C4′	0.1388 (4)	0.4720 (2)	0.18109 (13)	0.0262 (6)
C5′	0.0237 (4)	0.4225 (2)	0.13404 (14)	0.0349 (7)
C6′	−0.1566 (5)	0.4092 (5)	0.1553 (3)	0.0621 (12)
C7′	0.1496 (8)	0.3106 (4)	−0.0059 (2)	0.0642 (12)
O*W*1	0.7656 (3)	0.6345 (2)	0.24869 (12)	0.0351 (5)
O*W*2	0.0495 (4)	0.2220 (3)	0.3969 (2)	0.0657 (9)
O*W*3	0.6116 (3)	0.1296 (2)	0.17145 (11)	0.0376 (5)
O*W*4	−0.0628 (6)	0.1078 (5)	0.1632 (3)	0.178 (3)
Li1	0.5746 (6)	0.6378 (4)	0.1928 (2)	0.0339 (11)
Li2	0.2965 (6)	0.6337 (4)	0.2463 (3)	0.0368 (11)
HO4	0.3038 (41)	0.2131 (25)	0.3888 (14)	0.007 (9)
HO4′	−0.0108 (60)	0.5919 (38)	0.2180 (20)	0.084 (14)

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

Cu—O2′	1.910 (2)	O3′—C3′	1.416 (3)
Cu—O2	1.925 (2)	O4′—C4′	1.453 (4)
Cu—O3	1.944 (2)	O5′—C1′	1.416 (4)
Cu—O3′	1.947 (2)	O5′—C5′	1.442 (4)
O1—C1	1.412 (4)	C1′—C2′	1.524 (4)
O1—C7	1.438 (4)	C2′—C3′	1.523 (4)
O2—C2	1.416 (3)	C3′—C4′	1.524 (4)
O3—C3	1.419 (3)	C4′—C5′	1.523 (4)
O4—C4	1.433 (4)	C5′—C6′	1.529 (5)
O5—C1	1.412 (4)	Li1—O4^{i}	1.964 (6)
O5—C5	1.444 (3)	Li1—O3^{i}	1.991 (6)
C1—C2	1.516 (4)	Li1—O3′	1.932 (5)
C2—C3	1.527 (4)	Li1—O*W*1	1.975 (5)
C3—C4	1.523 (4)	Li1—Li2	2.529 (8)
C4—C5	1.527 (4)	Li2—O3^{i}	1.940 (6)
C5—C6	1.507 (5)	Li2—O*W*3^{i}	1.979 (6)
O1′—C1′	1.388 (4)	Li2—O3′	2.039 (6)
O1′—C7′	1.433 (5)	Li2—O4′	2.064 (5)
O2′—C2′	1.411 (3)	Li2—O*W*4^{ii}	2.772 (9)
O2—Cu—O3	86.97 (9)	O3^{i}—Li2—O*W*3^{i}	102.4 (2)
O2′—Cu—O3′	87.42 (10)	O3^{i}—Li2—O3′	96.8 (3)
O3′—Li1—O4^{i}	122.3 (3)	O*W*3^{i}—Li2—O3′	103.4 (2)
O4^{i}—Li1—O*W*1	116.3 (3)	O*W*3^{i}—Li2—O4′	141.1 (3)
O3′—Li1—O3^{i}	98.7 (3)	O3′—Li2—O4′	86.6 (2)
O4^{i}—Li1—O3^{i}	89.4 (2)		
O2—C2—C3—O3	48.4 (3)	O3′—C3′—C4′—O4′	63.2 (3)
O2′—C2′—C3′—O3′	46.5 (3)	O4—C4—C5—C6	−64.4 (3)
O3—C3—C4—O4	62.9 (3)	O4′—C4′—C5′—C6′	−63.4 (4)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4	HO4	O*W*2	0.65 (3)	2.05 (3)	2.700 (5)	174 (4)
O4′	HO4′	O*W*1^{i}	0.95 (5)	1.99 (5)	2.921 (4)	168 (4)
O*W*1	H*W*11	O2	0.88 (4)	1.75 (3)	2.591 (4)	160 (3)
O*W*1	H*W*12	O2′^{ii}	0.71 (4)	2.17 (4)	2.866 (4)	165 (4)
O*W*2	H*W*21	O1	0.71 (6)	2.25 (6)	2.881 (5)	148 (7)
O*W*2	H*W*22	O4′^{iii}	0.73 (5)	2.23 (5)	2.933 (5)	161 (5)
O*W*3	H*W*31	O2^{iv}	0.72 (3)	2.08 (3)	2.758 (4)	157 (3)
O*W*3	H*W*32	O2′	0.76 (4)	1.91 (3)	2.648 (4)	162 (3)
O*W*4	-	O*W*3^{i}	-	-	2.628 (6)	-
O*W*4	-	O5′	-	-	2.929 (7)	-

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Friedel opposites were not merged. Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*92 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976); *PLATON* (Spek, 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71692 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1071]

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Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane)barium

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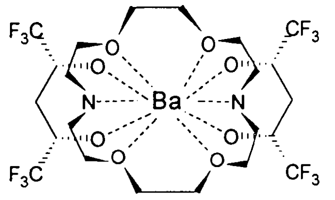
Abstract

In the title compound, $[Ba(C_5HF_6O_2)_2(C_{12}H_2N_2O_4)]$, the Ba^{2+} cation is ten-coordinated by four O and two N atoms from a crown ether, and by four O atoms from two β-diketone ligands. Ba—O and Ba—N distances range from 2.75 to 3.00 Å. The Ba atom is located near the center and 1.343 (1) Å above the mean plane of the crown ether. The two β-diketone ligands are located on the same side of

the complex. There are no significant intermolecular contacts.

Comment

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(1,4,-10,13-tetraoxa-7,16-diazacyclooctadecane)barium, [$Ba(hfa)_2$ diaza18-crown-6], (1), is a candidate for use as a barium precursor for metal-organic chemical-vapor deposition (MOCVD) because of its volatility at temperatures below 473 K. An *ORTEP* (Johnson, 1965) drawing, with numbering scheme, of the complex is shown in Fig. 1.



(1)

A twofold axis passes through the Ba^{2+} cation and the center of the crown ether so that the asymmetric unit contains only one half of the complex. The coordination geometry of (1) is different from the polymeric structure reported for $Ba(hfa)_2$ (Bradley *et al.*, 1992) and the monomeric structures of $Ba(hfa)_2$ 18-crown-6 (Norman & Pez, 1991) and $Ba(hfa)_2$ tetraglyme (van der Sluis, Spek, Timmer & Meinema, 1990). The 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa) ligands in $Ba(hfa)_2$ 18-crown-6 and $Ba(hfa)_2$ tetraglyme are located on opposite sides of the polyether mean plane. In contrast, both β-diketonate ligands in (1) are on the same side of the polyether mean plane. The orientation of the β-diketonate ligands in (1) is similar to that of the thiocyanate ligands in barium thiocyanate complexes containing 18-crown-6 and tetraglyme polyethers (Wei, Tinant, Declercq, van Meerssche & Dale, 1987, 1988).

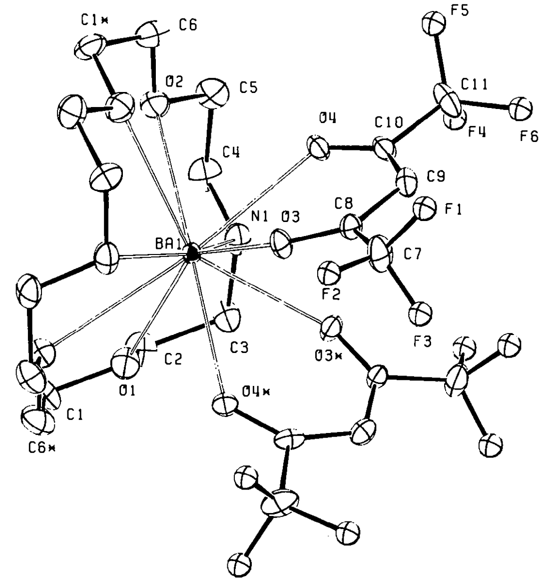


Fig. 1. *ORTEP* (Johnson, 1965) plot for (1). Only half of the molecule is unique and the two halves are related by crystallographic twofold symmetry. The atoms labeled with * have the symmetry equivalent position ($-x, y, \frac{1}{2}-z$).

The Ba–O(3)–O(4) and Ba–O(3^i)–O(4^i) planes of the hfa chelate rings in (1) intersect at an angle of 70.8 (1)° [symmetry code: (i) $-x$, y, $\frac{1}{2}-z$]. The polyether ligand is wrapped around the Ba atom such that the coordinating atoms are nonplanar. Of the polyether-coordinating atoms, N(1) exhibits the largest displacement [0.98 (1) Å] from the polyether mean plane. The Ba atom is located 1.343 (1) Å above the polyether mean plane. The average distance from the Ba atom to the β-diketone O atoms is 2.752 (6) Å. The distances from the Ba atom to the polyether O atoms range from 2.913 (9) to 3.002 (8) Å. The distance from the Ba atom to the polyether N atoms is 2.957 (9) Å. The angle N(1)—Ba—N(1^i) is 166.0 (2)°. In contrast, the angles O(1)—Ba—O(1^i) and O(2)—Ba—O(2^i) are 128.4 (2) and 110.4 (2)°, respectively. The C(2)—C(3)—N(1)—C(4) torsion angle in the $Ba(hfa)_2$ diaza18-crown-6 complex is −79 (1)° whereas the corresponding torsion angle for uncomplexed diaza18-crown-6 is 175.9 (9) Å (Herceg & Weiss, 1972). Thus, the structure of the diaza18-crown-6 ligand distorts significantly when complexed to Ba in $Ba(hfa)_2$ diaza18-crown-6.

As a result of the spacing between adjacent molecules being greater than 3.50 (1) Å, there are no significant intermolecular interactions in the solid-state structure of (1).

Experimental

$Ba(hfa)_2$(18-crown-6) (1) was prepared by mixing 69.6 g of BaH_2 (0.5 mmol), 132 mg of 18-crown-6 (0.5 mmol) and 0.14 ml of Hhfa (1 mmol) under nitrogen. After 2-3 h the mixture was vacuum dried. An alternative preparation method used thf as a solvent. In this method, 0.28 ml of Hhfa (2 mmol) was added by syringe to a stirred mixture containing 140 mg of BaH_2 (1 mmol) and 264 mg of 18-crown-6 (1 mmol) in 20 ml of freshly distilled thf. The mixture was stirred for 3 h under nitrogen and then the solvent was evaporated. Colorless crystals of (1) were obtained by sublimation at 443 K and reduced pressure (1.3 Pa) in evacuable glass sublimation apparatus.

Crystal data

$[Ba(C_5HF_6O_2)_2$-
$(C_{12}H_{26}N_2O_4)]$
$M_r = 813.66$

$D_x = 1.693$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å

Monoclinic
$C2/c$
$a = 22.812\ (7)$ Å
$b = 10.247\ (3)$ Å
$c = 17.015\ (5)$ Å
$\beta = 126.61\ (4)°$
$V = 3192.7$ Å^3
$Z = 4$

Cell parameters from 25 reflections
$\theta = 12–14°$
$\mu = 1.39$ mm^{-1}
$T = 295$ K
Parallelepiped
0.4 × 0.3 × 0.3 mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2723 measured reflections
2723 independent reflections
2121 observed reflections $[I > 2\sigma(I)]$

$\theta_{max} = 25°$
$h = -27 \rightarrow 21$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity variation: insignificant

Refinement

Refinement on F
$R = 0.052$
$wR = 0.061$
$S = 2.0$
2121 reflections
204 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 1.26$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
Ba(1)	0	0.02273 (6)	1/4	0.0443 (3)
F(1)	0.0771 (6)	0.5042 (10)	0.4960 (9)	0.222 (5)
F(2)	0.1493 (5)	0.3928 (10)	0.5077 (12)	0.379 (5)
F(3)	0.0990 (9)	0.5149 (13)	0.4076 (10)	0.281 (5)
F(4)	−0.2200 (4)	0.3101 (9)	0.1444 (6)	0.169 (4)
F(5)	−0.2006 (5)	0.2822 (14)	0.2773 (8)	0.252 (4)
F(6)	−0.1792 (4)	0.4607 (10)	0.2392 (8)	0.215 (4)
O(1)	−0.0111 (4)	−0.1010 (7)	0.0874 (5)	0.096 (3)
O(2)	−0.1179 (4)	−0.1443 (7)	0.2257 (6)	0.101 (4)
O(3)	0.0566 (3)	0.2293 (5)	0.3786 (4)	0.074 (3)
O(4)	−0.0965 (3)	0.1681 (6)	0.2608 (4)	0.078 (3)
N(1)	−0.1429 (4)	−0.0124 (7)	0.0576 (6)	0.089 (4)
C(1)	0.0406 (5)	−0.1992 (2)	0.1078 (8)	0.101 (4)
C(2)	−0.0796 (6)	−0.1307 (12)	0.0009 (8)	0.111 (4)
C(3)	−0.1344 (5)	−0.02111 (10)	−0.0204 (7)	0.091 (4)
C(4)	−0.1902 (5)	−0.1125 (11)	0.0458 (8)	0.104 (4)
C(5)	−0.1917 (4)	−0.1030 (12)	0.1409 (8)	0.100 (4)
C(6)	−0.1160 (7)	−0.1507 (13)	0.3072 (9)	0.118 (4)
C(7)	0.0872 (6)	0.4320 (10)	0.4468 (10)	0.102 (4)
C(8)	0.0323 (4)	0.3337 (8)	0.3816 (6)	0.066 (4)
C(9)	−0.0419 (5)	0.3703 (9)	0.3339 (7)	0.078 (4)
C(10)	−0.0978 (5)	0.2839 (9)	0.2786 (6)	0.072 (4)
C(11)	−0.1742 (6)	0.3330 (14)	0.2359 (9)	0.113 (4)

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

Ba(1)—O(1)	2.913 (9)	O(2)—C(5)	1.48 (1)
Ba(1)—O(2)	3.002 (8)	O(2)—C(6)	1.36 (2)
Ba(1)—O(3)	2.750 (6)	N(1)—C(3)	1.46 (2)
Ba(1)—O(4)	2.753 (7)	N(1)—C(4)	1.41 (1)
Ba(1)—N(1)	2.957 (9)	O(3)—C(8)	1.22 (1)
F(1)—C(7)	1.24 (2)	O(4)—C(10)	1.23 (1)
F(2)—C(7)	1.22 (2)	C(2)—C(3)	1.55 (2)
F(3)—C(7)	1.21 (2)	C(4)—C(5)	1.64 (2)
F(4)—C(11)	1.28 (2)	C(1)—C(6^i)	1.53 (2)
F(5)—C(11)	1.28 (2)	C(7)—C(8)	1.47 (1)
F(6)—C(11)	1.32 (2)	C(8)—C(9)	1.42 (1)
O(1)—C(1)	1.43 (1)	C(9)—C(10)	1.37 (1)
O(1)—C(2)	1.40 (1)	C(10)—C(11)	1.52 (2)
O(1)—Ba(1)—O(3)	145.5 (2)	Ba(1)—N(1)—C(3)	111.0 (6)
O(1)—Ba(1)—O(2^i)	56.4 (2)	Ba(1)—N(1)—C(4)	119.4 (7)
O(1)—Ba(1)—O(1^i)	128.4 (2)	C(3)—N(1)—C(4)	109.4 (9)
O(3)—Ba(1)—O(4)	63.0 (2)	O(1)—C(2)—C(3)	109 (1)
O(3)—Ba(1)—O(3^i)	79.4 (2)	N(1)—C(3)—C(2)	111 (1)
O(4)—Ba(1)—O(3^i)	67.8 (2)	N(1)—C(4)—C(5)	106 (1)
O(4)—Ba(1)—O(4^i)	114.5 (2)	O(2)—C(5)—C(4)	105.2 (8)
O(2)—Ba(1)—N(1)	58.1 (3)	O(1)—C(1)—C(6^i)	107.6 (9)
O(2)—Ba(1)—O(1^i)	56.4 (2)	F(1)—C(7)—F(2)	102 (1)
O(2)—Ba(1)—O(2^i)	110.4 (2)	F(1)—C(7)—C(8)	120 (1)
N(1)—Ba(1)—N(1^i)	166.0 (2)	O(3)—C(8)—C(7)	115.4 (8)
Ba(1)—O(1)—C(2)	120.3 (8)	O(3)—C(8)—C(9)	128.5 (8)
Ba(1)—O(1)—C(1)	119.0 (7)	C(7)—C(8)—C(9)	116.0 (8)
C(5)—O(2)—C(6)	109.4 (9)	C(8)—C(9)—C(10)	121.8 (8)
Ba(1)—O(3)—C(8)	134.3 (5)	O(4)—C(10)—C(9)	130.2 (8)
Ba(1)—O(4)—C(10)	132.5 (6)	O(4)—C(10)—C(11)	113.0 (9)
Ba(1)—O(2)—C(5)	112.0 (6)	C(9)—C(10)—C(11)	116.7 (9)
Ba(1)—O(2)—C(6)	113.9 (7)		
O(1)—C(2)—C(3)—N(1)	−62 (1)	C(4)—C(5)—O(2)—C(6)	−174.6 (9)
C(2)—C(3)—N(1)—C(4)	−79 (1)	C(1)—O(1)—C(2)—C(3)	−179 (1)
C(3)—N(1)—C(4)—C(5)	175.7 (7)	C(2)—O(1)—C(1)—C(6^i)	171 (1)
O(2)—C(5)—C(4)—N(1)	−69 (1)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

*SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1985), *ORTEP* (Johnson, 1965) and some locally written programs were used throughout this work. There was considerable difficulty during refinement resulting from significant disorder, especially of the F atoms, as indicated by unusually large displacement parameters and pseudosymmetry. The structure was refined in both Cc and $C2/c$ space groups, the space group $C2/c$ giving much better refinement. H atoms were not visible in the final difference map and were not included in the refinement.

Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71732 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1051]

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