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Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(2,5,8,11,14,17-hexaoxaoctadecane)-barium

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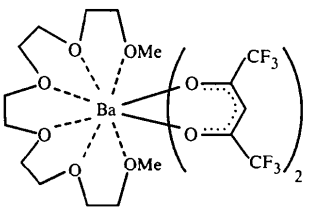
Abstract

The mononuclear title complex, bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato-O^2,O^4)(2,5,8,11,14,17-hexaoxaoctadecane-$O^2,O^5,O^8,O^{11},O^{14},O^{17}$)barium, $[Ba(C_5HF_6O_2)_2(C_{12}H_{26}O_6)]$, has a geometry similar to most other structurally characterized bis(β-diketonato)barium polyether adducts. The central Ba^{2+} ion has a coordination number of ten. The hexadentate polyether coordinates meridionally, with the β-diketonato ligands on opposite sides of the neutral-ligand mean plane. The Ba—O bond lengths range from 2.758 (3) to 2.858 (3) Å. All but one of the barium to polyether oxygen bonds are longer than the corresponding bonds to the β-diketonato ligands. The coordinative saturation of the Ba^{2+} ion ensures that there are no strong intermolecular interactions, consistent with the volatility of the title compound.

Comment

Fluorinated bis(β-diketonato)barium polyether complexes are important as precursors in chemical vapour deposition (CVD) of materials such as superconducting oxides (Dahmen & Gerfin, 1993; Watson, Atwood, Cumberbatch & Cardwell, 1994). Previous structure determinations have been carried out on volatile mononuclear complexes containing the 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfa) ligand and several different cyclic and acyclic polyether ligands (van der Sluis, Spek, Timmer & Meinema, 1990; Gardiner, Brown, Kirlin & Rheingold, 1991; Norman & Pez, 1991; Polyanskaya, Gatilov, Martynova & Nikulina, 1992; Inerowicz, Khan, Atkinson & White, 1994; Neumayer, Studebaker, Hinds, Stern & Marks, 1994; Motevalli, O'Brien & Watson, 1996). In most cases, meridional coordination of the central Ba^{2+} ion by the polyether is observed, with the β-diketonato ligands located on opposite sides of the neutral ligand plane. However, a different type of coordination geometry was found in two instances where crystals were obtained by sublimation rather than solution growth. Both hfa ligands are on the same side of the neutral ligand mean plane in $Ba(hfa)_2$–1,10-diaza-18-crown-6 (Inerowicz, Khan, Atkinson & White, 1994) and a monoclinic form of $Ba(hfac)_2$–18-crown-6 (Polyanskaya, Gatilov, Martynova & Nikulina, 1992). The tetragonal form of $Ba(hfa)_2$–18-crown-6 has the type of structure mentioned initially (Norman & Pez, 1991) and probably undergoes thermal isomerization in the solid state (Tobaly & Watson, 1995). The 2,5,8,11,14,17-hexaoxaoctadecane (pentaglyme) ligand in the title compound, (I), is of interest as the closest acyclic analogue of 18-crown-6 (Haymore, Lamb, Izatt & Christensen, 1982). We found striking differences in physical properties, however, between (I) and $Ba(hfa)_2$–18-crown-6; (I) melts at 419–420 K, whereas $Ba(hfa)_2$–18-crown-6 melts with decomposition only above 530 K, and (I) is also much more volatile than $Ba(hfa)_2$–18-crown-6 at around 400 K.



(I)

The title compound, (I), is a mononuclear coordinatively saturated complex (Fig. 1). All six pentaglyme O atoms are bonded to the Ba^{2+} ion in a meridional fashion, with the hfa ligands on opposite sides of the polyether mean plane, resulting in a coordination number of ten. The C3···Ba1···C8 angle is 163.1°. Within each hfa chelate ring, one of the Ba—O bonds is significantly longer than the other. As expected in this type of complex, the average barium to hfa oxygen distance of 2.787 (3) Å is shorter than the mean barium to polyether oxygen bond length of 2.837 (3) Å. The pentaglyme ligand has a pseudosymmetric conformation, as its two halves are nearly related by a twofold axis running through the Ba1 atom and the midpoint of the C16—C17 bond. Steric repulsions between the two ends of this ligand prevent its donor atoms achieving the almost coplanar arrangement observed in some other $Ba(hfa)_2$–polyether complexes containing acyclic pentadentate and cyclic hexadentate ligands (van der Sluis, Spek, Timmer & Meinema, 1990; Gardiner, Brown, Kirlin & Rheingold, 1991; Norman & Pez, 1991; Motevalli, O'Brien & Watson, 1996). This aspect of the structure of (I) is illustrated by tabulated O—Ba—O bond angles and by the fact that the O5···O10 separation is 3.417 Å, compared with an average O···O distance of 2.804 Å between other pairs of adjacent pentaglyme O atoms. A similar sterically enforced polyether conformation has been observed in the $Ba(hfa)_2$ adduct of the

potentially heptadentate ligand 2,5,8,11,14,17,20-heptaoxatetracosane (*n*-butylhexaglyme), where one polyether O atom is not bonded to the Ba^{2+} ion (Neumayer, Studebaker, Hinds, Stern & Marks, 1994). The angle between the Ba1, O1, O2 and Ba1, O3, O4 planes in (I) is 83.9 (1)°, which is close to the corresponding angle of 82.0 (4)° in $Ba(hfa)_2$–*n*-butylhexaglyme. All F atoms in compound (I) have high U_{eq} values and apparent anisotropic thermal motion (Fig. 1). These observations probably reflect torsional freedom of the CF_3 groups. Difficulties in locating F atoms are common in structure determinations of metal–hfa complexes and, for example, extend to the previously cited study of $Ba(hfa)_2$–*n*-butylhexaglyme performed at 153 K.

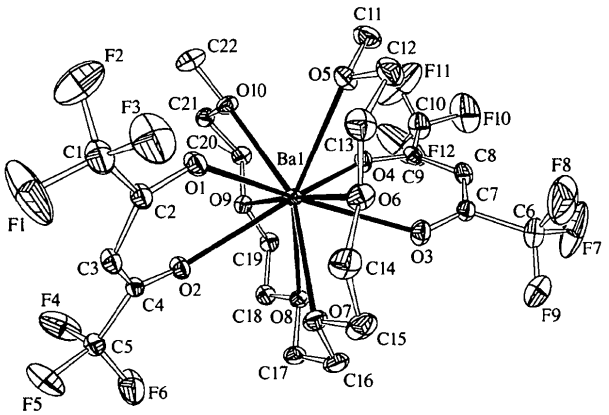


Fig. 1. The molecular structure of (I) showing 30% probability ellipsoids, with H atoms omitted for clarity.

Differential scanning calorimetry (DSC) showed that (I) undergoes a major endothermic transition between 300 K and temperatures at which its vapour pressure is useful for CVD applications. It is thus inappropriate to attempt a detailed explanation of the high volatility of (I) in comparison with other $Ba(hfa)_2$–polyether complexes in terms of the molecular packing observed at room temperature. The effective shielding of the central Ba^{2+} ion, however, which prevents any short intermolecular contacts with electronegative atoms, is certainly significant. There are short intermolecular contacts between pairs of F atoms, with six F···F distances in the range 2.88–3.26 Å, comparable to twice the fluorine van der Waals radius of 1.47 Å (Bondi, 1964).

Experimental

Pentaglyme was synthesized by a Williamson method described in detail previously (Haymore, Lamb, Izatt & Christensen, 1982). Compound (I) was prepared by treating the polyether with $Ba(hfa)_2.H_2O$ (Strem Chemicals) in toluene (Motevalli, O'Brien & Watson, 1996). Crystals were grown at room temperature by diffusion of pentane vapour into a saturated toluene solution. Microanalytical and spectroscopic characterization gave results consistent with the structure determination. A DSC measurement in which recrystallized (I) was heated from room temperature showed a major endotherm [onset 379.8 (2) K, maximum heat flow 382.7 (2) K, enthalpy change 22.3 (5) kJ mol^{-1}] preceding the melting peak [onset 418.9 (2) K, maximum heat flow 420.5 (2) K, enthalpy change 29.5 (5) kJ mol^{-1}].

Crystal data

$[Ba(C_5HF_6O_2)_2(C_{12}H_{26}O_6)]$
M_r = 817.78
Monoclinic
$C2/c$
a = 20.074 (4) Å
b = 14.331 (3) Å
c = 23.334 (5) Å
β = 106.77 (3)°
V = 6427 (2) Å^3
Z = 8
D_x = 1.690 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12.5–14.3°
μ = 1.352 mm^{-1}
T = 293 (2) K
Rhomb
0.62 × 0.45 × 0.45 mm
Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.49, T_{max} = 0.54
5954 measured reflections
5644 independent reflections
4890 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0078
θ_{max} = 24.97°
$h = -23 \rightarrow 0$
$k = -6 \rightarrow 17$
$l = -26 \rightarrow 27$
2 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.037
$wR(F^2)$ = 0.106
S = 1.107
5644 reflections
423 parameters
H atoms riding with *SHELXL*93 default geometry
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 20.3146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.097
$\Delta\rho_{max}$ = 0.818 e Å^{-3}
$\Delta\rho_{min}$ = −0.559 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Ba1	0.211011 (11)	0.95264 (2)	0.116637 (10)	0.04106 (11)
F1	0.0806 (4)	0.9299 (6)	0.3209 (2)	0.235 (5)
F2	0.0944 (4)	1.0612 (5)	0.2888 (3)	0.182 (3)
F3	0.1779 (3)	0.9859 (5)	0.3295 (2)	0.140 (2)
F4	−0.0391 (2)	0.7579 (4)	0.1044 (2)	0.155 (2)
F5	0.0033 (2)	0.6968 (3)	0.1849 (2)	0.120 (2)
F6	0.0452 (3)	0.6702 (4)	0.1170 (4)	0.193 (3)

F7	0.5093 (3)	0.9051 (8)	0.1036 (4)	0.254 (5)
F8	0.4933 (4)	0.9416 (6)	0.1790 (4)	0.234 (5)
F9	0.4674 (3)	0.8140 (5)	0.1468 (4)	0.202 (4)
F10	0.3835 (4)	1.1290 (6)	−0.0311 (3)	0.217 (4)
F11	0.2998 (7)	1.1791 (7)	−0.0226 (6)	0.326 (9)
F12	0.2931 (8)	1.0800 (9)	−0.0742 (3)	0.346 (10)
O1	0.1512 (2)	0.9843 (3)	0.2075 (2)	0.0640 (9)
O2	0.0929 (2)	0.8466 (2)	0.11647 (15)	0.0616 (8)
O3	0.3462 (2)	0.8999 (3)	0.1174 (2)	0.0729 (10)
O4	0.2663 (2)	1.0258 (3)	0.0308 (2)	0.0701 (10)
O5	0.2826 (2)	1.1107 (2)	0.1788 (2)	0.0682 (9)
O6	0.3098 (2)	0.9378 (3)	0.2314 (2)	0.0709 (10)
O7	0.2503 (2)	0.7748 (2)	0.1690 (2)	0.0659 (9)
O8	0.1934 (2)	0.7947 (2)	0.0427 (2)	0.0597 (8)
O9	0.1104 (2)	0.9557 (2)	0.00149 (14)	0.0540 (8)
O10	0.1223 (2)	1.1074 (2)	0.07574 (15)	0.0607 (8)
C1	0.1158 (4)	0.9741 (6)	0.2935 (3)	0.091 (2)
C2	0.1161 (2)	0.9376 (3)	0.2327 (2)	0.0565 (11)
C3	0.0788 (2)	0.8563 (3)	0.2133 (2)	0.0564 (11)
C4	0.0687 (2)	0.8197 (3)	0.1561 (2)	0.0482 (10)
C5	0.0194 (2)	0.7360 (4)	0.1397 (2)	0.0573 (11)
C6	0.4656 (3)	0.8989 (7)	0.1317 (4)	0.102 (2)
C7	0.3929 (2)	0.9350 (4)	0.1002 (2)	0.0615 (12)
C8	0.3873 (3)	1.0002 (4)	0.0555 (3)	0.0721 (15)
C9	0.3243 (3)	1.0379 (4)	0.0232 (2)	0.0615 (12)
C10	0.3251 (4)	1.1040 (7)	−0.0269 (4)	0.106 (3)
C11	0.2963 (4)	1.1863 (4)	0.1438 (3)	0.093 (2)
C12	0.3367 (3)	1.0983 (5)	0.2323 (3)	0.088 (2)
C13	0.3181 (3)	1.0196 (5)	0.2668 (3)	0.083 (2)
C14	0.3034 (4)	0.8538 (4)	0.2611 (3)	0.084 (2)
C15	0.3081 (4)	0.7743 (4)	0.2227 (3)	0.084 (2)
C16	0.2594 (3)	0.7078 (4)	0.1271 (3)	0.077 (2)
C17	0.1989 (3)	0.7078 (3)	0.0733 (3)	0.0699 (14)
C18	0.1348 (3)	0.7975 (4)	−0.0101 (3)	0.0729 (15)
C19	0.1288 (3)	0.8912 (4)	−0.0373 (2)	0.0668 (13)
C20	0.0980 (3)	1.0474 (4)	−0.0225 (2)	0.0658 (14)
C21	0.0714 (3)	1.1048 (4)	0.0194 (2)	0.0638 (13)
C22	0.1005 (4)	1.1628 (4)	0.1172 (3)	0.091 (2)

Table 2. *Selected geometric parameters (Å, °)*

Ba1—O1	2.758 (3)	Ba1—O10	2.832 (3)
Ba1—O4	2.762 (4)	Ba1—O7	2.837 (3)
Ba1—O8	2.806 (3)	Ba1—O6	2.844 (4)
Ba1—O3	2.811 (3)	Ba1—O5	2.846 (3)
Ba1—O2	2.815 (3)	Ba1—O9	2.858 (3)
O4—Ba1—O3	61.16 (11)	O10—Ba1—O5	74.00 (11)
O1—Ba1—O2	62.41 (10)	O6—Ba1—O5	57.82 (11)
O8—Ba1—O7	60.68 (11)	O8—Ba1—O9	60.33 (9)
O7—Ba1—O6	59.71 (11)	O10—Ba1—O9	57.72 (9)

Data collection: *CAD-4/PC* (Enraf–Nonius, 1992). Cell refinement: *CAD-4/PC*. Data reduction: local program (*CAD-4*; Davis, 1975). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1089). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Dahmen, K.-H. & Gerfin, T. (1993). *Prog. Cryst. Growth Charact.* **27**, 117–161.
Davis, J. (1975). *CAD-4. Program for Data Reduction.* University of London, England.
Enraf–Nonius (1992). *CAD-4/PC Software.* Version 1.5c. Enraf–Nonius, Delft, The Netherlands.
Gardiner, R., Brown, D. W., Kirlin, P. S. & Rheingold, A. L. (1991). *Chem. Mater.* **3**, 1053–1059.
Haymore, B. L., Lamb, J. D., Izatt, R. M. & Christensen, J. J. (1982). *Inorg. Chem.* **21**, 1598–1602.
Inerowicz, H. D., Khan, M. A., Atkinson, G. & White, R. L. (1994). *Acta Cryst.* C**50**, 688–690.
McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.
Motevalli, M., O'Brien, P. & Watson, I. M. (1996). *Polyhedron*, **15**, 1865–1875.
Neumayer, D. A., Studebaker, D. B., Hinds, B. J., Stern, C. S. & Marks, T. J. (1994). *Chem. Mater.* **6**, 878–880.
Norman, J. A. T. & Pez, G. P. (1991). *J. Chem. Soc. Chem. Commun.* pp. 971–972.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**42**, 351–359.
Polyanskaya, T. M., Gatilov, Yu. V., Martynova, T. N. & Nikulina, L. D. (1992). *Zh. Strukt. Khim.* **33**, 190.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sluis, P. van der, Spek, A. L., Timmer, K. & Meinema, H. A. (1990). *Acta Cryst.* C**46**, 1741–1743.
Tobaly, P. & Watson, I. M. (1995). *J. Chem. Thermodyn.* **27**, 1211–1219.
Watson, I. M., Atwood, M. P., Cumberbatch, T. J. & Cardwell, D. A. (1994). *J. Mater. Chem.* **4**, 1393–1401.

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Tris(*N*,*N*-diethyldithiocarbamato-*S*,*S*′)-nickel(IV) 1,1,2,3,3-Pentacyanopropenide

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Abstract

The title compound, $[Ni(C_5H_{10}NS_2)_3](C_8N_5)$, forms a structure with sheets consisting of alternate rows of cations and anions. The Ni atom in the cation has distorted octahedral geometry. The planar $[C_3(CN)_5]^-$ anion is significantly distorted from C_{2v} symmetry. The Ni—S distances range from 2.246 (2) to 2.257 (2) Å and the C—C distances in the allyl group of the anion are 1.19 (2) and 1.35 (2) Å.