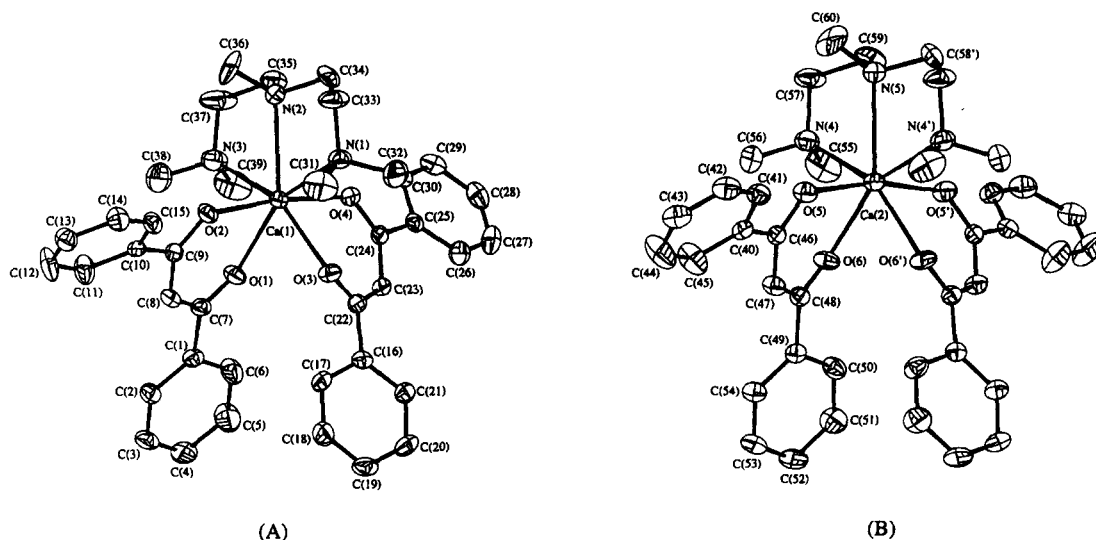
Fig. 1. Molecular structures of [Ca(dppd)₂(pmdeta)] (3) showing the atomic numbering scheme. Hydrogen atoms have been omitted and only one orientation of the disordered —CH₂N(Me)CH₂— moiety in each molecule is shown for clarity. (a) molecule in the general position; (b) molecule in the special position, with the primed atoms being generated by the two-fold axis passing through the Ca(2)—N(5) bond.

(OPh)₄(MeOH)₄] [22], 2.37 Å in [Ca₄(dppd)₈(EtOH)₂] [23], and 2.33 Å in [Ca₄(tmhd)₄(Me₂NCH₂CH₂)₂O] [24]. Examination of all the Ca—O bond lengths in the above complexes show considerable variations (average values 2.28–2.44 Å), which may be explained by different coordination numbers of calcium, the nature of Ca—O linkages (i.e. the number of bonds each oxygen makes with the metals) and steric interactions. The dppd ligands in the present complex are all symmetrically chelated to calcium, as indicated by the nearly equal Ca—O bonds for each ligand and O—Ca—O chelate angles lie in the close range 76.13(7)–77.04(7)°. These angles are comparable with those observed in other complexes with chelating β-diketonate ligands.

The pmdeta ligands chelate to the calcium atoms in a tridentate manner with Ca—N distances ranging from 2.582(3) to 2.678(3) Å, average 2.637 Å, much longer than what would be expected on the basis of atomic radii sum (2.49 Å) [25]. It is also observed that in each chelate the Ca—N bond with the terminal nitrogen is 0.05–0.08 Å longer than the bond with the central nitrogen (average distance 2.569 vs 2.593 Å). This relative lengthening of the terminal Ca—N bonds may be attributed to steric requirements of the two methyl groups on the terminal nitrogen atoms. The average Ca—N distance observed in the present compound is considerably longer than those (2.518 Å) in [Ca₄(tmhd)₄(Me₂NCH₂CH₂)O₂] [24] and (2.568 Å) in [Ca₂(OSiPh₃)₄(NH₃)₄]·0.5(toluene) [13], but shorter than the value (2.730 Å) in [Ca₄(tmhd)₄(OAr_N)₄(EtOH)₂] [21]. The N—Ca—N chelate angles are quite acute and lie in the very narrow range 68.48(6)–68.84(8)°. The bond lengths and angles associated with the chemically equivalent β-diketonate ligands are similar and have expected values. However, the independent ligands show considerable differences in terms of the non-planarity of the CaO₂C₃ chelate rings and also in the orientations of the phenyl rings with respect to the C₃O₂ moieties. All the chelate rings are non-planar with fold angles of 10.4(1), 24.8(1) and 20.1(2)°, respectively, along the O(1)...O(2), O(3)...O(4) and O(5)...O(6) axes in the two molecules. The values of the torsion angles O(1)—C(7)—C(1)—C(6), O(2)—C(9)—C(10)—C(15), O(3)—C(22)—C(16)—C(17), O(4)—C(24)—C(25)—C(30), O(5)—C(46)—C(40)—C(41) and O(6)—C(48)—C(49)—C(50) are 14.4(4), −31.3(4), 27.2(4), −18.4(4), −26.7(4) and 20.7(4)°, respectively. This suggests that the phenyl rings are also non-coplanar with the respective C₃O₂ planes and show considerable flexibility arising from intra- and inter- molecular non-bonded interactions.

CONCLUSIONS

An important point to note by way of conclusion is the total absence of any oxo or hydroxo ligands in all of these products. This effectively implies that our starting materials [M(OEt)₂(EtOH)₄]_n and synthetic strategy are highly reproducible and, therefore, important as a starting point to develop the chemistry of the alkoxides, β-diketonates and other oxygen based ligands of the heavier group 2 metals. By using 3 molar equiv. of ligand to the metal ethoxide, we have attempted to achieve a better tailoring of not only ligand to metal sets, but also more importantly control of the degree of oligomerization of the complexes. This latter point is of some importance if such materials are to find application as CVD precursors.

Surprisingly, our thermogravimetric data suggest that two of the Lewis base adducted calcium complexes display different weight loss behaviour and volatilities, which are directly attributable to the different neutral co-ligands, i.e. H-dppd and pmdeta. Our results suggest that subtle modifications in the coordination spheres of these metal centres thus appear to have a profound effect upon physical properties such as volatilities.

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