Group IIA Metal β-Diketonate Complexes; the Crystal Structures of $[Sr_3(tmhd)_6(Htmhd)]\cdot C_6H_5Me\cdot C_5H_{12}$ and $[Ba_4(tmhd)_8]$ (Htmhd = 2,2,6,6-tetramethylheptane-3,5-dione)†

Simon R. Drake,[*,a] **Michael B. Hursthouse,**[*,b] **K. M. Abdul Malik**[b] **and David J. Otway**[a]
[a] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK*
[b] *School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, P.O. Box 912, Cardiff CF1 3TB, UK*

Hydrocarbon-soluble Group IIA metal ethoxides $[\{M(OEt)_2(EtOH)_4\}_n]$ (M = Sr or Ba) react with the β-diketonate 2,2,6,6-tetramethylheptane-3,5-dionate (Htmhd) to yield the volatile complexes $[Sr_3(tmhd)_6(Htmhd)]$ and $[Ba_4(tmhd)_8]$ in excellent yield. These materials have been studied by classical spectroscopic techniques, differential scanning calorimetry and thermogravimetric analysis. They have also been characterised by single-crystal X-ray diffraction at 150 K, and shown to exist as a trimer and tetramer respectively, the former also incorporating a neutral Htmhd ligand.

In the last 2 to 3 years there has been considerable interest in the previously dormant area of alkaline-earth metallorganic complexes and this may be attributed to their potential application as molecular precursors for electroceramics such as superconductors, piezoelectrics and other speciality electronic materials. Metal β-diketonates, *e.g.* $[\{M(ROCCHCOR)\}_2]$, have generally found wider application in chemical vapour deposition (CVD) than the 'simple' metal alkoxides as they tend to have higher volatilities and improved chemical stability and mass-transport properties.

The synthesis of homoleptic strontium and barium β-diketonates [*e.g.* with [2,2,6,6-tetramethylheptane-3,5-dione (Htmhd) and hexafluoroacetylacetonate (Hhfa)], $[M(\beta\text{-dik})_2]$, has created innumerable difficulties for scientists over a considerable period of time.[1] These complexes are susceptible to ageing, moisture, oxygen and to incorporating co-ordinating solvents. For example, in aqueous media the barium aggregate $[Ba_5(OH)(tmhd)_9(H_2O)_3]$ has been obtained,[2] while other researchers have structurally characterised the hydrated compounds, $[\{Ca(hfa)_2(H_2O)_2\}_2]$ and $[\{Ba(hfa)_2(H_2O)\}_\infty]$.[3] If more rigorous anaerobic conditions are used, then products of high purity, *e.g.* the Lewis-base adducted complexes $[Ba_2(tmhd)_4L_2]$ (L = NH_3 or Et_2O), are obtained.[4]

Previous researchers have demonstrated the difficulties in the preparation of the homoleptic complex $[\{Ba(tmhd)_2\}_n]$, and most importantly its unstable high-temperature behaviour and poor vapour-pressure stability.[5,6] Our recent studies have concentrated in some depth on heavier alkaline-earth-metal alkoxides,[7] aryloxides[8] and siloxides,[9] using a wide range of synthetic strategies. A more comprehensive understanding of the diverse reaction products and detailed knowledge of the solvent dependence of the products is thus required.

A variety of synthetic approaches have been used to prepare barium β-diketonates, including the classical metal hydroxide–β-diketone route first reported by Cahours[10] over 130 years ago. It is only relatively recently that such materials have been definitely characterised. For examples, Sievers and co-workers[2] have formulated the product from this reaction to be $[Ba_5(OH)(tmhd)_9(H_2O)_3]$, based on incomplete structural data. Other workers have also studied the reaction of barium hydroxide with Htmhd and then recrystallised the product in methanol and obtained the complex $[Ba(tmhd)_2(MeOH)_3]\cdot 2MeOH$;[6] while more recently Drozdov and Trojanov[11] treated barium metal with Htmhd in pentane to yield $[Ba_4(tmhd)_8]$.

We therefore describe herein the synthesis and X-ray structural characterisation of two important examples of molecular β-diketonate compounds of strontium and barium. In the course of these studies, several other research groups have reported alternative routes to $[Ba_4(tmhd)_8]$ and two structural modifications of this.[11,12]

Results and Discussion

Our alternative strategy to the above routes utilises the hydrocarbon-soluble metal ethoxides $[M(OEt)_2(EtOH)_4]$,[13] which readily undergo a simple ligand exchange (1) with Htmhd

$$[M(OEt)_2(EtOH)_4] + 2Htmhd \xrightarrow{\text{hexane}} [\{M(tmhd)_2\}_n] + 6EtOH \quad (1)$$

(M = Sr or Ba). The crystalline ethanol-solvated metal ethoxides were dissolved in hexane and allowed to react with Htmhd, and the reactions found to be complete within 10 min. In both cases crystallisation from either pentane or hexane gave colourless crystals in excellent yield (> 70% non-optimised first crop). These are formulated as $[Sr_3(tmhd)_6(Htmhd)]$ **1** and $[Ba_4(tmhd)_8]$ **2** on the basis of single-crystal X-ray studies.

Spectroscopic Characterisation.—The IR spectra of the complexes **1** and **2** were studied as both hexachlorobutadiene and Nujol mulls between CsI windows. Selected bands are listed in the Experimental section. The bands are tentatively assigned on the basis of data for previously characterised transition-metal β-diketonates.[14] In the region 1500–1600 cm^{-1}, bands for

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: Torr ≈ 133 Pa, cal = 4.184 J.

1 at 1591, 1561 and 1537 cm^{-1} are assigned to the ν(C$\cdots$O) stretching modes and those at 1578 and 1504 cm^{-1} to the ν(C$\cdots$C) stretching modes. A peak is also observed at 1723 cm^{-1} which correlates well with the C=O stretch of the parent Htmhd ligand ($\approx$1700 cm^{-1}). In contrast, complex **2** only shows well resolved C$\cdots$O and C$\cdots$C stretching modes.

Multinuclear NMR spectroscopy (^{1}H and ^{13}C) for both complexes **1** and **2** in C_6D_6 shows only one time-averaged tmhd environment which suggests that these molecules are fluxional in solution at room temperature on the NMR time-scale.

Solid-state ^{13}C cross polarisation magic angle spinning (CP MAS) NMR spectra have also been recorded for both complexes at room temperature. Complex **1** reveals at least six well resolved Bu^t groups in the region δ 26–31, and also six quaternary carbon resonances. The resolution of the carbonyl groups was such that at least six environments were clearly observed, and at higher field, δ 211.8, a resonance due to a carbonyl group on the ligand Htmhd was seen. The solid-state ^{13}C NMR spectrum for compound **2** reveals only three clearly resolved tmhd Bu^t and quaternary carbon signals, further supported by the presence of only three CH resonances. Clearly at room temperature in the solid state we are observing the same structure as discussed in our single-crystal X-ray determination.

The electron-impact mass spectroscopic data for the complexes show a clear $[M_2L_3]^+$ species indicative of an oligomeric species. These results are in accord with those of other researchers, who have noted the marked tendency for such complexes to dissociate in the vapour phase.[2,15]

Physical Properties.—The molecular nature of these materials is also borne out by the observation that both are low-melting solids in the range 170–200 °C and sublime intact in high yield below 210 °C and 10^{-3} Torr. Such behaviour is strongly indicative of molecular ensembles with no short-range intermolecular contacts. Molecular mass cryoscopic studies in benzene have shown that both of these complexes remain intact in hydrocarbon solvents.

DSC/TGA Data.—The thermogravimetric analysis plot (see Fig. 1) of the strontium complex **1** (solvent-free material) shows more or less continuous behaviour over the temperature range 70–400 °C, but the first-derivative plot clearly reveals at least two major overlapping reaction processes, at (*i*) 70–240 and (*ii*) 240–400 °C. The presence of these reactions is also supported by the observation of the corresponding endotherms in the differential scanning calorimetry (DSC) curve. The first reaction corresponds to the simultaneous loss of the Htmhd molecule with a weight loss observed of 11.4% (calculated 10.75%). This is closely followed by a second isotherm, resulting in sublimation of the complex with 85 ± 2% weight loss, completed by 400 °C, leaving a 3–4% residue.

The DSC plot for $[Ba_4(tmhd)_8]$ **2** (Fig. 2) shows three endotherms, the first in the range 81–120 °C corresponds to the loss of a very small amount of lattice solvent, presumably hexane in the sample run. The second and third endotherms are in the range 189–220 °C and clearly result in the sample melting and subsequent chemical reaction (third endotherm). These features are also observed in the thermal gravimetric analysis (TGA) spectrum. In the corresponding TGA plot the onset temperature under flowing nitrogen gas is 260 °C with completion by 410 °C. Over this temperature range 92 ± 2% of the complex sublimes, leaving a small residue (*ca.* 5–6%). Our data yield a $T_{50\%}$ (50% of material sublimed) = 370 °C for **1** and 385 °C for **2**. These data may be contrasted with previously reported results on $[Ba_4(tmhd)_8]$. Yuhya *et al.*[16] reported a 25% residue at 500 °C and Cho and co-workers a 41% residue,[17] while Sievers and co-workers[2] who used the pentameric barium aggregate $[Ba_5(OH)(thd)_9(H_2O)_3]$ obtained a 20% residue at 500 °C. These results amply demonstrate the variable nature of the metal-tmhd sources, and also the inherent instability and difficulties in handling such materials, even under presumably anaerobic conditions.

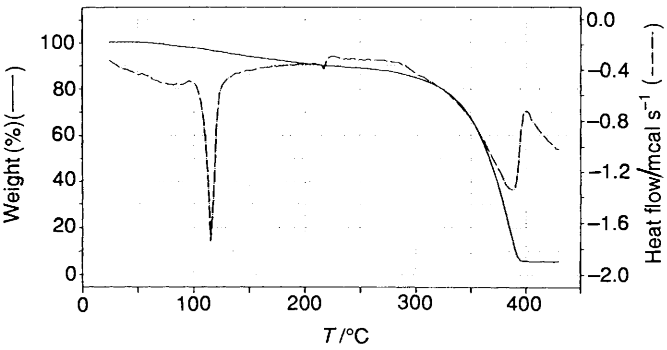

Fig. 1 Differential scanning calorimetry (- - - -) and thermogravimetric analysis curves (——) for the complex $[Sr_3(tmhd)_6(Htmhd)]$ **1**

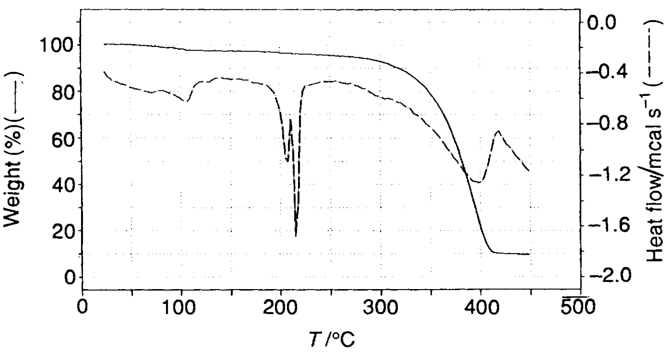

Fig. 2 Differential scanning calorimetry (- - - -) and thermogravimetric analysis curves (——) for the complex $[Ba_4(tmhd)_8]$ **2**

X-Ray Structural Determinations.—$[Sr_3(tmhd)_6(Htmhd)]\cdot C_6H_5Me\cdot C_5H_{12}$ **1**. The structure of $[Sr_3(tmhd)_6(Htmhd)]\cdot C_6H_5Me\cdot C_5H_{12}$ **1** is shown in Fig. 3, and selected bond lengths and angles are in Table 1. This molecule consists of a triangular array of strontium atoms, with metal–metal distances of Sr(2)···Sr(1) 4.110(5), Sr(3)···Sr(1) 3.631(5) and Sr(3)···Sr(2) 3.905(5) Å. The three strontium atoms each have a different co-ordination environment, but all have one common feature and that is the presence of one terminal chelating tmhd [*i.e.* O(1), O(2); O(7), O(8); O(11), O(12)] with an average Sr–O distance of 2.498(8) Å (see Fig. 4 for type 1 co-ordination mode); Sr(1) is also bonded to three oxygens, O(6), O(10) (both type 2 ligands) and O(14) (type 3 ligand) from three bridging tmhd ligands and a co-ordination number of six is completed by a triply bridging oxygen O(3) (type 5 ligand) with a Sr–O distance of 2.662(9) Å. Seven-co-ordination is observed for Sr(2) *via* the terminal chelating ligand [O(7), O(8)] (type 1), the two oxygens [O(5), O(6)] from a chelating/bridging ligand (type 2), two oxygens [O(3), O(4)] from an unusual μ,μ_3-chelate/bridging ligand (type 5) and one oxygen [O(13)] from a μ,μ-bridging tmhd (type 3). For Sr(3) there is one chelating tmhd ligand [O(11) and O(12)] (type 1), a μ,μ-bridging tmhd ligand [O(13) and O(14)] (type 3), a chelating/bridging tmhd ligand [O(9) and O(10)] (type 2), and the unique μ,μ_3-tmhd ligand [O(3), O(4)] (type 5).

The structure of complex **1** may be contrasted with that of the only previously structurally characterised strontium β-diketonate complex $[Sr_4(dpp)_8(Me_2CO)_2]$ (dpp = PhCOCH-COPh).[18] This molecule has the four strontium atoms arranged around a parallelepiped arrangement of oxygen atoms, and Sr–O (bridging) distances of 2.55 Å and Sr–O (chelating) of 2.44 Å. The shorter Sr–O bond distances observed for the purely chelating tmhd ligands are as expected for both **1** and $[Sr_4(dpp)_8(Me_2CO)_2]$.

Table 1 Selected interatomic distances (Å) and angles (°) for $[Sr_3(tmhd)_6(Htmhd)]\cdot C_6H_5Me\cdot C_5H_{12}$

O(1)–Sr(1)	2.479(8)	O(2)–Sr(1)	2.399(9)	O(13)–Sr(2)	2.507(8)	O(3)–Sr(3)	2.646(9)
O(3)–Sr(1)	2.662(9)	O(6)–Sr(1)	2.489(8)	O(4)–Sr(3)	2.526(8)	O(9)–Sr(3)	2.442(9)
O(10)–Sr(1)	2.605(9)	O(14)–Sr(1)	2.477(9)	O(10)–Sr(3)	2.648(10)	O(11)–Sr(3)	2.619(11)
O(3)–Sr(2)	2.638(9)	O(4)–Sr(2)	2.718(9)	O(12)–Sr(3)	2.618(9)	O(13)–Sr(3)	2.651(9)
O(5)–Sr(2)	2.513(10)	O(6)–Sr(2)	2.585(9)	O(14)–Sr(3)	2.557(6)	Sr(2) ··· Sr(1)	4.110(5)
O(7)–Sr(2)	2.437(8)	O(8)–Sr(2)	2.436(8)	Sr(3) ··· Sr(1)	3.631(5)	Sr(3) ··· Sr(2)	3.905(5)
O(2)–Sr(1)–O(1)	69.8(3)	O(3)–Sr(1)–O(1)	169.0(2)	O(13)–Sr(2)–O(5)	145.2(2)	O(13)–Sr(2)–O(6)	77.6(3)
O(3)–Sr(1)–O(2)	112.1(3)	O(6)–Sr(1)–O(1)	116.9(3)	O(13)–Sr(2)–O(7)	131.8(2)	O(13)–Sr(2)–O(8)	99.6(3)
O(6)–Sr(1)–O(2)	92.0(3)	O(6)–Sr(1)–O(3)	74.1(3)	O(4)–Sr(3)–O(3)	64.6(3)	O(9)–Sr(3)–O(3)	94.5(3)
O(10)–Sr(1)–O(1)	102.8(3)	O(10)–Sr(1)–O(2)	120.3(3)	O(9)–Sr(3)–O(4)	94.6(3)	O(10)–Sr(3)–O(3)	66.3(3)
O(10)–Sr(1)–O(3)	66.7(3)	O(10)–Sr(1)–O(6)	136.0(2)	O(10)–Sr(3)–O(4)	127.0(3)	O(10)–Sr(3)–O(9)	70.5(3)
O(14)–Sr(1)–O(1)	90.9(3)	O(14)–Sr(1)–O(2)	159.0(2)	O(11)–Sr(3)–O(3)	140.0(2)	O(11)–Sr(3)–O(4)	75.4(3)
O(14)–Sr(1)–O(3)	88.4(3)	O(14)–Sr(1)–O(6)	89.6(3)	O(11)–Sr(3)–O(9)	88.0(4)	O(11)–Sr(3)–O(10)	148.9(2)
O(14)–Sr(1)–O(10)	70.8(3)	O(4)–Sr(2)–O(3)	62.2(3)	O(12)–Sr(3)–O(3)	155.2(2)	O(12)–Sr(3)–O(4)	139.1(2)
O(5)–Sr(2)–O(3)	83.4(3)	O(5)–Sr(2)–O(4)	132.1(2)	O(12)–Sr(3)–O(9)	78.6(3)	O(12)–Sr(3)–O(10)	89.1(3)
O(6)–Sr(2)–O(3)	73.0(3)	O(6)–Sr(2)–O(4)	123.9(3)	O(12)–Sr(3)–O(11)	64.1(3)	O(13)–Sr(3)–O(3)	78.2(3)
O(6)–Sr(2)–O(5)	68.2(3)	O(7)–Sr(2)–O(3)	116.4(3)	O(13)–Sr(3)–O(4)	65.0(3)	O(13)–Sr(3)–O(9)	159.6(2)
O(7)–Sr(2)–O(4)	84.0(3)	O(7)–Sr(2)–O(5)	83.0(3)	O(13)–Sr(3)–O(10)	121.8(3)	O(13)–Sr(3)–O(11)	85.8(3)
O(7)–Sr(2)–O(6)	148.8(2)	O(8)–Sr(2)–O(3)	169.1(2)	O(13)–Sr(3)–O(12)	115.6(3)	O(14)–Sr(3)–O(3)	87.1(2)
O(8)–Sr(2)–O(4)	127.9(3)	O(8)–Sr(2)–O(5)	90.4(3)	O(14)–Sr(3)–O(4)	125.9(2)	O(14)–Sr(3)–O(9)	134.7(2)
O(8)–Sr(2)–O(6)	96.5(3)	O(8)–Sr(2)–O(7)	71.4(3)	O(14)–Sr(3)–O(10)	68.9(2)	O(14)–Sr(3)–O(11)	118.5(2)
O(13)–Sr(2)–O(3)	80.9(3)	O(13)–Sr(2)–O(4)	64.2(3)	O(14)–Sr(3)–O(12)	81.4(2)	O(14)–Sr(3)–O(13)	64.6(2)
Sr(1)–O(1)–C(2)	136.0(6)	Sr(1)–O(2)–C(4)	138.9(6)	Sr(2)–O(8)–C(37)	132.5(6)	Sr(3)–O(9)–C(46)	139.0(6)
Sr(2)–O(3)–Sr(3)	95.3(2)	Sr(1)–O(3)–Sr(3)	86.3(2)	Sr(1)–O(1)–Sr(3)	87.4(2)	Sr(3)–O(10)–C(48)	130.4(6)
Sr(1)–O(3)–Sr(2)	101.7(2)	Sr(3)–O(3)–C(13)	118.0(5)	Sr(1)–O(10)–C(48)	141.7(6)	Sr(3)–O(11)–C(57)	130.2(7)
Sr(2)–O(3)–C(13)	100.8(5)	Sr(1)–O(3)–C(13)	144.8(5)	Sr(3)–O(12)–C(59)	131.4(7)	Sr(2)–O(13)–Sr(3)	98.3(3)
Sr(2)–O(4)–Sr(3)	96.2(2)	Sr(3)–O(4)–C(15)	119.9(4)	Sr(3)–O(13)–C(68)	109.3(5)	Sr(2)–O(13)–C(68)	152.2(6)
Sr(2)–O(4)–C(15)	103.8(6)	Sr(2)–O(5)–C(24)	126.3(6)	Sr(1)–O(14)–Sr(3)	92.3(2)	Sr(3)–O(14)–C(70)	110.0(5)
Sr(1)–O(6)–Sr(2)	108.1(2)	Sr(2)–O(6)–C(26)	115.7(5)	Sr(1)–O(14)–C(70)	153.4(6)		
Sr(1)–O(6)–C(26)	131.9(6)	Sr(2)–O(7)–C(35)	129.3(6)				

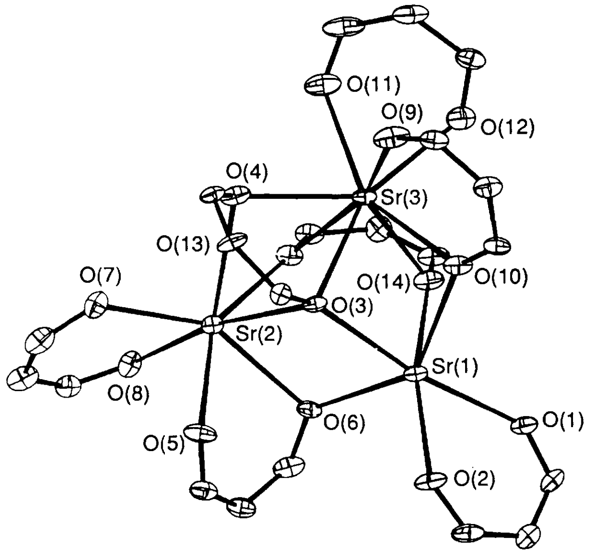

Fig. 3 The molecular structure of $[Sr_3(tmhd)_6(Htmhd)]$ **1** showing the atom numbering scheme; the $\mathrm{Bu^t}$ groups are omitted for clarity

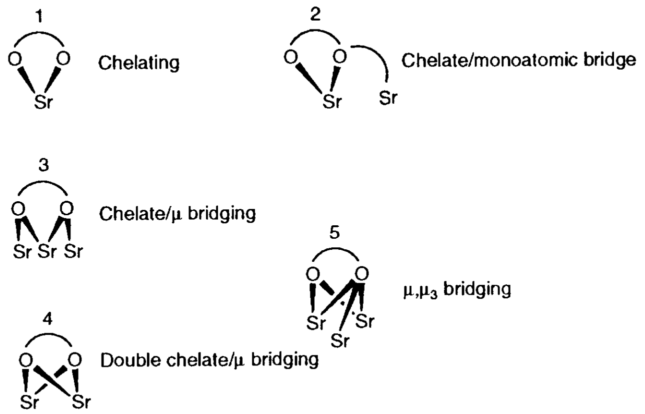

Fig. 4 Types of co-ordination modes observed for tmhd ligands in complexes **1** and **2**

Detailed analysis of ligand bond lengths and angles shows quite clearly that the Htmhd ligand is the chelating ligand on Sr(3). The C–O distances are 1.21(1) and 1.23(1) Å compared with 1.23(1)–1.30(1) Å for the other tmhd ligands and more importantly the tmhd ring C–C distances are 1.51(2) and 1.55(2) Å compared with 1.38(1)–1.44(1) Å in other ligands, and the C–C–C angle is 113(1)°, indicating quite clearly the presence of C–C single bonds and a CH_2 group in this unique ligand. The chelation of a protonated β-diketonate ligand, particularly in this form, is quite unusual and illustrates some of the complex equilibria occurring in solution for complex **1**.

A number of features are worthy of mention in regard to the structure of complex **1**. The appearance of a Sr_3 aggregate with no oxo or hydroxo ligands present in the final product attests to the high purity of the ethanol-solvated strontium ethoxide starting material, and the synthetic strategy applied here. The structure also displays a remarkable range of tmhd bonding patterns (see Fig. 4). In addition to the terminal chelating ligands mentioned earlier, we have not only the familiar chelating and monoatomic bridge [ligands containing O(5), O(6) and O(9), O(10)], but an unusual monoatomic 'perpendicular' μ,μ-bridging ligand, containing O(13) and O(14), and also an unusual double monoatomic perpendicular μ,μ_3-bridging ligand containing O(4) and O(3). Whilst there is some correlation between average Sr–O distances for the six-, seven- and eight-co-ordinated metal centres [2.518, 2.548 and 2.588 Å for Sr(1), Sr(2) and Sr(3) respectively], the very broad spread of values involving the different types of bridging oxygens does not conform to any simple pattern. This may be attributed to the strain involved in matching the aggregate geometry and oligomerisation.

Table 2 Selected interatomic distances (Å) and angles (°) for $[Ba_4(tmhd)_8]$

O(1)–Ba(1)	2.586(6)	O(2)–Ba(1)	2.584(6)
O(3)–Ba(1)	2.801(6)	O(4)–Ba(1)	2.843(6)
O(5)–Ba(1)	2.799(6)	O(6)–Ba(1)	2.831(6)
O(8)–Ba(1)	2.906(6)	O(3′)–Ba(2)*	2.664(6)
O(4)–Ba(2)	2.659(6)	O(5′)–Ba(2)	2.670(6)
O(6)–Ba(2)	2.715(6)	O(6′)–Ba(2)	3.140(6)
O(7)–Ba(2)	2.479(5)	O(8)–Ba(2)	3.034(6)
Ba(2) · · · Ba(1)	4.213(5)	Ba(2) · · · Ba(2′)	4.099(5)
Ba(2) · · · Ba(1′)	4.144(5)		
O(2)–Ba(1)–O(1)	66.5(2)	O(3)–Ba(1)–O(1)	100.0(2)
O(3)–Ba(1)–O(2)	131.8(1)	O(4)–Ba(1)–O(1)	114.8(2)
O(4)–Ba(1)–O(2)	169.9(1)	O(4)–Ba(1)–O(3)	58.2(2)
O(5)–Ba(1)–O(1)	121.0(2)	O(5)–Ba(1)–O(2)	86.8(2)
O(5)–Ba(1)–O(3)	59.9(2)	O(5)–Ba(1)–O(4)	100.2(2)
O(6)–Ba(1)–O(1)	170.7(1)	O(6)–Ba(1)–O(2)	104.6(2)
O(6)–Ba(1)–O(3)	88.0(2)	O(6)–Ba(1)–O(4)	73.3(2)
O(6)–Ba(1)–O(5)	59.3(2)	O(8)–Ba(1)–O(1)	110.4(2)
O(8)–Ba(1)–O(2)	104.9(2)	O(8)–Ba(1)–O(3)	122.7(2)
O(8)–Ba(1)–O(4)	65.1(2)	O(8)–Ba(1)–O(5)	127.5(2)
O(8)–Ba(1)–O(6)	68.3(2)		
O(4)–Ba(2)–O(3′)	146.2(2)	O(5′)–Ba(2)–O(3′)	63.2(2)
O(5′)–Ba(2)–O(4)	105.3(2)	O(6)–Ba(2)–O(3′)	90.7(2)
O(6)–Ba(2)–O(4)	78.1(2)	O(6)–Ba(2)–O(5′)	138.7(2)
O(6′)–Ba(2)–O(3′)	84.4(2)	O(6′)–Ba(2)–O(4)	64.4(2)
O(6′)–Ba(2)–O(5′)	56.6(2)	O(6′)–Ba(2)–O(6)	91.4(2)
O(7)–Ba(2)–O(3′)	100.4(2)	O(7)–Ba(2)–O(4)	113.1(2)
O(7)–Ba(2)–O(5′)	98.8(2)	O(7)–Ba(2)–O(6)	118.0(2)
O(7)–Ba(2)–O(6′)	149.9(2)	O(8)–Ba(2)–O(3′)	139.0(2)
O(8)–Ba(2)–O(4)	65.4(2)	O(8)–Ba(2)–O(5′)	151.7(2)
O(8)–Ba(2)–O(6)	67.9(2)	O(8)–Ba(2)–O(6′)	128.5(2)
O(8)–Ba(2)–O(7)	64.4(2)		
C(2)–O(1)–Ba(1)	137.9(3)	C(4)–O(2)–Ba(1)	138.5(3)
Ba(1)–O(3)–Ba(2′)	98.6(2)	C(13)–O(3)–Ba(1)	98.0(4)
C(13)–O(3)–Ba(2′)	154.3(4)	Ba(2)–O(4)–Ba(1)	99.9(2)
C(15)–O(4)–Ba(1)	100.0(4)	C(15)–O(4)–Ba(2)	152.6(3)
Ba(1)–O(5)–Ba(2′)	98.5(2)	C(24)–O(5)–Ba(1)	108.8(4)
C(24)–O(5)–Ba(2′)	127.4(4)	Ba(2)–O(6)–Ba(1)	98.8(2)
Ba(2′)–O(6)–Ba(1)	87.7(2)	Ba(2′)–O(6)–Ba(2)	88.6(2)
C(26)–O(6)–Ba(1)	103.7(4)	C(26)–O(6)–Ba(2)	143.4(3)
C(26)–O(6)–Ba(2′)	120.5(4)	C(35)–O(7)–Ba(2)	147.3(3)
Ba(2)–O(8)–Ba(1)	90.3(2)	C(37)–O(8)–Ba(1)	142.1(3)
C(37)–O(8)–Ba(2)	127.5(4)		

* The primed atoms are generated from the unprimed ones by the symmetry relation $-x, 1 - y, -z$.

$[Ba_4(tmhd)_8]$ **2**. We have determined the structure of $[Ba_4(tmhd)_8]$ **2** at low temperature (150 K); two room-temperature determinations were reported whilst this manuscript was in preparation.[11,12] The molecular structure is shown in Fig. 5, and some important geometry parameters are in Table 2. The structure is centrosymmetric and consists of a distorted parallelpiped of oxygen atoms (from the tmhd ligands), and comprises O(2), O(5), O(6) and O(8) and their symmetry-related atoms. This framework is further supported by the four barium atoms which lie over each of the faces of this parallelepiped arrangement. In fact, the molecule may be considered to be constructed of two symmetry-related $Ba_2(tmhd)_4$ dimeric subunits which are linked by a range of tmhd bridge-bonding modes. The two dimeric units are bridged by six oxygens of six separate tmhd ligands. This tetrameric compound has structural similarities to that of $[Ca_4(dpp)_8(EtOH)_2]$.[18] The ethanol ligands in the latter bind to only two of the four available metal centres thus giving six- and seven-co-ordinate metal atoms. In **2** these sites are occupied by further Ba–O contacts from semi-bridging tmhd ligands. The four barium atoms occupy the corners of a fairly regular rhombohedron with an average Ba · · · Ba 'distance' of 4.152(5) Å, and the angles of the rhombohedron are *ca.* 60 and 120°. Each of the two unique barium atoms is seven-co-ordinate.

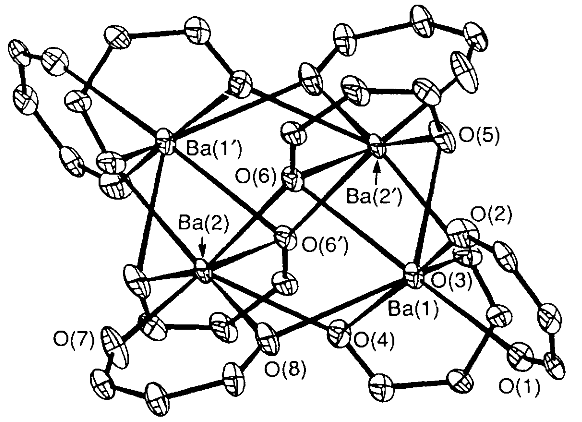

Fig. 5 The structure of $[Ba_4(tmhd)_8]$: the Bu^t groups are omitted for clarity

Atom Ba(1) is bonded to one chelating tmhd ligand [O(1), O(2)] (type 1 chelate, see Fig. 3). The second tmhd [O(3) and O(4)] also chelates, but each oxygen then bridges to another metal centre [Ba(2) and Ba(2′)] and is a type 3 ligand. For Ba(2) one chelating tmhd [O(7) and O(8)] also forms one bridge to Ba(1) (type 2 ligand) and the other forms a bridge to Ba(1) through O(5) and two bridges to Ba(1) and Ba(2) through O(6) (type 5 ligand).

This result may be contrasted with the recent room-temperature studies of Drozdov and Trojanov,[11] and Gleizes *et al.*,[12] who suggested that the two unique barium atoms were six- and seven-co-ordinate, with the six-co-ordinate Ba(2) having a 'possible seventh co-ordinating oxygen' at a distance of 3.426(23) Å. Our analysis identified a 'seventh' Ba(2)–O(6′) distance of 3.140(6) Å. We attribute this distance to a definite bonding interaction, albeit weak in nature. The presence of two formally μ,μ_3 tmhd ligands (type 5) in this structure results in a far more compact form of $[Ba_4(tmhd)_8]$ than has hitherto been observed and more importantly a rare observation of this type of β-diketonate co-ordination. It is to be noted that the $[Ba_4(tmhd)_8]$ species reported by Gleizes *et al.*[12] was obtained from $[Ba(tmhd)_2(MeOH)_3]$ by vacuum sublimation and crystallised in the orthorhombic space group *Pbca*, whilst that reported by Drozdov and Trojanov[11] was obtained from pentane and crystallised in the triclinic space group $P\bar{1}$ as in our case. The overall structure in the two crystalline modifications is basically the same, but both the above studies failed to establish the Ba(2)–O(6′) contact as a definite bonding interaction, and thus the exact μ,μ_3 bridging nature of two tmhd ligands was missed.

The fusing of two dimeric subunits of this type has been previously demonstrated in tungsten and molybdenum alkoxide chemistry by Chisholm *et al.*[19] The appearance of this Ba_4 aggregate with *no oxo or hydroxy ligands in the final product* again attests to the remarkably high purity of the ethanol-solvated barium ethoxide starting material and the synthetic strategy applied here.

Noticeably shorter Ba–O distances are observed in the partially chelating tmhd ligands with an average bond distance of 2.607(6) Å. In comparison, the bridging Ba–O distances [average 2.908(6) Å] are significantly longer than the 'chelating Ba–O' distances as is to be expected. The average value for all Ba–O distances in the molecule is 2.765(6), slightly longer than that found in the recently structurally characterised dimeric $[Ba_2(tmhd)_4L_2]$ (L = NH_3 or Et_2O) species (average of 2.73 Å).[4] This increase in average Ba–O bond length is accounted for by the observation of the tridentate co-ordination mode of the ligands in this molecule. Other workers have used sequestering agents such as crown ethers,[20] multidentate glymes[21] or β-diketonates with pendant groups,[22] to reduce the degree of oligomerisation.

Conclusion

Our volatility and thermal gravimetric analysis data indicate that these strontium and barium β-diketonates are thermally stable and volatilise readily into the gas phase, and compare well with recently characterised barium β-diketoiminate complexes.[22] Our observations support the assertion that the tmhd complexes of Sr and Ba are either trimers or tetramers in the solid state, solution and the gas phase. These materials have been shown in the solid state to exhibit a diverse range of co-ordination modes for the tmhd β-diketonate ligands attached to the metal centres. However, most importantly the exact nature of such complexes may not be derived unambiguously from conventional spectroscopic techniques, and also from the room-temperature X-ray data.

Given the complete characterisation of these materials, we are now evaluating their chemistry with a wide variety of possible Lewis bases. For example we have recently reported the monomeric complex [Sr(tmhd)$_2$L] [L = 2,5,8,11-tetraoxadodecane (triglyme)] and other related compounds.[23] In our current studies we are using suitable modifications of this and other strategies which we envisage will improve not only their thermal stability but more importantly air and moisture stability.

Experimental

General Procedures.—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 (using 'greaseless' J. Youngs joints/valves). All hydrocarbon solvents were rigorously predried, distilled 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.

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 4A 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 (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 ^{1}H spectra and the ^{13}C resonance of the solvent as a reference 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. Mass spectra were run on a Kratos MS30 instrument in electron-impact (EI) positive-ion mode at the Royal School of Pharmacy Mass Spectrometry Service, University of London.

Controlled thermal analysis of the complexes was investigated using a Polymer Laboratories 1500H simultaneous thermal analyser, controlled by a Omni Pro 486DX-33 personal computer connected to a Rioch 1200 laser printer. The mass 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 and 2,2,6,6-tetramethylheptane-3,5-dione were obtained from Aldrich Chemicals and dried over 4A molecular sieves prior to use. The metal ethoxides were prepared *via* a standard route.[13]

Table 3 X-Ray crystallographic data for complexes **1** and **2**[a]

	1	**2**
Formula	$C_{89}H_{154}O_{14}Sr_3$	$C_{88}H_{152}Ba_4O_{16}$
M	1711.05	2015.473
Crystal size/mm	0.30 × 0.20 × 0.18	0.40 × 0.35 × 0.25
a/Å	14.413(4)	14.969(3)
b/Å	14.658(5)	13.836(3)
c/Å	24.352(9)	14.822(3)
α/°	97.20(1)	62.47(2)
β/°	100.20(2)	65.98(1)
γ/°	109.82(2)	60.78(2)
U/Å^3	4666.8	2476.54
Z	2	1
D_c/g cm^{-3}	1.218	1.351
μ(Mo-Kα)/cm^{-1}	17.1	16.2
F(000)	1828	1032
Total reflections	15 627	9934
No. of unique reflections	13 177	6773
No. of observed reflections [$F_o > 3\sigma(F)$]	7473	5888
θ range/°	1.9–25.5	1.9–25.4
R^b	0.0538	0.0274
R'^c	0.0699	0.0340

[a] Details in common: clear blocks; triclinic; space group $P\bar{1}$; T 150 K; λ(Mo-Kα) 0.710 69 Å. [b] $R = \Sigma(\Delta F)/\Sigma(F_o)$. [c] $R' = \{\Sigma[w(\Delta F)^2]/\Sigma[w(F_o)^2]\}^{\frac{1}{2}}$.

Preparations.—[Sr$_3$(tmhd)$_6$(Htmhd)]·C_6H_5Me·C_5H_{12} **1**. To a solution of strontium ethoxide (6.0 g, 16.5 mmol) in toluene (25 cm^3) was added 2,2,6,6-tetramethylheptane-3,5-dione (6.93 cm^3, 33.15 mmol) and the resulting clear solution stirred for 1 h. This was then reduced to dryness *in vacuo* to yield a white paste which was kept at 70 °C for 2 h yielding a white solid. The solid was redissolved in pentane (10 cm^3) and left to stand at 0 °C overnight to crystallise as large colourless blocks. These were filtered off and the liquor reduced to half volume to obtain two further crops of crystals. Yield 5.84 g (78%), m.p. 172–176 °C, sublimes 180–210 °C (10^{-3} Torr). Consistent analyses were obtained on the sublimed solid (Found: C, 59.50; H, 8.50. Calc. for $C_{77}H_{134}O_{14}Sr_3$: C, 59.75; H, 8.65%). Infrared data: (Nujol) 1723m, 1591vs, 1578vs, 1561vs, 1537vs, 1504vs, 1417vs, 1359vs, 1274m, 1223s, 1185s, 1132s, 1082m, 1063m, 1027m, 954w, 933w, 867s, 802m, 792m, 755m, 729s, 695w, 596vw, 475m and 397vw; (hexachlorobutadiene) 2962vs, 2868s, 1725vw, 1505vs, 1452vs, 1417vs, 1390vs, 1359vs, 1275w, 1244m, 1224s, 1185s, 1132s, 1022w, 759w, 730m, 596vw, 477m and 389vw cm^{-1}. NMR: ^{1}H (C_6D_6, 270 MHz, 20 °C), δ 1.17 (br s, CH$_3$) and 5.79 (br s, CH); toluene and pentane peaks omitted; ^{13}C (C_6D_6, 67.94 MHz, 20 °C), δ 28.19 (br s, CH$_3$), 40.81 [s, *C*(CH$_3$)$_3$], 90.82 (br s, CH) and 201.07 (s, CO); ^{13}C (CP MAS, 75.468 MHz, 25 °C), δ 27.44, 28.13, 28.59, 29.08, 29.74, 30.06 (s, CH$_3$), 39.71, 40.43, 41.21, 41.61, 42.01, 42.43 [s, *C*(CH$_3$)$_3$], 89.43, 90.44, 91.09, 92.45, 92.97, 94.66 (s, CH), 197.01, 198.06, 201.03, 202.63, 203.82, 205.15 (s, C$\cdots$O) and 211.81 (s, C=O). Cryoscopy [benzene (5–34) × 10^{-3} mol dm^{-3}]: M_o = 1530 ± 60 (using sublimed solid). Mass spectroscopy (EI): *m*/*z* 725, [Sr$_2$L$_3$]$^+$, 40; 454, [SrL$_2$]$^+$, 10; 397, [SrL{(CH$_3$)$_3$COCHCO(H)}]$^+$, 50; and 271, [SrL]$^+$, 100%.

[Ba$_4$(tmhd)$_8$] **2**. To a solution of barium ethoxide (7.95 g, 19.32 mmol) in hexane (25 cm^3) was added 2,2,6,6-tetramethylheptane-3,5-dione (8.05 cm^3, 38.64 mmol) and the resulting clear solution stirred for 1 h. This was then reduced to dryness *in vacuo* to yield a white paste which was kept at 70 °C for 2 h yielding a white solid. The solid was redissolved in hexane (10 cm^3) and left to stand at 0 °C overnight to crystallise as large colourless blocks. These were filtered off and the liquor reduced to half volume to obtain a further crop of crystals. Yield 7.01 g (72%), m.p. 194–197 °C, decomp. > 305 °C, sublimes 190–210 °C (10^{-3} Torr) (Found: C, 52.70; H, 7.85. Calc. for $C_{88}H_{152}Ba_4O_{16}$: C, 52.45; H, 7.55%). Infrared data: (Nujol)

Table 4 Fractional atomic coordinates (× 10^4) for $[Sr_3(tmhd)_6(Htmhd)]\cdot C_6H_5Me\cdot C_5H_{12}$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sr(1)	2 497.4(6)	6 387.1(6)	3 356.6(4)	C(40)	−370(9)	3 237(9)	247(5)
Sr(2)	2 108.5(6)	4 203.2(6)	2 004.6(4)	C(41)	−848(9)	1 387(9)	3(5)
Sr(3)	4 354.0(6)	6 763.5(6)	2 492.2(4)	C(42)	1 930(10)	510(9)	1 821(6)
O(1)	2 775(5)	7 008(5)	4 390(3)	C(43)	22(10)	−173(8)	1 457(6)
O(2)	924(5)	6 309(5)	3 586(3)	C(44)	814(13)	859(9)	2 437(6)
O(3)	2 346(4)	6 087(4)	2 238(2)	C(45)	4 603(8)	9 658(7)	1 669(4)
O(4)	3 495(4)	5 504(4)	1 574(3)	C(46)	4 414(7)	9 003(7)	2 126(4)
O(5)	288(5)	3 924(5)	2 002(3)	C(47)	4 097(7)	9 359(7)	2 603(4)
O(6)	1 857(4)	4 560(4)	3 024(3)	C(48)	3 719(6)	8 835(7)	3 017(4)
O(7)	1 389(5)	3 359(4)	1 012(3)	C(49)	3 423(8)	9 384(7)	3 492(4)
O(8)	1 754(5)	2 442(4)	1 947(3)	C(50)	5 535(8)	9 598(9)	1 457(5)
O(9)	4 530(5)	8 192(5)	2 042(3)	C(51)	3 652(8)	9 189(8)	1 175(4)
O(10)	3 594(4)	7 932(4)	3 021(3)	C(52)	4 781(9)	10 748(7)	1 887(5)
O(11)	5 850(5)	6 566(5)	2 079(3)	C(53)	3 643(10)	10 482(7)	3 481(5)
O(12)	6 178(5)	7 979(5)	3 041(3)	C(54)	2 254(9)	8 874(9)	3 429(6)
O(13)	3 896(4)	4 892(4)	2 596(3)	C(55)	4 020(9)	9 311(8)	4 070(4)
O(14)	4 261(4)	6 442(4)	3 493(3)	C(56)	7 234(8)	6 909(9)	1 619(5)
C(1)	2 792(8)	7 449(8)	5 366(4)	C(57)	6 602(8)	7 197(8)	1 995(5)
C(2)	2 223(8)	7 037(7)	4 730(4)	C(58)	6 889(8)	8 284(7)	2 237(5)
C(3)	1 155(8)	6 730(7)	4 588(4)	C(59)	6 882(7)	8 496(7)	2 875(4)
C(4)	569(7)	6 374(7)	4 019(4)	C(60)	7 726(8)	9 400(8)	3 251(5)
C(5)	−594(7)	6 018(8)	3 892(4)	C(61)	7 247(10)	7 491(12)	1 122(5)
C(6)	3 537(9)	8 512(9)	5 419(5)	C(62)	6 738(12)	5 779(10)	1 373(6)
C(7)	3 357(11)	6 758(11)	5 526(5)	C(63)	8 326(9)	7 221(12)	1 970(6)
C(8)	2 060(10)	7 443(10)	5 773(4)	C(64)	7 485(11)	9 541(10)	3 841(5)
C(9)	−1 021(9)	5 966(10)	4 443(5)	C(65)	8 746(9)	9 217(11)	3 305(7)
C(10)	−907(9)	6 781(10)	3 601(6)	C(66)	7 792(12)	10 313(9)	2 996(6)
C(11)	−1 034(9)	4 988(10)	3 510(6)	C(67)	4 931(7)	3 919(7)	2 685(4)
C(12)	986(7)	6 496(6)	1 745(4)	C(68)	4 661(6)	4 800(6)	2 897(4)
C(13)	1 886(6)	6 186(6)	1 753(4)	C(69)	5 251(7)	5 462(7)	3 410(4)
C(14)	2 157(7)	6 010(7)	1 244(4)	C(70)	4 988(7)	6 188(7)	3 699(4)
C(15)	2 959(7)	5 700(6)	1 168(4)	C(71)	5 594(8)	6 714(7)	4 313(4)
C(16)	3 255(7)	5 608(8)	595(4)	C(72)	4 457(12)	3 074(9)	2 996(6)
C(17)	670(7)	6 482(8)	2 326(4)	C(73)	4 488(11)	3 548(11)	2 039(5)
C(18)	55(7)	5 794(7)	1 267(4)	C(74)	6 097(9)	4 207(11)	2 823(7)
C(19)	1 300(7)	7 582(6)	1 637(4)	C(75)	5 441(9)	7 697(8)	4 462(5)
C(20)	2 445(8)	5 599(9)	90(4)	C(76)	6 744(8)	6 913(10)	4 378(5)
C(21)	4 245(8)	6 537(8)	663(4)	C(77)	5 153(10)	6 002(9)	4 704(4)
C(22)	3 505(8)	4 670(8)	498(4)	C(78)*	4 690(17)	1 785(16)	371(9)
C(23)	−1 374(7)	2 931(7)	2 068(4)	C(79)*	4 165(14)	959(12)	0(7)
C(24)	−220(7)	3 445(7)	2 310(4)	C(80)*	3 129(19)	602(17)	−193(10)
C(25)	208(7)	3 316(7)	2 860(4)	C(81)*	2 604(16)	1 088(16)	106(9)
C(26)	1 189(7)	3 838(7)	3 168(4)	C(82)*	2 915(22)	1 758(21)	435(12)
C(27)	1 585(7)	3 623(7)	3 751(4)	C(83)*	4 407(19)	2 417(17)	642(10)
C(28)	−1 539(9)	2 016(10)	1 626(6)	C(84)*	3 744(36)	2 243(31)	626(17)
C(29)	−1 992(8)	2 631(9)	2 520(5)	C(85)*	5 931(33)	1 762(33)	383(18)
C(30)	−1 742(9)	3 679(10)	1 778(6)	C(86)*	5 877(19)	2 223(20)	566(11)
C(31)	1 954(10)	4 557(9)	4 214(4)	C(87)*	−714(25)	−770(24)	5 190(13)
C(32)	764(10)	2 768(10)	3 916(5)	C(88)*	−178(16)	−885(14)	5 019(8)
C(33)	2 520(9)	3 328(9)	3 700(5)	C(89)*	−1 303(21)	−408(22)	5 389(11)
C(34)	54(8)	2 404(8)	212(4)	C(90)*	−527(28)	875(24)	5 233(14)
C(35)	712(8)	2 496(7)	804(4)	C(91)*	−458(26)	−12(30)	5 133(15)
C(36)	573(7)	1 676(7)	1 056(4)	C(92)*	−1 147(36)	438(37)	5 375(18)
C(37)	1 119(7)	1 688(6)	1 606(4)	C(93)*	5 563(28)	2 717(27)	744(15)
C(38)	949(8)	696(7)	1 818(5)	C(94)*	3 809(38)	1 689(35)	407(19)
C(39)	732(9)	2 500(8)	−222(4)	C(95)*	5 060(46)	1 143(40)	130(23)

* Atom belongs to the disordered solvent molecules, C_6H_5Me or C_5H_{12}. All these atoms were refined isotropically with fixed partial occupancies: C(78) 0.69, C(79) 0.88, C(80) 0.69, C(81) 0.77, C(82) 0.66, C(83) 0.71, C(84) 0.51, C(85) 0.46, C(86) 0.63, C(87) 0.58, C(88) 0.78, C(89) 0.70, C(90) 0.56, C(91) 0.51, C(92) 0.52, C(93) 0.49, C(94) 0.43, C(95) 0.43, which total 12.

1589s, 1575s, 1561s, 1502s, 1412vs, 1355vs, 1271m, 1243m, 1223m, 1199m, 1178m, 1128m, 1019m, 953w, 931w, 864m, 820w, 799m, 791m, 779w, 756w, 733m, 592w, 472m and 390vw; (hexachlorobutadiene) 2958s, 2907m, 2868m, 1588s, 1504s, 1452s, 1412vs, 1388s, 1356s, 1273w, 1243m, 1223m, 1174s, 1129m, 1019w, 735w, 593w, 559w, 476m and 390w cm^{-1}. NMR: ^{1}H (C_6D_6, 270 MHz, 20 °C), δ 1.19 (s, CH_3) and 5.86 (s, CH); ^{13}C (C_6D_6, 67.94 MHz, 20 °C), δ 28.55 (CH_3), 41.01 [s, *C*$(CH_3)_3$], 91.32 (CH) and 200.21 (s, CO); ^{13}C (CP MAS, 75.468 MHz, 25 °C), δ 22.02, 29.98, 30.92 (s, CH_3), 41.21, 42.06, 42.87 [s, *C*$(CH_3)_3$], 89.74, 92.88, 94.06 (s, CH), 195.75, 196.37, 199.31, 200.78, 202.23 and 203.76 (s, C$\cdots$O). Mass spectroscopy (EI): *m*/*z* 827, $[Ba_2L_3]^+$, 100; 504, $[BaL_2]^+$, 5; 447 $[BaL\{(CH_3)_3COCHCO(H)\}]^+$, 5; and 321, $[BaL]^+$, 85%. Cryoscopy [benzene (4–39) × 10^{-3} mol dm^{-3}]: M_o = 1980 ± 85.

X-Ray Crystallography.—Single crystals of complexes **1** and **2** were obtained as outlined in the Experimental section. They were suspended in silicon oil and subsequently mounted onto the goniostat in a nitrogen stream at 150 K. Cell dimensions and slightly more than one hemisphere of intensity data were recorded using a FAST TV area-detector

Table 5 Fractional atomic coordinates (× 10^4) for $[Ba_4(tmhd)_8]$

Atom	*x*	*y*	*z*
Ba(1)	2036.1(2)	3582.1(2)	1454.3(2)
Ba(2)	−985.2(2)	4299.9(2)	1259.5(2)
O(1)	3764(3)	2053(3)	1967(3)
O(2)	2763(3)	4014(3)	2457(3)
C(1)	5173(4)	623(4)	2748(4)
C(2)	4330(4)	1798(4)	2555(4)
C(3)	4220(4)	2479(4)	3024(4)
C(4)	3459(4)	3525(4)	2972(4)
C(5)	3444(4)	4148(4)	3577(4)
C(6)	5849(4)	461(4)	1695(4)
C(7)	4575(5)	−161(4)	3318(5)
C(8)	5897(4)	330(4)	3419(4)
C(9)	3585(4)	3393(5)	4692(4)
C(10)	4344(5)	4568(5)	2969(5)
C(11)	2394(5)	5113(5)	3666(5)
O(3)	2542(3)	3808(3)	−659(3)
O(4)	992(2)	3002(3)	696(3)
C(12)	4262(4)	2609(4)	−1211(4)
C(13)	3116(4)	2812(4)	−584(4)
C(14)	2739(4)	1965(4)	44(4)
C(15)	1689(4)	2092(4)	609(4)
C(16)	1389(4)	1072(4)	1218(4)
C(17)	4723(4)	3057(5)	−827(5)
C(18)	4940(4)	1409(4)	−1089(4)
C(19)	4272(4)	3263(5)	−2385(4)
C(20)	195(5)	1419(5)	1553(6)
C(21)	1815(5)	473(5)	2197(5)
C(22)	1848(6)	311(6)	590(5)
O(5)	2031(3)	5591(3)	−99(3)
O(6)	118(2)	5373(2)	1143(2)
C(23)	2542(4)	6849(4)	−48(4)
C(24)	1778(4)	6274(4)	337(4)
C(25)	844(4)	6480(4)	1123(4)
C(26)	88(4)	6021(4)	1512(4)
C(27)	−812(4)	6279(4)	2458(4)
C(28)	3621(5)	5961(5)	85(6)
C(29)	2245(6)	7604(6)	546(6)
C(30)	2611(6)	7470(6)	−1222(5)
C(31)	−1595(4)	5750(5)	2753(4)
C(32)	−304(4)	5772(5)	3381(4)
C(33)	−1397(5)	7515(5)	2221(5)
O(7)	−1928(3)	3415(3)	3015(3)
O(8)	231(2)	3050(3)	2957(3)
C(34)	−2966(4)	2720(4)	4669(4)
C(35)	−1930(4)	2893(4)	3974(4)
C(36)	−1089(4)	2486(4)	4407(4)
C(37)	−83(4)	2543(4)	3916(4)
C(38)	665(4)	1975(4)	4666(4)
C(39)	−3827(4)	3845(4)	4651(4)
C(40)	−2925(4)	2000(5)	5806(4)
C(41)	−3215(4)	2166(4)	4189(4)
C(42)	815(5)	768(5)	5180(5)
C(43)	175(5)	2510(5)	5520(5)
C(44)	1741(5)	2041(7)	4078(5)

diffractometer following previously described procedures.[24] An absorption correction was made using DIFABS[25] (adapted by A. Karaulov, University of Wales (Cardiff). A summary of the crystal data, data collection and refinement parameters is given in Table 3. The structures of **1** and **2** were solved by Patterson methods (SHELX 86)[26] and refined by full-matrix least squares (SHELX 80),[27] using anisotropic thermal parameters for non-hydrogen atoms. The H atoms in **1** were ignored; those in **2**, all located from difference maps, were not refined but included in F_c calculations with an assumed U_{iso} of 0.05 Å^2. Compound **1** contained one molecule of toluene and one molecule of pentane, both disordered in the lattice; a total of 18 positions with fixed partial occupancies were refined for the total of 12 carbons, each fractional atom being assigned an individual isotropic thermal parameter.

All calculations were made on a T800 transputer hosted by an IBM/AT personal computer. The fractional coordinates of the non-hydrogen atoms are given in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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