The X-ray Crystal Structures of $[Ca(hfa)_2(OH_2)_2]$ and $[Ba(hfa)_2(OH_2)]$† (Hhfa = 1,1,1,5,5,5-Hexafluoropentane-2,4-dione)

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The X-ray crystal structures of $[Ca(hfa)_2(OH_2)_2]$ and $[Ba(hfa)_2(OH_2)]$ show the presence of dimeric and polymeric species respectively, in which the alkaline earth cations are bridged both by oxygens of chelating (hfa) ligands and fluorines of CF_3 groups.

There is a considerable interest in metal–organic chemical vapour deposition (MOCVD) as a technique for the growth of high T_c superconducting films.[1–4] Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)barium(II), $[Ba(hfa)_2]$, has been successfully used at UMIST to grow oxide and mixed oxide films[5] and is now commercially available[6] as an MOCVD precursor. However, its behaviour is erratic, and in line with several other similar complexes used as MOCVD precursors[7] it has been suspected that an increase in metal coordination occurs with ensuing polymerisation and a lowering of the vapour pressure.

Similarly, the volatility of $[Ca(hfa)_2]$ makes it a suitable precursor for the deposition of CaF_2 by low-pressure MOCVD.[8–10] However, unless exceptional precautions are taken to exclude moisture it is difficult to obtain anhydrous $[Ca(hfa)_2]$ and the hydrated compounds which are readily obtained are unsuitable for the deposition of CaF_2.‡

Although we have not been able to isolate single crystals of the anhydrous compounds, our continuing investigations into these systems has led us, independently, to isolate hydrated forms of $[M(hfa)_2]$, the X-ray structure determinations of which have identified a common feature which may have relevance to the volatility and decomposition behaviour of the parent materials. $[Ca(hfa)_2(OH_2)_2]$§ exists in a centrosymmetric dimeric form as depicted in Fig. 1 which shows that each calcium is bonded to one chelating hfa, two water molecules (*cis* to one another) and a second chelating hfa which also bridges the two calciums through one of the oxygens.¶ However, it can be seen that each calcium is also involved in

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† As hydrogen atoms were not located in this structure determination the alternative hydrogen configuration, $[Ba(Hhfa)(hfa)(OH)]$, is also possible.

‡ Commercial samples of $[Ca(hfa)_2]$ are usually contaminated with the hydrated forms.

§ Some $[Ca(hfa)_2]$ which had been exposed to air for 24 h was crystallized from diethyl ether–petroleum (b.p. 40–60 °C) (1:1) giving $[Ca(hfa)_2(OH_2)_2]$ for which satisfactory elemental analyses were obtained; ^1H NMR (80 MHz, C_6D_6) δ 6.2 (s, 2H, hfa) and 4.34 (s, 4H, H_2O); IR (Nujol, KBr), ν_{OH} 3340–3580, ν_{CO} 1680, 1651 cm^{-1}.

¶ *Crystal data* for $[Ca(hfa)_2(OH_2)_2]$: $M = 980.3$, triclinic, space group $P\bar{1}$, $a = 11.205(1)$, $b = 9.838(1)$, $c = 9.095(1)$ Å, $\alpha = 115.87(1)$, $\beta = 96.19(1)$, $\gamma = 96.17(1)°$, $U = 883.37(1)$ Å^3, $Z = 2$, $D_c = 1.2$ g cm^{-3}. 2441 Unique reflections were obtained of which 1882 having $I > 3\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by least squares to $R = 0.05$.

Crystal data for $[Ba(hfa)_2(OH_2)]$: $M = 569.5$, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.659(4)$, $b = 8.752(3)$, $c = 22.527(9)$ Å, $\beta = 100.46(4)°$, $U = 1678.8$ Å^3, $Z = 4$, $D_c = 2.25$ g cm^{-3}, $F(000) = 1072$, λ(Mo-Kα) = 0.7103 Å, $\mu = 2.33$ mm^{-1}. 3020 Unique reflections were measured of which 1534 having $I > 2\sigma(I)$ were used in the refinement. The structure was solved *via* the heavy atom method and refined by full-matrix least-squares to $R = 0.074$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. Seen Notice to Authors, Issue No. 1.

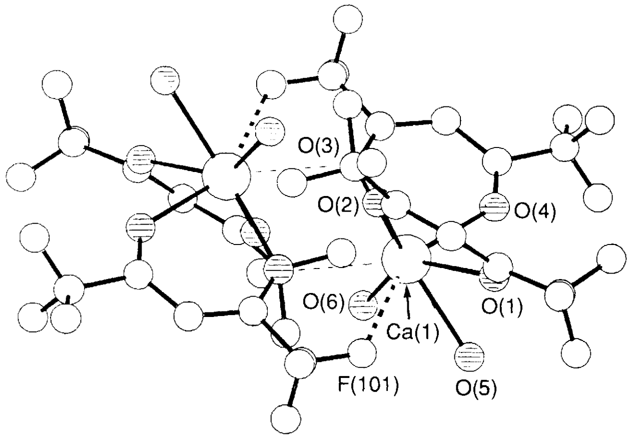

Fig. 1 Structure of $[Ca(hfa)_2(OH_2)_2]$. Principal bond lengths are Ca(1)–O(1) 2.446(5), Ca(1)–O(2) 2.401(5), Ca(1)–O(3) 2.473(5), Ca(1)–O(4) 2.353(5), Ca(1)–O(5) 2.429(6), Ca(1)–O(6) 2.346(7), Ca(1)–F(101) 2.524(5), Ca(1)–O(3′) 2.623(5) Å, where ′ = $-x$, $-y$, $-z$. O(3) is behind by C(5).

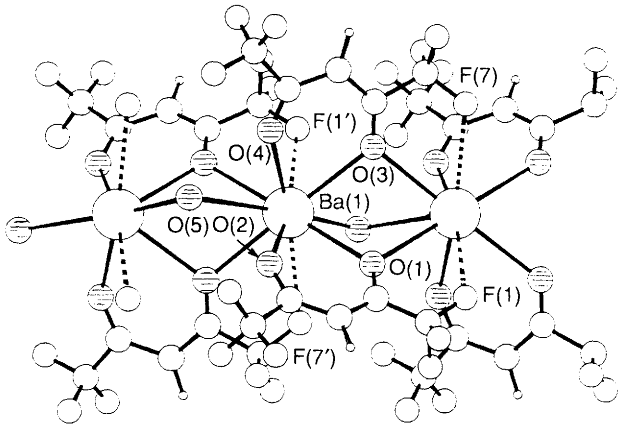

Fig. 2 Structure of $[Ba(hfa)_2(OH_2)]$. Principal bond lengths are Ba(1)–O(1) 2.81(1), Ba(1)–O(2) 2.67(1), Ba(1)–O(3) 2.85(1), Ba(1)–O(4) 2.67(2), Ba(1)–O(5) 3.12(1), Ba(1)–O(1′) 2.92(2), Ba(1)–O(3′) 2.86(2), Ba(1)–O(5′) 2.74, Ba(1)–F(1′) 2.92(2), Ba(1)–F(7′) 2.97(2) Å, where ′ = $-x$, $y - 0.5$, $0.5 - z$.

Ca···F–C bridging *via* a CF_3 group on a neighbouring hfa ligand (Ca···F interatomic distance, 2.52 Å). This interaction makes each calcium eight-coordinate with a distorted dodecahedral configuration. Not surprisingly the Ca···F bond length is slightly longer than Ca–F bonds in eight-coordinated complexes but is considerably longer than the bridging Ca···O distance, and the former is clearly important in promoting the formation of dimeric molecules.

$[Ba(hfa)_2(OH_2)]$†‖ exists in the crystal in polymeric form. Part of the polymeric chain including atomic labelling is displayed in Fig. 2.¶ The structure is composed of approximately mirror-symmetric $[Ba(hfa)_2(OH_2)]$ units, which are linked into infinite polymeric chains along the crystallographic screw axis by two shared fluoropentane-dionato and water oxygens from each unit. This packing brings two fluorines into the barium coordination at distances of 2.92(2) and 2.97(2) Å, which suggests considerable Ba–F interaction when one considers that the sum of F(van der Waals' radius) and Ba(atomic radius) is 3.57 Å.[11] The 10-fold coordination of Ba is not unique and may be compared to bis(*o*-nitrophenolato)-barium(II),[12] in which the Ba–O bonds range from 2.711(3) to 3.117(5) Å.

To our knowledge, these results are the first examples of bridges involving alkaline earth metals and fluorine atoms of a CF_3 group. A Ru···F interaction has been described[13] and Stalke and Whitmire have recently reported a similar feature for a structure containing the more highly polarising Li^+ ion,[14] but the Cs···F interactions (3.21–3.75 Å) observed in $[CsY(hfa)_4]$[15] and the Rb···F interactions (2.80–3.35 Å) in $[Rb_2Na(hfa)_3]$[16] appear to be rather weaker than the Ca···F interactions reported here. We have also identified similar interactions in some lanthanide complexes of trifluoromethyl alkoxy ligands.[17] It is likely, therefore, that this feature may occur quite frequently in complexes containing fluorinated alkyl groups.

The lower volatility of $[Ca(hfa)_2]$ (sublimes at 140 °C and 10^{-3} Torr) suggests that the anhydrous compound must be oligomeric and fragment ions of a hexamer have been reported in the mass spectrum. Using only μ-O bridging hfa ligands the calcium would probably be constrained to six-coordination whereas supplementary bridging *via* fluorine (CF_3) would lead to a higher coordination number. Extensive fluorine bridging in $[Ca(hfa)_2]$ might explain the facility with which this compound decomposed to CaF_2.[9,10] We are currently attempting to grow single crystals of the anhydrous compound suitable for X-ray study.

On the other hand, it is possible that the presence of the water molecule may be advantageous for the decomposition of the Ba complex to give oxide species and so further studies into $[Ba(hfa)_2]$ synthesised and recrystallized in the absence of water, together with related barium precursors are in progress.

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‖ $[Ba(hfa)(OH_2)]$ was synthesised by the reaction of $Ba(OH)_2$ and $CF_3COCH_2COCF_3$ in an aqueous medium and then extracted into ether. Recrystallization from ethanol-water yielded X-ray-quality crystals.