C7—Pd1—C8	34.65 (8)	34.80 (8)
C7—Pd1—Cr1	85.41 (7)	85.70 (7)
C8—Pd1—Cr1	50.79 (5)	50.92 (5)
C2—Cr1—C3	86.21 (12)	86.84 (11)
C2—Cr1—C1	84.14 (12)	84.18 (12)
C3—Cr1—C1	95.87 (12)	96.17 (11)
C2—Cr1—Pd1	134.95 (8)	135.75 (8)
C3—Cr1—Pd1	69.77 (9)	69.92 (8)
C1—Cr1—Pd1	62.19 (8)	62.60 (8)
C8—Cr1—Pd1	59.75 (6)	59.43 (6)
O1—C1—Cr1	171.3 (2)	171.2 (2)
O2—C2—Cr1	178.6 (2)	178.7 (2)
O3—C3—Cr1	175.1 (3)	174.8 (2)
C6—C5—C4	123.6 (5)	122.9 (4)
C4—C5′—C6′	118.3 (12)	123.5 (17)
C8—C7—C14	120.4 (2)	118.9 (2)
C8—C7—Pd1	88.34 (14)	88.13 (14)
C14—C7—Pd1	111.0 (2)	112.9 (2)
C13—C8—C9	115.4 (2)	115.9 (2)
C13—C8—C7	123.9 (2)	123.5 (2)
C9—C8—C7	120.4 (2)	120.3 (2)
C13—C8—Pd1	108.8 (2)	108.09 (15)
C9—C8—Pd1	100.37 (15)	100.65 (15)
C7—C8—Pd1	57.02 (12)	57.07 (12)
C10—C9—C8	122.5 (2)	121.8 (2)
C9—C10—C11	119.9 (2)	120.6 (2)
C12—C11—C10	119.5 (2)	119.1 (2)
C13—C12—C11	120.6 (2)	120.8 (2)
C12—C13—C8	121.9 (2)	121.7 (2)
C15—C14—C19	117.0 (2)	117.3 (2)
C15—C14—C7	119.8 (2)	123.1 (2)
C19—C14—C7	123.2 (2)	119.6 (2)
C16—C15—C14	121.3 (3)	121.1 (3)
C17—C16—C15	120.5 (3)	120.6 (2)
C16—C17—C18	119.7 (3)	119.4 (2)
C17—C18—C19	119.8 (3)	120.1 (3)
C18—C19—C14	121.7 (3)	121.5 (2)

The structure was solved by direct methods. The Pd and Mo atoms were located in the *E* map; all other atoms were found in difference Fourier syntheses. Careful inspection of the difference map and subsequent refinement of the site occupation factors (s.o.f.) revealed disorder of the allyl-group C atoms over two positions. Constrained refinement of the s.o.f.'s yielded values of 0.81(2) and 0.78(2) for the prevailing isomer for each of the independent molecules. In the final stages of refinement, these values were fixed at 0.8 for both independent molecules; the s.o.f.'s of the alternative isomer were fixed at 0.2. The H atoms corresponding only to the prevailing diastereomer were located and refined, although some of their positions seem to be biased as a result of the contribution of the H atoms of the alternative isomer.

The final refinement was performed on F^2 for all reflections, including those generally believed to be unobserved [$F^2 < 2\sigma(F^2)$] and even those having negative F^2 but larger than $-3\sigma(F^2)$ (no reflections were rejected according to the latter criterion); 15 reflections obscured by the primary beam stop or thought to be affected by temperature instability were omitted. The final conventional *R* factor was 0.0302 for all reflections and 0.0237 for the 6032 observed reflections with $F > 4\sigma(F)$. The weighted *wR*2 factor (calculated on F^2) was 0.0632 for all data and 0.0567 for the observed data.

Both independent molecules are virtually geometrically identical (see *Comment*) and the coordinates of the corresponding atoms satisfy the following approximate relationship:

$$x(A) + x(B) = 0.5; \quad y(A) + y(B) = 1.$$

However, careful geometric analysis of the unit-cell parameters leaves no possibility for metric symmetry higher than triclinic.

0108-2701/93/040808-03$06.00

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55783 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1029]

References

Bender, R., Braunstein, P., Jud, J.-M. & Dusausoy, Y. (1983). *Inorg. Chem.* **22**, 3394-3407.

Kalinin, V. N., Cherepanov, I. A., Moiseev, S. K., Batsanov, A. S. & Struchkov, Yu. T. (1991). *Mendeleev Commun.* pp. 77-78.

Robinson, W. & Sheldrick, G. M. (1988). *SHELXS86*. In *Crystallographic Computing* 4, edited by N. W. Isaacs & M. R. Taylor, pp. 366-392. Oxford Univ. Press.

Rybinskaya, M. I., Kreindlin, A. Z., Struchkov, Yu. T. & Yanovsky, A. I. (1989). *J. Organomet. Chem.* **359**, 233-243.

Sheldrick, G. M. (1992). *SHELXL92*. Beta-test version. Program for the refinement of crystal structures. Univ. of Göttingen, Germany.

Watts, W. E. (1979). *J. Organomet. Chem. Libr.* **7**, 399-459.

Acta Cryst. (1993). C**49**, 808–810

Barium Bis(trimethylacetate)–18-crown-6 (1/1)

ARNOLD L. RHEINGOLD,* CORBET B. WHITE AND BRIAN S. HAGGERTY

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

PETER KIRLIN AND ROBIN A. GARDINER

Advanced Technology Materials, Inc., Danbury, CT 06810, USA

(*Received* 12 *May* 1992; *accepted* 13 *October* 1992)

Abstract

The (1,4,7,10,13,16-hexaoxacyclooctadecane)bis(trimethylacetato)barium molecule is contained in a $P\bar{1}$ triclinic cell. The Ba atom is located on an inversion center. There are two trimethylacetate ligands coordinated to the Ba atom which is encapsulated by an 18-crown-6 ether ring. The Ba atom is ten coordinate with an average Ba—O(18-crown-6) bond distance of 2.823 (6) Å and an average Ba—O(trimethylacetate) bond distance of 2.835 (8) Å.

Comment

This compound is the first barium crown ether useful for superconductor fabrication. The six crown-ether O atoms bonded to the Ba atom assume an almost

planar arrangement but deviate by ±0.19 Å from the least-squares plane. Fig. 2 shows the crystal packing viewed down the short *a* axis.

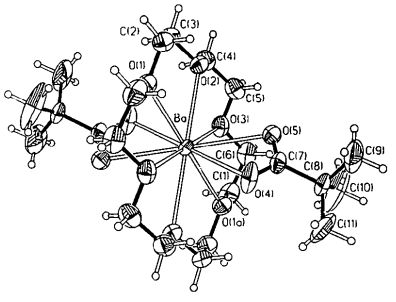


Fig. 1. Thermal ellipsoid diagram for barium bis(trimethylacetate)–18-crown-6.

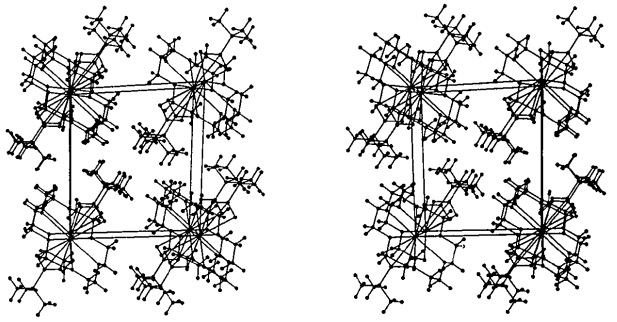


Fig. 2. Unit-cell packing diagram for barium bis(trimethylacetate)–18-crown-6. As viewed down the *a* axis.

Dyer, Metcalf, Ghirardelli, Palmer & Holt (1986) reported a related Ba-salt crown-ether structure with a nitrate ion replacing the trimethylacetate ion and containing additional methyl groups bonding directly to the Ba. The Ba—O(18-crown-6) bond distances (average 2.833 Å) are similar to those in the title compound.

Experimental

Crystal data

$[Ba(C_5H_9O_2)_2(C_{12}H_{24}O_6)]$
M_r = 603.9
Triclinic
$P\bar{1}$
a = 7.705 (11) Å
b = 9.664 (10) Å
c = 11.285 (14) Å
α = 82.17 (9)°
β = 70.42 (9)°
γ = 71.75 (9)°
V = 751.7 (15) Å^3
Z = 1
D_x = 1.334 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 20–25°
μ = 1.365 mm^{-1}
T = 295 K
Cube
0.48 × 0.40 × 0.40 mm
Colorless
Crystal source: recrystallization from toluene

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2085 measured reflections
1966 independent reflections
1922 observed reflections $[F_o > 4\sigma(F_o)]$
R_{int} = 0.0276
θ_{max} = 45.0°
$h = -7 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 197 reflections
intensity variation: <2%

Refinement

Refinement on F
Final R = 0.0561
wR = 0.0732
S = 1.72
1922 reflections
152 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o)+0.001F_o^2]$
$(\Delta/\sigma)_{max}$ = 0.035
$\Delta\rho_{max}$ = 2.91 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}
Extinction correction: empirical isotropic
Extinction coefficient: 1.88553, 0.00211
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ba	0	0	0	0.040 (1)
O(1)	0.3316 (9)	0.0095 (7)	−0.2014 (6)	0.061 (3)
O(2)	0.3641 (9)	−0.1747 (7)	0.0119 (6)	0.061 (3)
O(3)	0.0229 (10)	−0.2266 (7)	0.1868 (6)	0.063 (3)
O(4)	−0.0919 (13)	0.2695 (7)	0.1103 (6)	0.082 (4)
O(5)	0.0445 (9)	0.0834 (7)	0.2184 (6)	0.063 (3)
C(1)	−0.3247 (17)	−0.1386 (13)	0.2724 (11)	0.081 (6)
C(2)	0.5112 (14)	−0.0488 (13)	−0.1778 (11)	0.076 (5)
C(3)	0.5108 (14)	−0.1945 (13)	−0.1082 (11)	0.080 (5)
C(4)	0.3582 (16)	−0.3078 (11)	0.0819 (11)	0.072 (5)
C(5)	0.2055 (15)	−0.2758 (11)	0.2055 (10)	0.070 (5)
C(6)	−0.1325 (17)	−0.1925 (11)	0.3016 (10)	0.074 (5)
C(7)	−0.0573 (13)	0.2085 (10)	0.2116 (9)	0.053 (4)
C(8)	−0.1570 (15)	0.3008 (10)	0.3332 (9)	0.062 (4)
C(9)	−0.0123 (24)	0.3625 (19)	0.3547 (15)	0.146 (11)
C(10)	−0.2251 (33)	0.2059 (19)	0.4426 (13)	0.185 (15)
C(11)	−0.3216 (29)	0.4263 (24)	0.3227 (17)	0.241 (16)

Table 2. *Bond lengths* (Å) *and angles* (°)

Ba—O(1)	2.813 (6)	Ba—O(2)	2.825 (6)
Ba—O(3)	2.832 (6)	Ba—O(4)	2.822 (8)
Ba—O(5)	2.847 (8)	Ba—C(7)	3.160 (11)
O(1)—C(2)	1.423 (13)	O(1)—C(1*A*)	1.384 (13)
O(2)—C(3)	1.436 (11)	O(2)—C(4)	1.419 (12)
O(3)—C(5)	1.416 (15)	O(3)—C(6)	1.433 (11)
O(4)—C(7)	1.283 (12)	O(5)—C(7)	1.228 (10)
C(1)—C(6)	1.540 (19)	C(2)—C(3)	1.515 (17)
C(4)—C(5)	1.489 (14)	C(7)—C(8)	1.572 (13)
C(8)—C(9)	1.513 (26)	C(8)—C(10)	1.483 (19)
C(8)—C(11)	1.482 (22)		
O(1)—Ba—O(2)	60.2 (2)	O(5)—Ba—O(1*A*)	72.8 (2)
O(2)—Ba—O(3)	60.6 (2)	O(2)—Ba—O(2*A*)	180.0 (1)
O(2)—Ba—O(4)	109.5 (3)	O(4)—Ba—O(2*A*)	70.5 (3)
O(1)—Ba—O(5)	107.2 (2)	C(7)—Ba—O(2*A*)	86.0 (2)
O(3)—Ba—O(5)	66.7 (2)	O(3)—Ba—O(3*A*)	180.0 (1)
O(1)—Ba—C(7)	109.7 (2)	O(5)—Ba—O(3*A*)	113.3 (2)
O(3)—Ba—C(7)	85.8 (2)	O(4)—Ba—O(4*A*)	180.0 (1)
O(5)—Ba—C(7)	22.8 (2)	C(7)—Ba—O(4*A*)	156.1 (2)
O(2)—Ba—O(1*A*)	119.8 (2)	C(7)—Ba—O(5*A*)	157.2 (2)
O(4)—Ba—O(1*A*)	78.8 (2)	O(5*A*)—Ba—C(7*A*)	22.8 (2)
C(7)—Ba—O(1*A*)	70.3 (2)	Ba—O(1)—C(1*A*)	116.8 (5)

O(3)—Ba—O(2A)	119.4 (2)	Ba—O(2)—C(3)	113.8 (6)
O(5)—Ba—O(2A)	106.1 (2)	C(3)—O(2)—C(4)	112.9 (7)
O(1A)—Ba—O(2A)	60.2 (2)	Ba—O(3)—C(6)	112.8 (5)
O(4)—Ba—O(3A)	70.8 (2)	Ba—O(4)—C(7)	93.0 (6)
C(7)—Ba—O(3A)	94.2 (2)	C(6)—C(1)—O(1A)	109.1 (10)
O(5)—Ba—O(4A)	134.0 (2)	O(1)—C(2)—C(3)	107.4 (10)
O(5)—Ba—O(5A)	180.0 (1)	O(2)—C(4)—C(5)	108.8 (7)
C(7)—Ba—C(7A)	180.0 (1)	O(3)—C(6)—C(1)	109.6 (10)
Ba—O(1)—C(2)	117.1 (6)	Ba—C(7)—O(5)	64.1 (6)
C(2)—O(1)—C(1A)	111.2 (9)	Ba—C(7)—C(8)	159.5 (7)
Ba—O(2)—C(4)	113.2 (6)	O(5)—C(7)—C(8)	119.3 (9)
Ba—O(3)—C(5)	112.8 (6)	C(7)—C(8)—C(10)	109.4 (10)
C(5)—O(3)—C(6)	113.1 (9)	C(7)—C(8)—C(11)	113.0 (11)
Ba—O(5)—C(7)	93.1 (7)	C(10)—C(8)—C(11)	108.9 (12)
O(1)—Ba—O(3)	119.4 (2)	O(2)—C(3)—C(2)	110.4 (8)
O(1)—Ba—O(4)	101.2 (2)	O(3)—C(5)—C(4)	109.6 (10)
O(3)—Ba—O(4)	109.2 (2)	Ba—C(7)—O(4)	63.1 (5)
O(2)—Ba—O(5)	73.9 (2)	O(4)—C(7)—O(5)	123.8 (9)
O(4)—Ba—O(5)	46.0 (2)	O(4)—C(7)—C(8)	116.9 (7)
O(2)—Ba—C(7)	94.0 (2)	C(7)—C(8)—C(9)	108.7 (9)
O(4)—Ba—C(7)	23.9 (2)	C(9)—C(8)—C(10)	109.8 (14)
O(1)—Ba—O(1A)	180.0 (1)	C(9)—C(8)—C(11)	107.0 (14)
O(3)—Ba—O(1A)	60.6 (2)		

Structure solved by direct methods (*SOLV*) and refined by full-matrix least squares. All non-H atoms anisotropic, all H-atom parameters assumed [*d*(C—H) = 0.960 Å, fixed isotropic U = 0.08 Å^2]. Calculations were performed using *SHELXTL-Plus* (Sheldrick, 1990).

Atomic coordinates and isotropic thermal parameters are given in Table 1, bond lengths and angles in Table 2.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55738 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1022]

References

Dyer, R. B., Metcalf, D. H., Ghirardelli, R. G., Palmer, R. A. & Holt, E. M. (1986). *J. Am. Chem. Soc.* **108**, 3621–3627.

Sheldrick, G. M. (1990). *SHELXTL-Plus*, version 4.21/V. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Acta Cryst. (1993). C**49**, 810–813

3,4,5-Trihydroxybenzohydroxamic Acid Monohydrate, a Ribonucleotide Reductase Inhibitor

BETTINA BRYDE NIELSEN AND INGRID KJØLLER LARSEN

Department of Organic Chemistry, Royal Danish School of Pharmacy, DK-2100 Copenhagen, Denmark

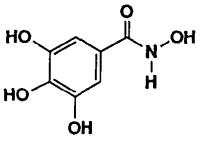
(*Received* 7 *August* 1992; *accepted* 27 *October* 1992)

Abstract

The 3,4,5-trihydroxybenzohydroxamic acid molecule consists of two approximately planar parts: the hydroxamic acid moiety and the phenyl ring with the hydroxy substituents. These two planes are twisted relative to each other with a dihedral angle of 34.3 (1)°. The conformation of O=C—N—O is synperiplanar with a torsion angle of −5.4 (4) °. The crystal structure is stabilized by an intensive and complex pattern of hydrogen bonding, in which the water molecule plays a central role.

Comment

The anticancer agent hydroxyurea exerts its ribonucleotide reductase (RNR) inhibitory activity by destroying the tyrosyl free radical in RNR, thereby leaving the enzyme inactive (Atkin, Thelander, Reichard & Lang, 1973; Gräslund, Ehrenberg & Thelander, 1982; Thelander, Gräslund & Thelander, 1985; Howell, Sanders-Loehr, Loehr, Roseman, Mathews & Slabaugh, 1992). In a search for anticancer drugs with the same target of action Elford, Wampler & van't Riet (1979) tested a series of compounds including polyhydroxylated benzohydroxamic acids. 3,4-Dihydroxybenzohydroxamic acid (3,4-OHBHA), 2,3,4-trihydroxybenzohydroxamic acid (2,3,4-OHBHA) and 3,4,5-trihydroxybenzohydroxamic acid (3,4,5-OHBHA) were all found to have strong inhibitory activities on partially purified RNR from Novikoff hepatoma cells. These



3,4,5-OHBHA

compounds were found to have stronger inhibitory effects than hydroxyurea on the mammalian RNR (Elford, van't Riet, Wampler, Lin & Elford, 1981), whereas the *E. coli* RNR and the phage T4 RNR were found to be more sensitive towards hydroxyurea than towards the polyhydroxylated benzohydroxamic acids (Kjøller Larsen, Sjöberg & Thelander, 1982). In an early structure–activity study of hydroxyurea analogues using HeLa cells it was shown that an unsubstituted OH group at the N atom was required for activity (Young, Schochetman, Hodas & Balis, 1967). On the other hand, Elford *et al.* (1979) found that polyhydroxylated benzamides and methyl benzoates were also inhibitors of RNR, indicating that in these compounds the hydroxamic acid moiety is not essential for RNR inhibitory activity. The polyhydroxylated aromatic part of the compounds seems to be the part interfering with the tyrosyl radical of the enzyme.

By testing a series of hydroxyurea analogues (Larsen, 1980; Kjøller Larsen *et al.*, 1982) or polyhydroxybenzene derivatives (Elford *et al.*, 1981) it has been found that the ability of a compound to undergo one-electron oxidation is correlated with its inhibitory activity towards RNR. In addition, the most potent inhibitors were approximately planar molecules. The crystal structure of the small sub-

0108-2701/93/040810-04$06.00