DALTON

Monomeric Group 2 metal β-diketonates stabilised by protonated amine ligands as tight cation–anion pairs; crystal structure of $[Htmen]_2[Sr(tfpd)_4]$ (tfpd = 1,1,1-trifluoropentane-2,4-dionate, tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)

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The *in situ* reactions of the tetraethanol-solvated alkaline-earth metal ethoxides $[\{M(OEt)_2(EtOH)_4\}_n]$ (M = Ca, Sr or Ba) with selected β-diketones and multidentate amines, resulted in the formation of tight cation–anion pairs, $[H(L-L)]_2[M(\beta\text{-diket})_4]$ [β-diket = 1,1,1-trifluoropentane-2,4-dionate (tfpd) or 1,1,1,5,5,5-hexafluoropentane-2,4-dionate (hfpd); L−L = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen) or *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (pmdien)] in relatively low yields. The products have been characterised by microanalysis, IR, ^1H and ^{13}C NMR and mass spectrometry. The complex $[Htmen]_2[Sr(tfpd)_4]$ has been further characterised by X-ray crystallography. The structure contains a monomeric eight-co-ordinate $[Sr(tfpd)_4]^{2-}$ dianion in which the four chelating tfpd ligands are in a square-prismatic arrangement, while the protonated tmen ligands are strongly hydrogen bonded to the tfpd chelates. The Sr−O distances lie in the range 2.530(2)–2.593(2) Å, average 2.571 Å.

The use of metal alkoxides or β-diketonates as metal organic chemical vapour deposition (MOCVD) precursors for metal oxide superconductors *via* a low-temperature deposition route is an area of intense current interest. Their potential application in the field of electroceramics, *e.g.* $BaTiO_3$, $K_{0.4}Ba_{0.6}BiO_3$ and $BaMg_{0.33}Ta_{0.6}O_3$, is of great prominence.[1] In the course of research into alkaline-earth-metal chemistry, we and others have been confronted with a number of complications using the bulk metals as starting materials to a range of metal alkoxides or aryl oxides.[2] Difficulties encountered include contamination of the metal surfaces by either oxide or hydroxide groups, which has resulted in either oxo- or hydroxy-groups embodied in the product. For example, Bradley *et al.*[3] isolated the hydrated metal species $[\{M(hfpd)_2(H_2O)_2\}_n]$ (Hhfpd = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) from calcium or barium hydroxide sources. A further constraint has been the passivation of the metal surface, which has led to poor reproducibility of reactions. Similarly, the solubility of such materials has proven to be modest, due mainly to the fact that they are generally polymeric in nature, involatile and insoluble in most organic solvents.

Metal alkoxides and β-diketonates have been used as precursors for a large number of metal oxide materials because of their beneficial properties and inherent advantages over traditional ceramic routes to these materials.[4] These compounds are readily accessible as crystalline solids of known stoichiometry, soluble in hydrocarbon solvents (aliphatic or aromatic), stable in an inert atmosphere and are sufficiently reactive that most reactions occur at or slightly above room temperature.

In the course of our research directed towards volatile single-source CVD precursors we have used the metal ethoxides, $[\{M(OEt)_2(EtOH)_4\}_n]$ (M = Ca, Sr or Ba), as soluble sources of these metals.[5,6] We have observed a facile reaction between these metal ethoxides and a range of β-diketones in hexane or chloroform at room temperature, analogous to the previous work on transition-metal-based complexes.[6,7] Given the high-co-ordination numbers generally observed for these complexes, we have also attempted to inhibit the formation of oligomers by the use of multidentate chelating glyme or amine ligands (Scheme 1).[8]

$$[\{Ca(OEt)_2(EtOH)_4\}_n] + 2\ Hdppd + pmdien \xrightarrow{(i),\ (ii)} [Ca(dppd)_2(pmdien)] + 6\ EtOH$$

Scheme 1 Hdppd = 1,3-Diphenylpropane-1,3-dione, pmdien = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine. (*i*) CH_2Cl_2; (*ii*) C_6H_5Me, heat

In the above reactions involving metal β-diketonates there are very few examples in which the multidentate ligands are not co-ordinated directly to the metal centres. We report here what we believe to be a general synthetic route to complexes of the type $[H(L-L)]_2[M(\beta\text{-diket})_4]$, and the crystal structure of $[Htmen]_2[Sr(tfpd)_4]$ (tmen = $Me_2NCH_2CH_2NMe_2$). There is strong evidence to suggest that the protonated amine cations observed in these complexes are obtained as a result of proton transfer from free ethanol to the amines in solution.

Results and Discussion

Syntheses

A notable feature of the Group 2 metals is their strong Lewis acidity, which ensures that in the absence of Lewis-base solvents they generally form polymeric insoluble materials. On the addition of Lewis-base solvents to Group 2 organometallics the polymeric ensembles are cleaved to yield simpler molecular species.[8] A wide variety of molecular geometries is available, provided that judicious choice of hydrocarbyl ligands (or other organic substrates) and/or Lewis bases is used to achieve co-ordinative saturation of the large M^{2+} cations, to reduce potential polymerisation processes. For such a strategy a precedent is indeed available, with prior use of macrocyclic ligands, *e.g.* crown ethers and cryptands.[9–11] We consider that the formally unsaturated Group 2 metal β-diketonate complexes may show a reactivity pattern similar to that of the pentamethylcyclopenta-

$$[\{M(OEt)_2(EtOH)_4\}_n] + H(\beta\text{-diket}) \longrightarrow [\{M(\beta\text{-diket})_2\}_n] + 6\ EtOH$$

Scheme 2 H(β-diket) = Hpd (pentane-2,4-dione), Hdppd, Htfpd (1,1,1-trifluoropentane-2,4-dione), Hhfpd or Htmhd

dienyl complexes, *e.g.* with ethers, phosphines, halides, nitriles, *etc.*[12]

The reaction of the metal ethoxides $[\{M(OEt)_2(EtOH)_4\}_n]$ (M = Ca, Sr or Ba), formed from the pure metal in an excess of ethanol *via* the prewash method,[5] with for example 2,2,6,6-tetramethylheptane-3,5-dione (Htmhd) in hexane at room temperature has been previously shown to give the homoleptic complexes, according to Scheme 2.[5,6] These materials have, however, proven to be sensitive to the atmosphere and to the presence of external Lewis bases (*e.g.* H_2O and NH_3). We have undertaken to eliminate these problems. In order to achieve saturation of the cationic metal centre prior knowledge suggests that we need high co-ordination numbers. The *in situ* reaction of the preformed metal β-diketonates (Scheme 2) with O-donor ligands has been found to yield air-stable monomeric complexes of the form $[M(\beta\text{-diket})_2(n\text{-glyme})]$.[13,14] An obvious extension of these findings is the replacement of O- with N-donor Lewis basis [*e.g.* tmen, pmdien and hmteta (*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexamethyltriethylenetetramine)]. Under the same conditions, *in situ* prepared ‘$[\{Sr(tfpd)_2\}_n]$’ reacts in an exothermic manner on addition of tmen to form $[Htmen]_2[Sr(tfpd)_4]$ **1**. Similar reactions occur between *in situ* prepared ‘$[\{Sr(tfpd)_2\}_n]$’ and pmdien to form $[Hpmdien]_2[Sr(tfpd)_4]$ **2**, and the reaction of the metal hexafluoropentanedionates ‘$[\{M(hfpd)_2\}_n]$’ with pmdien results in the formation of similar complexes, $[Hpmdien]_2[M(hfpd)_4]$ (M = Ca **3**, Sr **4** or Ba **5**) [equation (1)]. These

$$2(‘[\{M(\beta\text{-diket})_2\}_n]’ + EtOH + L{-}L) \longrightarrow ‘[\{M(OEt)_2\}_n]’ + [H(L{-}L)]_2[M(\beta\text{-diket})_4] \quad (1)$$

exothermic reactions and proton migration (presumably from the liberated ethanol ligands *in situ*) are not unique, but appear to be confined to the smaller amines (tmen and pmdien) and reactions for fluorinated β-diketonates, *i.e* tfpd and hfpd. When other amines such as hmteta are used with more rigorous work-ups prior to the addition of the amine then proton migration is not observed.[15] This strongly suggests that in the absence of the proton donor (ethanol in solution) the reaction is unable to proceed in this manner.

A 4:1 ratio of β-diketonate ligand:metal is observed in the products, despite a ratio of only 2:1 being employed for the reagents. Also, the low yields observed for all these complexes suggest that, following proton migration from ethanol ligands to the amines, a significant amount of metal ethoxide is reformed and remains in solution as a by-product of the reactions [equation (1)]. However, when a 2:1 molar ratio of β-diketone:amine is used, yields of up to *ca.* 80% are obtained.[8]

Physical properties

All of these compounds have good solubility in an extensive range of organic solvents especially in co-ordinating solvents such as ethers [tetrahydrofuran (thf) and diethyl ether]. This pronounced solubility even in aromatic hydrocarbon solvents (*i.e.* toluene) is most likely to be due to the co-ordinative saturation of the metal centres. It ensures that the metal is surrounded by an organic sheath, giving excellent solubility. A further important observation (especially if these materials are to have industrial applications) is their stability to both air and moisture, which suggests that water co-ordination is unlikely to occur.

All the compounds show a significant drop in their melting points upon complexation of the amine ligand. Complex **1** melts between 86 and 88 °C and may be contrasted with the starting compound $[\{Sr(tfpd)_2\}_n]$ which decomposes over the range 227–230 °C. Complex **2** also melts at a considerably lower temperature than that of the starting homoleptic compound, in the range 98–102 °C. The three hfpd-based compounds **3**–**5** also have relatively low melting points, *e.g.* $[Hpmdeta]_2[Ba(hfpd)_4]$ melts in the range 53–56 °C.

Table 1 Proton NMR chemical shifts (δ) for complexes **1**–**5** in $(CD_3)_2SO$

Compound	CH_3	NMe	NMe_2	CH_2	CH	NH
1	1.89	—	2.10	2.25 (m)	5.69	10.91 (br)
2	1.85	1.87	2.08	2.26 (m), 2.28	5.68	11.31 (br)
3	—	1.75	1.95	1.99 (m), 2.07	6.23	9.86 (br)
4	—	2.09	2.23	2.43 (m), 2.47	5.19	9.89 (br)
5	—	2.62	2.77	2.91 (m), 3.32	5.78	9.74 (br)

br = Broad, m = multiplet.

Infrared spectra

The complexes **1**–**5** were studied as both Nujol and hexachlorobutadiene mulls between KBr windows. The IR bands are assigned on the basis of data for the previously characterised hydrated and anhydrous β-diketonates.[16–18] In the region 1640–1500 cm^{-1} bands at 1638 and 1541 cm^{-1} are assigned to the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ stretching modes and those at 1513 and 1496 cm^{-1} to the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ stretches for compound **1**. Similar frequencies are observed for all other compounds. These results may be compared with the IR spectra of base-free homoleptic compounds $[\{M(\beta\text{-diket})_2\}_\infty]$ where several bands are observed due to the different co-ordination geometries of the β-diketonate ligands.[6] Precise assignment of $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ modes is not possible as they are undoubtedly coupled. The main difference from the IR spectra of the homoleptic compounds is the presence of an N–H stretch in the hexachlorobutadiene spectra of complexes **1**–**5**, observed at *ca.* 3324 cm^{-1} for **1**, as expected. No obvious differences occur on alternating between ligands or metals.

Nuclear magnetic resonance spectra

The ^1H and ^{13}C NMR data are in accord with the structures described herein (Tables 1 and 2 respectively). In the ^1H NMR spectra it is noted that there is no ethanol present from the metal ethoxide starting materials. The spectrum for compound **1** reveals a single characteristic methyl peak of the β-diketonate at δ 1.89, suggesting only one environment for the ligand in solution (this is also supported by the infrared data). For **2** this peak shifts only slightly to δ 1.85 with the change in Lewis base to the larger amine. The methyl and methylene signals for the amine ligands in **1** are observed at δ 2.10 (δ 1.87 and 2.08 for **2**) and 2.25 (2.26 and 2.28 for **2**) respectively. The CH peak of the tfpd lies at δ 5.69 (5.68 for **2**). A low-field peak is also observed at δ 10.91 (11.31 for **2**) which is assigned to the NH hydrogen of the protonated amine ligands (Table 1).

The ^{13}C NMR spectra for compounds **1** and **2** show a tfpd methyl peak at δ 28.8 and 28.5 respectively. An *N*-methyl peak for the amine ligands is also observed at δ 43.9 for **1** (δ 41.4 and 43.5 for **2**) (Table 2). Methylene and methyne peaks for the amine and tfpd ligands respectively are observed at δ 54.5 and 94.1 for **1** and 52.4, 55.3 and 93.8 for **2**. Two quartets due to the splitting by ^{19}F are observed, the first at δ 123.5 ($^1J = 300$ Hz) [δ 119.7 ($^1J = 305$ Hz) for **2**] is due to the CF_3 carbon, and the second at δ 169.1 ($^2J = 29$ Hz) [176.8 ($^2J = 30$ Hz) for **2**] to the adjacent carbonyl carbon. The second carbonyl signal is observed at lower field, as expected (δ 196.5 and 194.0 for **1** and **2** respectively) due to the increased electron density in the $M{-}O{-}C_3{-}O$ ring.

The ^1H NMR spectra of the hfpd compounds **3**–**5** show the expected NMe peak at δ 1.75 (**3**), 2.09 (**4**) and 2.62 (**5**), and the NMe_2 peak of the amine ligand at δ 1.95 (**3**), 2.23 (**4**) and 2.77

Table 2 Carbon-13 NMR chemical shifts (δ, *J*/Hz) for complexes **1**–**5** in $(CD_3)_2SO$

Compound	CH_3	NMe	NMe_2	CH_2	CH	CF_3	CO
1	28.79	—	43.90	54.45	94.11	123.50 (q, $^1J = 300$)	169.05 (q, $^2J = 29$), 196.54
2	28.50	41.36	43.54	52.41, 55.29	93.82	119.70 (q, $^1J = 305$)	176.80 (q, $^2J = 30$), 193.98
3	—	43.17	45.24	54.95, 56.72	88.82	126.70 (q, $^1J = 301$)	176.80 (q, $^2J = 33$)
4	—	42.68	44.48	52.60, 52.93	84.19	118.45 (q, $^1J = 302$)	172.49 (q, $^2J = 31$)
5	—	42.86	44.65	52.81, 56.10	94.10	118.15 (q, $^1J = 293$)	172.41 (q, $^2J = 29$)

Table 3 Bond lengths (Å) and angles (°) involving non-H atoms for $[Htmen]_2[Sr(tfpd)_4]$ **1**

Sr–O(1)	2.577(2)	Sr–O(2)	2.583(2)	N(1)–C(11)	1.468(4)	N(2)–C(15)	1.484(4)
Sr–O(3)	2.530(2)	Sr–O(4)	2.593(2)	N(2)–C(16)	1.486(4)	N(2)–C(14)	1.495(4)
F(1)–C(1)	1.320(4)	F(2)–C(1)	1.329(4)	C(1)–C(2)	1.541(4)	C(2)–C(3)	1.397(4)
F(3)–C(1)	1.318(4)	F(4)–C(6)	1.338(4)	C(3)–C(4)	1.407(4)	C(4)–C(5)	1.501(4)
F(5)–C(6)	1.326(4)	F(6)–C(6)	1.331(4)	C(6)–C(7)	1.538(4)	C(7)–C(8)	1.383(4)
O(1)–C(2)	1.237(3)	O(2)–C(4)	1.266(3)	C(8)–C(9)	1.421(5)	C(9)–C(10)	1.502(4)
O(3)–C(9)	1.243(3)	O(4)–C(7)	1.257(3)	C(13)–C(14)	1.513(5)		
N(1)–C(12)	1.452(5)	N(1)–C(13)	1.462(5)				
O(3)–Sr–O(3′)*	90.37(9)	O(3)–Sr–O(1′)	152.15(6)	F(1)–C(1)–F(2)	105.4(3)	F(3)–C(1)–C(2)	114.9(3)
O(3)–Sr–O(1)	76.75(6)	O(1′)–Sr–O(1)	124.62(8)	F(1)–C(1)–C(2)	110.9(3)	F(2)–C(1)–C(2)	111.8(3)
O(3′)–Sr–O(2)	109.20(6)	O(3)–Sr–O(2)	136.35(7)	O(1)–C(2)–C(3)	130.5(3)	O(1)–C(2)–C(1)	113.3(3)
O(1′)–Sr–O(2)	71.49(6)	O(1)–Sr–O(2)	67.89(6)	C(3)–C(2)–C(1)	116.1(2)	C(2)–C(3)–C(4)	124.0(3)
O(2)–Sr–O(2′)	83.42(8)	O(3)–Sr–O(4′)	70.14(7)	O(2)–C(4)–C(3)	124.1(2)	O(2)–C(4)–C(5)	118.4(2)
O(1)–Sr–O(4′)	127.26(6)	O(2)–Sr–O(4′)	153.12(6)	C(3)–C(4)–C(5)	117.6(3)	F(5)–C(6)–F(6)	106.4(3)
O(3)–Sr–O(4)	68.25(7)	O(1)–Sr–O(4)	82.11(6)	F(5)–C(6)–F(4)	107.2(3)	F(6)–C(6)–F(4)	106.3(3)
O(2)–Sr–O(4)	81.97(7)	O(4′)–Sr–O(4)	119.49(9)	F(5)–C(6)–C(7)	111.6(3)	F(6)–C(6)–C(7)	110.7(2)
C(2)–O(1)–Sr	126.5(2)	C(4)–O(2)–Sr	128.8(2)	F(4)–C(6)–C(7)	114.2(3)	O(4)–C(7)–C(8)	130.0(3)
C(9)–O(3)–Sr	133.4(2)	C(7)–O(4)–Sr	127.9(2)	O(4)–C(7)–C(6)	112.0(3)	C(8)–C(7)–C(6)	118.0(3)
C(12)–N(1)–C(13)	110.4(3)	C(12)–N(1)–C(11)	109.7(3)	C(7)–C(8)–C(9)	124.4(3)	O(3)–C(9)–C(8)	123.7(3)
C(13)–N(1)–C(11)	111.0(3)	C(15)–N(2)–C(16)	111.6(3)	O(3)–C(9)–C(10)	117.7(3)	C(8)–C(9)–C(10)	118.6(3)
C(15)–N(2)–C(14)	110.9(3)	C(16)–N(2)–C(14)	112.7(3)	N(1)–C(13)–C(14)	111.1(3)	N(2)–C(14)–C(13)	113.4(3)
F(3)–C(1)–F(1)	106.7(3)	F(3)–C(1)–F(2)	106.5(3)				

* The primed atoms belong to one and the same complex anion and are generated by the symmetry operation $\frac{1}{2} - x, \frac{1}{2} - y, z$.

(**5**). The two methylene peaks of the amine ligand follow a similar pattern, with peaks observed at δ 1.99 and 2.07 (**3**), 2.43 and 2.47 (**4**), and 2.91 and 3.32 (**5**). The NH hydrogen of the protonated pmden ligand is once again observed at very high field for these complexes at δ 9.86 (**3**), 9.89 (**4**) and 9.74 (**5**). The methyne signals for the hfpd ligands do not follow any particular pattern and are observed as single peaks at δ 6.23 (**3**), 5.19 (**4**) and 5.78 (**5**).

The ^{13}C NMR spectra for complexes **3**–**5** reveal an NMe peak at δ 43.2 (**3**), 42.7 (**4**) and 42.9 (**5**), while NMe_2 peaks are seen at δ 45.2 (**3**), 44.5 (**4**) and 44.7 (**5**). The CH_2 signals for the amine are observed at δ 55.0 and 56.7 (**3**), 52.6 and 52.9 (**4**), and 52.8 and 56.1 (**5**). The CH peak of the hfpd ligand is observed at δ 88.8 (**3**), 84.2 (**4**) and 94.1 (**5**). Once again a CF_3 quartet is observed in the region δ 118.2–126.7 with a ^1J coupling of about 300 Hz, and the corresponding CO quartet in the region δ 172.4–176.8. The two carbonyl carbons in the hfpd ligand are equivalent in solution, therefore only one CO peak is observed (Table 2).

Mass spectrometry

The positive-ion mass spectra of compounds **1**–**5** show a wide range of fragments. Compound **1** shows distinct $[ML_5 - CF_2]$ and $[ML_4]^{2-}$ ions which are not observed for any of the other compounds. The frequently observed $[M_2L_3]^+$ fragment is observed for all five complexes, as are fragments involving the various breakdowns of the tfpd and hfpd ligands in conjunction with the metal. It is immediately noticeable that for all the complexes except **5** the amine ligand is not observed to be attached to the metal centre in the mass spectrometric data. In contrast the barium complex **5** shows the pmdien ligand is co-ordinated in a number of cases, *e.g.* *m/z* 518, [Ba(hfpd)(pmdien)]$^+$; a breakdown of the pmdien ligand is also seen to occur in the form of an Me_2NH fragment, *e.g.* *m/z* 389, $[Ba(hfpd)(Me_2NH)]^+$. To elucidate the unambiguous identity of one of these complexes a single-crystal-X-ray study of **1** was made.

Crystal structure of $[Htmen]_2[Sr(tfpd)_4]$ 1

The X-ray determination showed that complex **1** consists of monomeric $[Sr(tfpd)_4]^{2-}$ anions and $[Htmen]^+$ cations (in the ratio 1:2) held together by hydrogen bonds and van der Waals forces. The stoichiometry thus determined is in good agreement with the spectroscopic data. The complex anion (Fig. 1) contains an eight-co-ordinate strontium atom sited on a crystallographic two-fold axis of symmetry and bonded to four tfpd ligands which are all chelating. The co-ordination polyhedron may be described as a distorted square prism.

The Sr–O (tfpd) bond lengths (Table 3) are in the range 2.530(2)–2.593(2) Å, average 2.571 Å. These distances are somewhat larger than those in other strontium complexes involving chelating β-diketonates, *e.g.* 2.399(9)–2.619(9) Å, average 2.498(9) Å, in $[Sr_3(tmhd)_6(Htmhd)]$,[6] 2.468(1)–2.519(1) Å, average 2.495(1) Å in $[Sr(tmhd)_2(triglyme)]$ [triglyme = $CH_3O(CH_2CH_2O)_3CH_3$],[13] 2.459(6)–2.520(7) Å, average 2.487(7) Å, in $[Sr_2(tmhd)_4(diglyme)_2(H_2O)]$[13] [diglyme = $CH_3O(CH_2CH_2O)_2CH_3$] and 2.500(6)–2.564(6) Å, average 2.540(6) Å, in $[Sr(dppd)_2(tetraglyme)]$ [tetraglyme = $CH_3O(CH_2CH_2O)_4CH_3$],[16] but smaller, as expected, than the Sr–O distances involving the glyme or bridging oxygens of the β-diketonate ligands in the above compounds. In fact the Sr–O distances in this type of compound show large variations which may result from a variety of factors including co-ordination number of the metal centre, modes of bonding of the ligands and steric interactions.

The bond lengths and angles involving the tfpd ligands and Htmen moieties are in Table 3 and found to be very close to the expected values. However, one of the two unique tfpd ligands is chelated symmetrically to the metal [Sr–O(1) 2.577(2), Sr–O(2) 2.583(2) Å] whilst the other is quite asymmetric [Sr–O(3) 2.530(2), Sr–O(4) 2.593(2) Å]. The β-diketonate moieties are

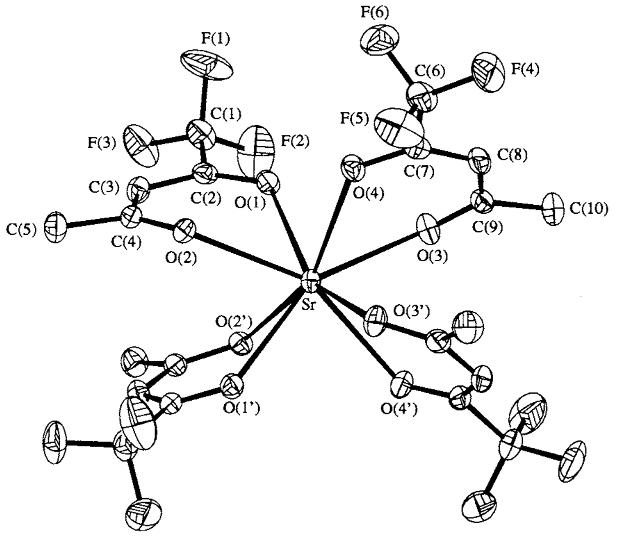

Fig. 1 Structure of the $[Sr(tfpd)_4]^{2-}$ dianion in complex **1**, showing the atom numbering scheme; H atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level

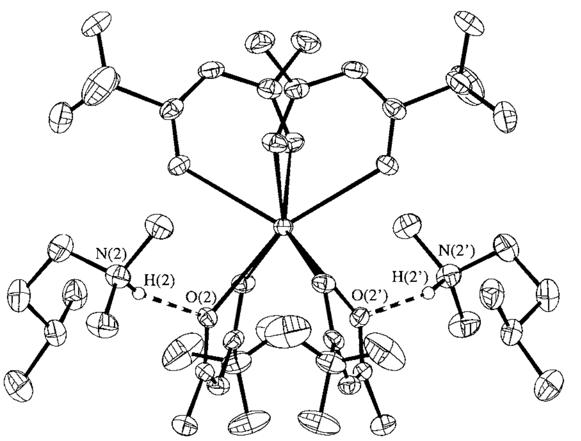

Fig. 2 Hydrogen-bonded interactions between the $[Sr(tfpd)_4]^{2-}$ dianion and $[Htmen]^+$ cations in complex **1**

folded about the O ··· O axis by 31.7(3) and 25.4(3)°, which are rather large, and probably result from interligand steric interactions.

One of the most interesting features of complex **1** is the observation that the diamine ligands do not bind directly to the metal as might have been expected. Instead, the protonated nitrogen, N(2), on the cationic amine ligand comes into close contact with one of the tfpd oxygens, O(2), and forms a strong N(2)–H(2) ··· O(2) hydrogen bond [N(2) ··· O(2) 2.745(5), N(2) ··· H(2) 0.88(4), H(2) ··· O(2) 1.90(2) Å, N(2)–H(2)–O(2) 159(1)°]. These hydrogen-bonded interactions between the $[Sr(tfpd)_4]^{2-}$ anion and two protonated tmen cations are shown clearly in Fig. 2. A similar phenomenon has recently been observed in the barium chelate $[H_2en]_{1.5}[Ba(hfpd)_5]\cdot EtOH$ (en = ethane-1,2-diamine), where the protonated en molecules in the lattice are weakly hydrogen bonded to the chelate anions.[17]

Clearly the central $[Sr(tfpd)_4]^{2-}$ moiety has the β-diketonate ligands wrapped around in the observed orientation because this allows not only the hydrogen bonding between the tfpd ligand and protonated tmen, but also the diamine nitrogens can orientate the methyl groups in a way that results in several weak Me ··· F interactions [C(5) ··· F(1) 3.342(5), C(16) ··· F(1) 3.499(5) and C(10) ··· F(3) 3.491(5) Å]. It is suggested that this situation which results in what may be described as a tight cation–anion pair alleviates the excess of negative charge on the strontium atom. In addition, this mode of bonding of the protonated amine to the carbonyl group of a tfpd ligand appears to be an unusual example of hydrogen bonding giving rise to an interesting structural motif.

Conclusion

Our strategy uses hydrocarbon-soluble metal ethoxides which are readily prepared from the bulk metal. These materials have the advantage that they yield reproducible oxo-, hydroxy- and water-free products, providing that rigorous anaerobic techniques are employed. This factor is important in that we may now control more precisely the stoichiometry which has previously been difficult. Synthetic design of this type of precursor will no doubt be invaluable and not only in the field of metal–oxygen based chemistry where Group 2 metals are currently being used for control of thin-film preparation by CVD due to their high stability.

Experimental

General procedures

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

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 1720 FT-IR spectrometer as either Nujol or hexachlorobutadiene mulls, in the region 4000–400 cm^{-1}, NMR solution spectra on a JEOL GS 270 MHz spectrometer, ^1H at 270.16 MHz (at 25 °C) and $^{13}C-\{^1H\}$ spectra at 67.94 MHz. Chemical shifts were referenced to the protio impurities of the deuteriated solvent $[(CD_3)_2SO]$. Elemental analyses were performed by Imperial College, and all compounds were handled in an inert atmosphere. Mass spectroscopic data were obtained on a Kratos MS30 instrument by the Royal School of Pharmacy Mass Spectrometry Service, University of London. The melting points recorded are uncorrected values.

Starting materials

1,1,1,5,5,5-Hexafluoropentane-2,4-dione (Hhfpd) and 1,1,1-trifluoropentane-2,4-dione (Htfpd) were obtained from Inorgtech of Mildenhall, Suffolk, UK. The metal ethoxides $[\{M(OEt)_2(EtOH)_4\}_n]$ were prepared according to published procedures.[5] The compounds tmen and pmdien were obtained from Aldrich and stored over 4 Å molecular sieves.

Preparations

$[Htmen]_2[Sr(tfpd)_4]$ 1. The compound $[\{Sr(OEt)_2(EtOH)_4\}_n]$ (1.92 g, 5.71 mmol) was weighed into a Schlenk tube and hexane (25.0 cm^3) added. To the resulting clear solution was added Htfpd (1.40 cm^3, 11.42 mmol) and the reaction left to stir for 5 min. Then, tmen (1.72 cm^3, 11.42 mmol) was slowly added, whereupon a highly exothermic reaction occurred and a large amount of gas was liberated. The reaction was then allowed to stir for 10 min. The solvent and liberated ethanol were removed *in vacuo* to give a pale orange solid. This was redissolved in hot toluene (20.0 cm^3) and then placed at 0 °C, which over a period of 12 h yielded a crop of colourless crystals (2.53 g, 47.7% with respect to Sr), m.p. 86–88 °C (Found: C, 40.8; H, 5.65. $C_{32}H_{50}F_{12}N_4O_8Sr$ requires C, 41.1; H, 5.35%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 3330w, 1638s, 1541m, 1513m, 1496m, 1409m, 1355m, 1285s, 1216m, 1181m, 1126m, 1043m, 1009m, 938m, 919w, 843m, 792m, 765m, 723m, 604w, 584m and 548s; (hexachlorobutadiene) 3318w, 1637m, 1384m, 1275s, 1126m, 1043m, 893w, 756m, 721m, 605w, 584m and 547m. Positive-ion electron-impact (EI) mass spectrum: *m/z* 806 [$SrL_4(L - CF_2)$], 700 (SrL_4), 635 (Sr_2L_3), 498 [$SrL_2(L - CF_2)$], 394 (SrL_2) and 241 (SrL). Solubility studies: insoluble in aliphatic solvents (hexane), but soluble in aromatic (benzene or toluene) and co-ordinating solvents (thf and Me_2SO).

[Hpmdien]$_2$[Sr(tfpd)$_4$] 2. The compound [{$Sr(OEt)_2$-$(EtOH)_4$}$_n$] (2.00 g, 5.88 mmol) was weighed into a Schlenk tube and hexane (25.0 cm^3) added. To the resulting clear solution was added Htfpd (1.42 cm^3, 11.72 mmol) and the reaction left to stir for 5 min. Then pmdien (2.33 cm^3, 11.72 mmol) was slowly added, whereupon the reaction proceeded as for complex **1**. The solid was redissolved in hot toluene (20.0 cm^3) and left to crystallise at room temperature (r.t.), which over a period of 12 h yielded a crop of colourless crystals (3.03 g, 49.9% with respect to Sr), m.p. 98–102 °C (Found: C, 40.45; H, 6.7; N, 7.65. $C_{38}H_{64}F_{12}N_6O_8Sr$ requires C, 43.5; H, 6.1; N, 8.0%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 3306w, 1638m, 1384m, 1275s, 1126m, 1043m, 893w, 756m, 721m, 605w, 584m and 547m; (hexachlorobutadiene) 3385w, 1612s, 1460s, 1384m, 1357m, 1130s, 1033m, 893w, 723m, 695w, 607w and 548m. Positive ion EI mass spectrum: *m/z* 635 (Sr_2L_3), 498 [$SrL_2(L - CF_2)$], 394 (SrL_2) and 241 (SrL). Solubility studies: insoluble in aliphatic solvents (hexane), but soluble in aromatic (benzene or toluene) and co-ordinating solvents (thf and Me_2SO).

[Hpmdien]$_2$[Ca(hfpd)$_4$] 3. The compound [{$Ca(OEt)_2$-$(EtOH)_4$}$_n$] (2.00 g, 6.37 mmol) was weighed into a Schlenk tube and toluene (25.0 cm^3) added. To the resulting clear solution was added Hhfpd (1.28 cm^3, 12.75 mmol) and the reaction left to stir for 5 min. Then pmdien (2.52 cm^3, 12.75 mmol) was slowly added, whereupon the reaction proceeded as for **1**. The solid was redissolved in hot toluene at 45 °C (20.0 cm^3) and left to crystallise at r.t., which over a period of 12 h yielded a crop of pale yellow crystals (3.54 g, 49.6% with respect to Ca), m.p. 83–86 °C (Found: C, 36.65; H, 4.2; N, 6.85. $C_{38}H_{52}CaF_{24}N_6O_8$ requires C, 37.55; H, 4.3; N, 6.9%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 3357w, 3316w, 1527m, 1414m, 1255m, 1146m, 1032m, 987m, 932m, 794m, 765m, 737m, 660m and 580m; (hexachlorobutadiene) 3365w, 1603s, 1421m, 1364m, 1253m, 1145s, 1032m, 983s, 940m, 897m and 738m. Positive-ion EI mass spectrum: *m/z* 701 (Ca_2L_3), 623 [$CaL_2(L - 2F)$], 454 (CaL_2) and 247 (CaL). Solubility studies: insoluble in aliphatic solvents (hexane), but soluble in aromatic (benzene or toluene) and co-ordinating solvents (thf and Me_2SO).

[Hpmdien]$_2$[Sr(hfpd)$_4$] 4. The compound [{$Sr(OEt)_2$-$(EtOH)_4$}$_n$] (2.71 g, 8.05 mmol) was weighed into a Schlenk tube and toluene (25.0 cm^3) added. To the resulting clear solution was added Hhfpd (2.28 cm^3, 16.1 mmol) and the reaction left to stir for 5 min. Then pmdien (3.19 cm^3, 16.1 mmol) was slowly added, whereupon the reaction proceeded as for **1**. The solid was redissolved in hot toluene at 45 °C (20.0 cm^3) and left to crystallise at r.t., which over a period of 12 h yielded a crop of pale yellow crystals (4.12 g, 46.7% with respect to Sr), m.p. 155–158 °C (Found: C, 35.15; H, 4.0; N, 6.3. $C_{38}H_{52}F_{24}N_6O_8Sr$ requires C, 36.15; H, 4.1; N, 6.65%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 3334w, 3329w, 1672s, 1605m, 1569s, 1541m, 1496m, 1414w, 1256s, 1200m, 1146s, 1030m, 998m, 945w, 933w, 788m, 751m, 737m, 728m, 694m, 660w and 578s; (hexachlorobutadiene) 3361w, 3027m, 2960m, 2920m, 2863m, 1671s, 1542s, 1495s, 1467s, 1414w, 1378m, 1255s, 1147s, 1083s, 1030s, 895w, 752m, 729s, 695m and 579w. Positive-ion EI mass spectrum: *m/z* 806 [SrL_3-(CF_3CO)], 609 [$SrL_2(L - 2CF_2)$], 521 (SrL_2F) and 295 (SrL). Solubility studies: insoluble in aliphatic solvents (hexane), but soluble in aromatic (benzene or toluene) and co-ordinating solvents (thf and Me_2SO).

[Hpmdien]$_2$[Ba(hfpd)$_4$] 5. The compound [{$Ba(OEt)_2$-$(EtOH)_4$}$_n$] (3.03 g, 7.36 mmol) was weighed into a Schlenk tube and toluene (25.0 cm^3) added. To the resulting clear solution was added Hhfpd (2.10 cm^3, 14.7 mmol) and the reaction left to stir for 5 min. Then pmdien (2.55 cm^3, 14.7 mmol) was slowly added, whereupon the reaction proceeded as for **1**. The solid was redissolved in hot toluene at 45 °C (20.0 cm^3) and left to crystallise at r.t., which over a period of 12 h yielded a crop of pale yellow crystals (4.33 g, 44.7% with respect to Ba), m.p. 53–56 °C (Found: C, 31.65; H, 3.8; N, 6.0. $C_{38}H_{52}BaF_{24}N_6O_8$ requires C, 34.8; H, 3.95; N, 6.4%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 3342w, 3308w, 1668s, 1558m, 1540m, 1414m, 1258s, 1192m, 1126m, 1079m, 1023m, 998m, 943m, 932w, 799m, 788m, 753m, 737m, 728m, 660w and 578s; (hexachlorobutadiene) 3436w, 2960m, 2920m, 2856m, 1668s, 1467s, 1414w, 1368m, 1255s, 1186s, 1147m, 1080s, 1057m, 1023m, 895w, 752m, 737s and 579w. Positive-ion EI mass spectrum: *m/z* 707 [BaL(L − F)(pmdien)], 590 (BaL_2F_2), 551 (BaL_2), 518 [BaL(pmdien)], 389 [BaL-(Me_2NH)] and 344 (BaL). Solubility studies: insoluble in aliphatic solvents (hexane), but soluble in aromatic (benzene or toluene) and co-ordinating solvents (thf and Me_2SO).

Crystallography

Crystals of complex **1** suitable for X-ray work were grown from toluene at 0 °C, and mounted on the goniostat at 150 K using silicone oil which acted both as a coating and an adhesive.

Crystal data. $C_{32}H_{50}F_{12}N_4O_8Sr$, $M = 934.38$, orthorhombic, space group *Fdd*2 (no. 43), $a = 27.095(4)$, $b = 28.416(3)$, $c = 11.154(1)$ Å, $U = 8588(2)$ Å^3 (by least-squares refinement of diffractometer angles for 250 reflections within $\theta = 2.9$–$29.9°$, $\lambda = 0.710\,69$ Å), $Z = 8$, $D_c = 1.445$ g cm^{-3}, $F(000) = 3840$, $\mu = 13.56$ cm^{-1}, $T = 150$ K, colourless parallelepiped, crystal size 0.40 × 0.20 × 0.15 mm.

Data collection and processing.[19] Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator and an Oxford Cryostream low-temperature cooling system; 11 417 reflections measured ($2.9 \leqslant \theta \leqslant 29.9°$; index ranges $-29 \leqslant h \leqslant 37$, $-38 \leqslant k \leqslant 33$, $-15 \leqslant l \leqslant 14$), 5491 unique (merging $R = 0.0376$ after absorption correction using DIFABS;[20] maximum and minimum absorption correction factors = 0.892, 1.009).

Structure analysis and refinement. The structure was solved *via* direct methods (SHELXS 86)[21] {most of the atoms in the $[Sr(tfpd)_4]^{2-}$ moiety} followed by difference syntheses. Full-matrix least-squares refinement on *F* using SHELX 80[22] with all non-hydrogen atoms anisotropic resulted in a model which appeared to be chemically correct but the conventional *R* value was rather high (*ca.* 0.09). The refinement was continued using the program SHELXL 93[23] employing all the unique F^2 data, which immediately suggested that the working model was the wrong enantiomorph. The correct enantiomorph was then obtained by transforming the existing atom coordinates by ($\frac{1}{4} - x$, $\frac{1}{4} - y$, $1 - z$). The hydrogen atoms were all located from difference maps and refined isotropically. The non-hydrogen atoms were anisotropic. The refinement finally converged at $wR2 = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}} = 0.0842$ and $R1 = \Sigma(\Delta F)/\Sigma(F_o) = 0.0428$ for all 5491 data and 358 parameters; ρ_{min}, ρ_{max} −0.22, 0.51 e Å^{-3}; $(\Delta/\sigma)_{max}$ 0.035. The corresponding *wR*2 and *R*1 values for 3486 data with $F_o > 4\sigma(F_o)$ were 0.0585 and 0.0262 respectively. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2]$, which gave acceptable agreement analyses. The Flack parameter[24] refined to a value of −0.015(5) confirming that the absolute structure was determined correctly. Sources of scattering factor data are given in ref. 23. The diagrams were drawn with SNOOPI.[25] The calculations were done on a Pentium P5-90 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 reference number 186/381.

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