

Synthesis and X-Ray Structure of Hexafluoroacetylacetonatobarium (Diethyl Ether Solvate) [$\{\text{Ba}_2(\text{hfa})_4 \cdot \text{Et}_2\text{O}\}_\infty$]

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The X-ray study of the crystals of [$\{\text{Ba}_2(\text{hfa})_4 \cdot \text{Et}_2\text{O}\}_\infty$] reveals its chain structure to be responsible for the low volatility of this compound.

Although hexafluoroacetylacetonatobarium¹ and its adducts with O-donor ligands^{2,3} are volatile and therefore used in metal-organic chemical vapour deposition (MOCVD), the structural data for these compounds are limited. In contrary to dipivaloylmethanatobarium, which sublimes *in vacuo* almost

quantitatively, the analogous complex with Hhfa possesses lower volatility. This fact combined with mass spectral data⁴ indicates a higher degree of oligomerization of the Ba-hfa chelate with respect to the tetranuclear $\text{Ba}_4(\text{thd})_8$ ⁵ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate). To confirm this we

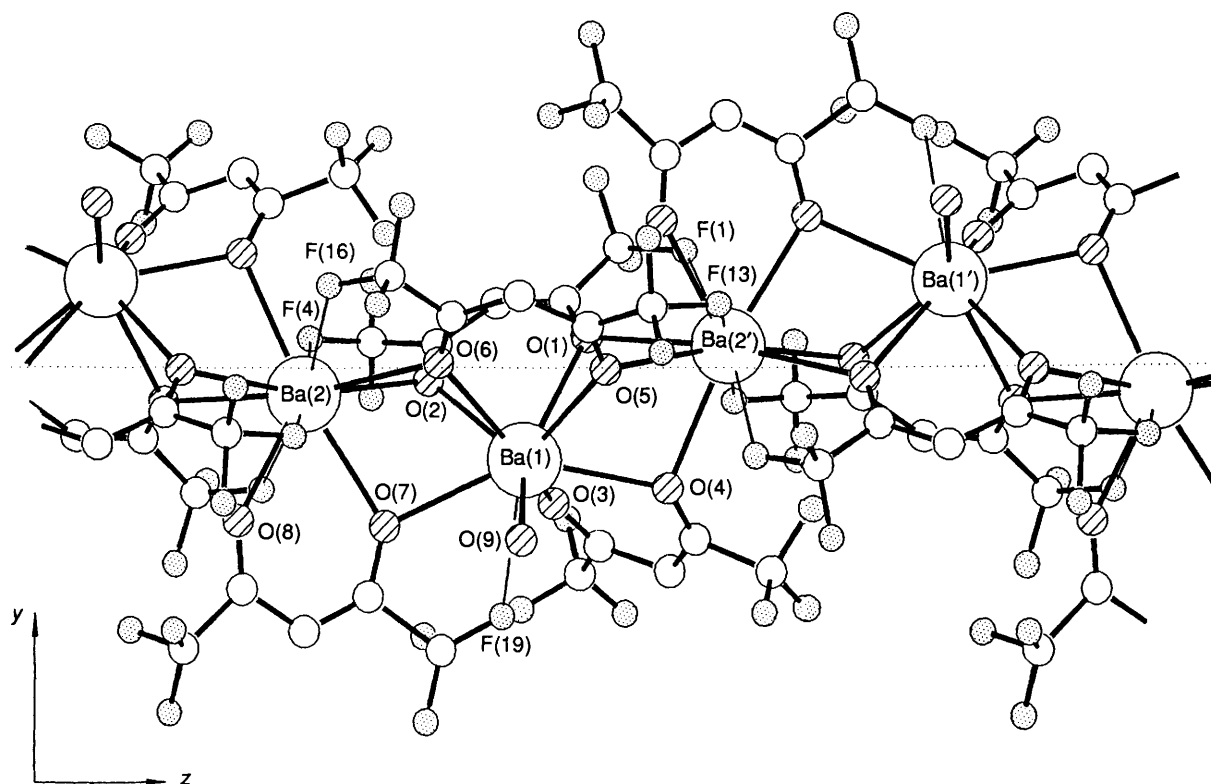


Fig. 1 Projection on O_{yz} plane. The Et-groups of the ether molecules are omitted. The c -glide plane is marked by a dotted line.

have studied the crystal structure of hexafluoroacetylacetonatobarium solvated with diethyl ether [$\{Ba_2(hfa)_4 \cdot Et_2O\}_\infty$] **1**. Compound **1** was prepared as follows: Barium metal was dissolved in a pentane–diethyl ether (1 : 1) solution of Hhfa (with a slight excess of Hhfa with respect to the stoichiometry) under nitrogen. Recrystallization of the precipitate formed gave colourless prismatic crystals of **1** (97%). As this substance is hygroscopic, the crystals were placed into glass capillaries.

An X-ray study of **1** shows that it consists of the infinite zigzag chains $Ba(2)Ba(1)Ba(2')Ba(1')$ directed along the c -axes (Fig. 1).[†] The three neighbouring barium atoms $Ba(2), Ba(1), Ba(2')$ are connected by two hfa ligands $[O(1)O(2), O(5)O(6)]$, which act as bidentate, bridging towards $Ba(1)$, and monodentate, bridging towards both $Ba(2)$ and $Ba(2')$ atoms. The other two ligands $[O(3)O(4), O(7)O(8)]$ are bidentate to $Ba(1)$ and monodentate bridging to $Ba(2')$. The Ba–O distances in **1** lie in the range 2.68–2.82 Å, *i.e.* close to 2.68–2.71 Å in $Ba(hfa)_2(\text{tetraglyme})_2$ and 2.70–2.80 Å in $Ba(hfa)_2(18\text{-crown-6})$.⁶

[†] Crystal data for **1**: $C_{24}H_{16}F_{24}O_9Ba_2$, $M = 1177.02$, monoclinic, space group $P2_1/c$, $a = 11.276(2)$, $b = 22.368(2)$, $c = 15.531(3)$ Å, $\beta = 100.01(2)^\circ$, $V = 3857.6$ Å³, $D_c = 2.026$ Mg m⁻³, $Z = 4$. Monochromatic Mo–K α radiation, $\lambda = 0.7107$ Å, $\mu = 21.85$ cm⁻¹, $T = 293$ K. A total of 9988 reflections were measured ($1 < \theta < 28^\circ$) on a CAD 4 diffractometer (no absorption correction); 3418 reflections with $I > 3\sigma(I)$ were used in calculations with the SDP program package.⁹ The structure was solved using a combination of direct and Fourier methods and refined by the full-matrix least-squares technique with the anisotropic thermal parameters for all non-hydrogen atoms except six fluorine atoms of the disordered trifluoromethyl groups and eight carbon atoms of the disordered trifluoromethyl or ethyl groups of the diethyl ether molecule. The position of the hydrogen atoms were not determined or calculated. The final R -values were $R = 0.071$ and $R_w = 0.075$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

A characteristic feature of this structure is the additional coordination of the fluorine atoms from the CF_3 -groups of hfa to the barium atoms. In both $O(1)O(2)$ and $O(5)O(6)$ hfa-anions one fluorine atom in every trifluoromethyl group is coordinated to $Ba(2)$ or $Ba(2')$, the Ba–F distances are in the range 2.97–3.09 Å. The other two hfa ligands $[O(3)O(4)$ and $O(7)O(8)]$ differ from those already discussed. Among them only the latter forms an additional Ba–F bond [$Ba(1)$ – $F(19)$ 2.76 Å]. Thus, taking into consideration these Ba–F interactions the coordination number (CN) of the barium atoms is rather high. $Ba(1)$ ($CN = 9$) forms eight Ba–O bonds with six O-atoms from two chelate rings, one bridging O(7) atom and the O(9) of the diethyl ether molecule, and one Ba–F bond. The environment of the $Ba(2)$ atom ($CN = 11$) consists of two O-atoms forming a chelate ring, five bridging O-atoms and four F-atoms. The Ba–F distances in **1** are longer with respect to those in barium fluoride [Ba – F 2.685 Å, $CN(Ba) = 8$] that can be accounted for the greater coordination number of barium in the former compound (although a comparison is loosely correct because of wide difference in ionicity of Ba–F bonds). The four F-atoms [$F(1), F(4), F(13), F(16)$] and the $Ba(2)$ atom all lie in the same plane. It is interesting to note that an analogous interaction between the metal and the covalently-bonded fluorine was found in $Cs[Ce(hfa)_4]$.⁷

We suppose that the loss of ether molecule from **1** would cause only small changes in the coordination of the atoms; with the polymeric structure as a whole being preserved. The structure under discussion is appreciably similar to that of $Ba(hfa)_2$ which is also polymeric with weak Ba–F interactions.⁸ It is possible that the additional coordination of the fluorine atoms is responsible for the stability of their polymeric structures and, consequently, for the low volatility of both compounds as well as for the formation of barium fluoride as a decomposition product. In the monomeric adducts formed by the reaction of $Ba(hfa)_2$ with Lewis bases [*e.g.* $Ba(hfa)_2(\text{tetraglyme})_2$] such additional Ba–F interactions

were not found as the coordination sphere of the barium atom (CN = 9) is already completed.

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