Volatile Barium, Strontium and Calcium Bis(hexafluoroacetylacetonate)(crown ether) Complexes

J. A. T. Norman* [a] **and G. P. Pez*** [b]

[a] *Schumacher Co., 1969 Palomar Oaks Way, Carlsbad, CA 92009-1307, USA*
[b] *Corporate Science and Technology Center, Air Products and Chemicals, Inc., Allentown, PA 18195-1501, USA*

New compositions of general formula M(hexafluoroacetylacetonate)(crown ether), where M = Ba, Sr and Ca have been prepared and found to be unusually volatile; the structure of the monomeric Ba complex has been determined by X-ray crystallography.

There is a growing interest in the use of organometal chemical vapour deposition (OMCVD) methods for the preparation of thin films of high temperature superconductors, particularly $YBa_2Cu_3O_{7-x}$[1,2] but also recently, Bi–Sr–Ca–Cu–O[3] compositions. While there are satisfactory OMCVD sources for copper and yttrium, compounds of barium having an adequate volatility and reactivity at CVD process conditions where it is required to form metal oxides have not been available. The currently employed precursors, $Ba(hfa)_2$ (hfa = hexafluoroacetylacetonate) and $Ba(dpm)_2$ (dpm = 2,2,6,6-tetramethylheptane-3,5-dionate) have a very limited volatility, which can, however, be increased by the addition of appropriate ligand additives during CVD processing.[4] Use of the former precursor lends to a significant co-deposition of barium fluoride.[1]

The volatility requirement should ideally be met by a monomeric barium complex that is totally 'encapsulated' in an organic or fluoro-organic ligand environment. Satisfying the up to 12-fold coordination requirement of a Ba^{2+} ion[5] in a monomeric structure appears to be particularly difficult. Thus even bis(pentamethylcyclopentadienyl)barium(II), in which there might be expected to be a sufficient shielding of the metal ion, exists in the solid as an infinite chain coordination polymer.[6] We approached the problem by attempting to incorporate the desirable metal chelating ligand features of $Ba(crown ether)(SCN)_2$[7] and barium bis(β-diketonate)[8] complexes into a single molecule.

Reaction of barium hydride, 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and hexafluoroacetylacetone at *ca.* 25 °C in a 1 : 1 : 2 molar ratio in tetrahydrofuran (THF) under N_2 followed by removal of solvent, afforded a white THF soluble solid which was purified by repeated sublimation at 150–200 °C, 10^{-3} Torr. The crystalline sublimate product was shown by its NMR spectrum and an X-ray structural determination† to be $Ba(hfa)_2$(18-crown-6) **1**. Its molecular structure is shown in Fig. 1. It consists of a barium atom at the centre and in the plane of a molecule of 18-crown-6 which is also coordinated by two chelating hfa ligands. Whereas the $Ba(hfa)_2$ portion of the structure is well defined, considerable disorder was encountered in the molecule of 18-crown-6. It was possible to resolve only partially the various fractionally occupied ring atom positions; the polyether ring shown in Fig. 1 represents just one of many possible locations for the atoms of this ligand. The assignment of the complete ten-coordinate barium environment to a structural type is difficult due to the uncertainties in the polyether ring positions. The average hfa Ba–O distances of 2.82 Å and O–Ba–O angle of 61.2(3)° are within normal ranges. Consistent with the apparently unusual degree of volatility of the complex, there are no significant intermolecular contacts in the crystal lattice.

The structure of **1** is similar to that recently reported for $Ba(hfa)_2$(2,5,8,11,14-pentaoxapentadecane) **2**,[9] which consists of two hfa ligands one above and one below the planar barium-coordinating polyether. However, there is a surprisingly different relative orientation of the hfa ligands in the two molecules. Thus, in **1** the two BaO_2 planes of the hfa chelate rings intersect at an angle of 85.2(2)°, so that the primary well-defined coordination about barium is that of a slightly flattened tetrahedron. In **2** the corresponding angle is 12.9° and the hfa oxygens are thus coordinated in an almost planar configuration.

By a similar synthetic procedure, $Sr(hfa)_2$(18-crown-6) **3** and $Ca(hfa)_2$(18-crown-6) **4** were prepared. Using 4,13-diaza-18-crown-6(1,7,10,16-tetraoxa-4,13-diazacyclooctadecane) as the macrocyclic ligand afforded the series of $M(hfa)_2$(4,13-diaza-18-crown-6) complexes with M = Ba **5**, Sr **6** and Ca **7**.‡

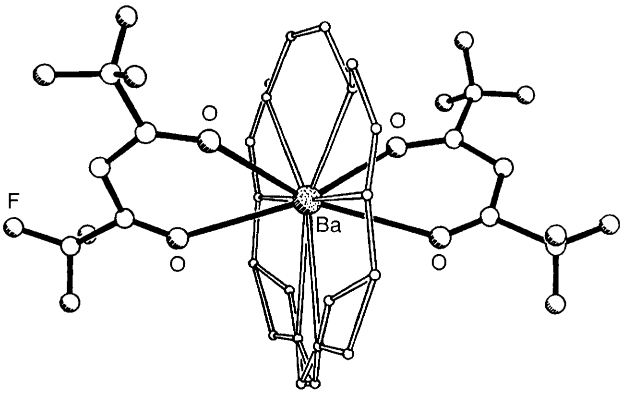

Fig. 1 Molecular structure of $Ba(hfa)_2$ (18-crown-6) **1**

---

† The X-ray structural determination was done by Dr A. L. Rheingold, University of Delaware, Newark, DE, USA.

Crystal data for $Ba(hfa)_2$18-crown-6 **1**: $C_{22}H_{26}Ba_{12}O_{10}$, tetragonal, space group $P4_12_12$, $a = 14.421(2)$, $c = 15.494(2)$ Å, $V = 3222.4\ (8)$ Å^3, $Z = 4$, $D_c = 1.683$ g cm^{-3} Data were collected on a Nicolet R3m diffractometer using graphite monochromated Mo-Kα radiation, over a 2θ scan range of 4–52°. A total of 6859 (3170 independent) intensities were collected of which 2522 had $F_0 > 5\sigma(F_0)$. The structure was solved by heavy atom methods and completed by a series of difference Fourier syntheses. All non-H $Ba(hfa)_2$ atoms were refined with anisotropic thermal parameters while those of the disordered polyether ring were refined with isotropic parameters. Hydrogen atoms were treated as idealized contributions. Site occupancies for the polyether-ring atoms were constrained to values consistent with the crown ether formula. In the final cycle of refinement $R(F) = 5.60$ and $R\,(wF) = 6\%$; the residual electron density peak, $\Delta(l)$ was 1.21 e Å^{-3}. 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.

‡ *NMR characterization data* ([$^2H_6$]acetone) for **1**: ^1H NMR δ 3.8 (s, 24 H) and 5.65 (s, 2H); ^{19}F NMR δ −77.6 (s, 12 F); ^{13}C NMR δ 71.0 (s, 12 C), 87.0 (s, 2C), 120.0 (q, 4C) and 17.0 (q, 4C). For **3**: ^1H NMR δ 3.7 (s, 24 H) and 5.7 (s, 2H); ^{19}F NMR δ −81.1; ^{13}C NMR δ 71 (s, 12C), 87 (s, 2C), 120 (q, 4C) and 175 (q, 4C). For **4**: ^1H NMR δ 3.8 (br s, 24H) and 5.8 (s, 2H); ^{19}F NMR δ −76.8 (s, 12F); ^{13}C NMR δ 65 (br s, 12C), 88 (s, 2C), 119 (q, 4C) and 176 (q, 4C). For **5**: ^1H NMR δ 2.9 (s, 8H), 3.7 (s, 16H) and 5.62 (s, 2H); ^{19}F NMR δ −77.6 (s, 12F); ^{13}C NMR δ 48.9 (s, 4C), 70.9 (s, 4C), 71.7 (s, 4C), 86.0 (s, 2C), 119.2 (q, 4C) and 174.3 (q, 4C). For **6**: ^1H NMR δ 2.8 (br s, 8H), 3.7 (s, 16H) and 5.75 (s, 2H); ^{19}F NMR δ −81.1; ^{13}C NMR δ 69 (s, 12C), 95.5 (s, 2C), 119 (q, 4C) and 175 (q, 4C). For **7**: ^1H NMR δ 2.84 (m, 8H), 3.70 (s, 16H) and 5.75 (s, 2H); ^{19}F NMR δ −76.7; ^{13}C NMR δ 49 (s, 4C), 71 (s, 4C), 72 (s, 4C), 87 (s, 2C), 119 (q, 4C) and 175 (q, 4C).

All these compositions (which are believed to be monomeric on the basis of their volatility), were isolated and purified by vacuum sublimation at the conditions stated above. Surprisingly, no volatile Ba bis(pentane-2,4-dionate) (18-crown-6) or Ba(dpm)$_2$(18-crown-6) complexes could be isolated by this means. From NMR spectra of reaction product mixtures it appears that the latter complex is formed but decomposes on heating with sublimation of free 18-crown-6. There are presumably stringent steric and electronic requirements for accommodating both macrocyclic and β-diketonate ligands around barium such that the entire ensemble remains intact during sublimation. An evaluation of the new volatile complexes in OMCVD processes is in progress.§

The chemical synthesis efforts of Mrs B. Muratore are gratefully acknowledged.

Received, 5th February 1991; Com. 1/00554E

References

1 J. Zhao, K. H. Dahmen, H. O. Marcy, L. M. Tonge, T. J. Marks, B. W. Wessels and C. R. Kannewurf, *Appl. Phys. Lett.*, 1988, **53**, 1750; A. P. Purdy, A. D. Berry, R. T. Holm, M., Fatemi and D. K. Gaskill, *Inorg. Chem.*, 1989, **28**, 2799.

2 A. J. Panson, R. G. Charles, D. N. Schmidt, J. R. Szedon, G. J. Machiko and A. I. Braginski, *Appl. Phys. Lett.*, 1988, **53**, 1756; H. Yamane, H. Kurosawa, T. Hirai, K. Watanabe, H. Iwasaki, N. Kobayashi and Y. Muto, *Supercond. Sci. Technol.*, 1989, **2**, 115; P. H. Dickinson, T. H. Geballe, A. Sanjurjo, D. Hildenbrand, G. Craig, M. Zisk, J. Collman, S. A. Banning and R. E. Sievers, *J. Appl. Phys.*, 1989, **66**, 444; K. Kanehori, N. Sughii, T. Fukazawa and K. Miyauchi, *Thin Solid Films*, 1989, **182**, 265.

3 M. Nemoto and M. Yanmanaka, *J. Mater. Res.*, 1990, **5**, 1.

4 A. R. Barron, in *The Strem Chemiker*, Strem Chemicals, Newburyport, MA, USA, 1990, vol. XIII No. 1.

5 C. J. M. van Veggel, M. Bos, S. Harkema, W. Verboom and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 746; K. G. Caulton, M. H. Chisholm, S. R. Drake and J. C. Huffman, *J. Chem. Soc., Chem. Commun.*, 1990, 1498; K. G. Caulton, M. H. Chisholm, S. R. Drake and K. Folting, *J. Chem. Soc., Chem. Commun.*, 1990, 1349.

6 R. A. Williams, T. P. Hanusa and J. C. Huffman, *J. Chem. Soc., Chem. Commun.*, 1988, 1045.

7 N. K. Dalley, D. E. Smith, R. M. Izatt and J. Christensen, *J. Chem. Soc., Chem. Commun.*, 1972, 90.

8 R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon Press, Oxford, 1965.

9 P. van der Sluis, A. L. Spek, K. Timmer and D. A. Meinema, *Acta Crystallogr., Sect. C.*, 1990, **46**, 1741.

---

§ *Note added in proof*: Since the submission of this paper a European Patent Application has appeared (K. Timmer, C. I. M. A. Spee, A. Mackor and H. A. Meinema, EP 0 405 634 A2, 1991), which claims the synthesis of Ba(hfa)$_2$(18-crown-6) **1**, but gives no structural information.