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Barium(II)–2,4-dinitrophenolate–18-crown-6 at 183 K

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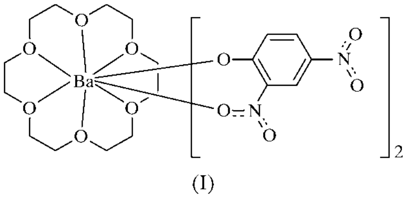
The title compound, bis(2,4-dinitrophenolato-κ^2O,O')(1,4,7,10,13,16-hexaoxadecane-κ^6O)barium(II), $[Ba(C_6H_3N_2O_5)_2(C_{12}H_{24}O_6)]$, is a 1:1 complex of barium(II)–2,4-dinitrophenolate and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6). Its structure is located on a crystallographic inversion centre. The temperature dependence of the crystal structure has been studied. The monoclinic β angle of the $P2_1/n$ space group increases with increasing temperature. The packing structure of the complex is stabilized by intermolecular C—H···O interactions.

Comment

Complexes of alkaline-earth metal cations with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) have been investigated intensively (Dyer *et al.*, 1986; Wei *et al.*, 1988; Luger *et al.*, 1992; Rheingold *et al.*, 1993). In general, the studies are on the structures of the complexes, including the conformation of the macrocycle and the position of the metal cation relative to the crown centre. Interest has centred on the different nature of the metal cation and the counter-anion.



(I)

In this study, we prepared the title complex, (I), whose counter-anion is 2,4-dinitrophenolate, in which the nitro groups are expected to be involved in intermolecular C—H···O interactions. The cell parameters of (I) were evaluated in the temperature range 123–300 K in order to explore the temperature dependences of the crystal cell parameters, while the geometry and weak interactions were analyzed for the data collected at 183 K.

In the temperature range studied, complex (I) belongs to the monoclinic $P2_1/n$ space group. Fig. 1 shows the continuous temperature dependence of the a, b and c lattice parameters, and the monoclinic β angle. Though a and b increase, the c lattice parameter decreases with increasing temperature (Fig. 1). The important observation is the variation of the β angle with temperature for this structure. Since the monoclinic system is determined by the value of β, any variation of the monoclinic β angle with temperature implies that the crystal of (I) exhibits a temperature-dependent crystal structure.

The crystallographic data for complex (I) at the chosen temperature (183 K) show that the asymmetric unit of the monoclinic $P2_1/n$ system consists of only one half of the molecule of (I) and the other half of the molecule is related by a centre of inversion at the Ba atom. The unit cell contains two molecules. The Ba atom lies at the crown centre, and the C1 and C6 atoms of the first half of the 18-crown-6 are connected to the C6*A* and C1*A* atoms of the second half and *vice versa*, while the whole 2,4-dinitrophenolate (dnp) moiety is inverted to the opposite side of the 18-crown-6 ring. The Ba atom is ten-coordinated to the six O atoms of the 18-crown-6 and the four O atoms of the two 2,4-dinitrophenolate moieties.

The atomic numbering scheme and molecular conformation of (I) are shown in Fig. 2. The bond lengths and angles are

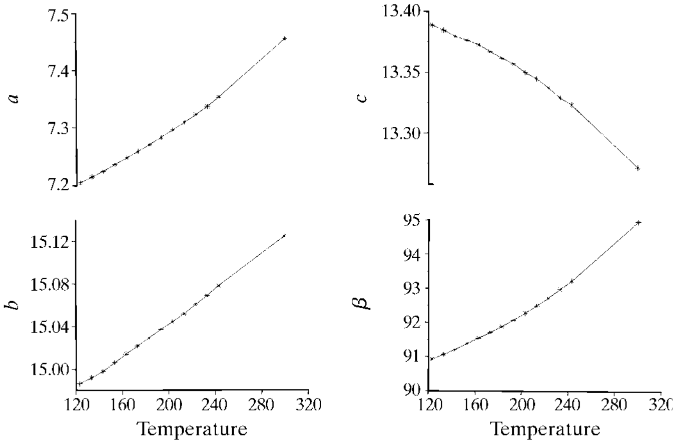


Figure 1
Temperature (K) variation of the cell parameters (Å, °) of complex (I).

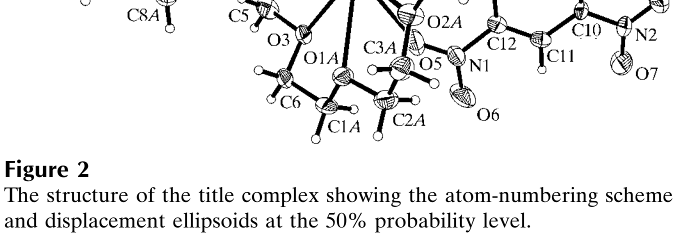


Figure 2
The structure of the title complex showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

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normal (see Table 1). The average Ba—O$_{crown}$ and Ba—O$_{dnp}$ distances are 2.801 (3) and 2.842 (3) Å. The average Ba—O$_{crown}$ distance in (I) is slightly shorter than that in the room-temperature structure of bariumbis(trimethylacetate)–18-crown-6 [2.823 (6) Å; Rheingold *et al.*, 1993], while the average Ba–O$_{dnp}$ distance is slightly shorter that the sum of the covalent radii for Ba and O atoms of 2.87 Å (Shannon, 1976).

Both the 2,4-dinitrophenolate moieties are essentially planar, with a maximum deviation of 0.012 (4) Å. The dihedral angle between the planes through the 2,4-dinitrophenolate moiety and Ba/O4/O5 is 12.8 (2)°, and that of the planes through the 18-crown-6 and 2,4-dinitrophenolate moieties is 66.7 (1)°.

In the 18-crown-6 macrocycle, the C atoms deviate from its least-squares plane to within ±0.355 (4) Å, with average C—O and C—C distances of 1.427 (7) and 1.501 (7) Å, respectively. The C—O bond lengths are normal for C—O single bonds (Allen *et al.*, 1987), whereas the C—C bond lengths are considerably shorter than the average value for a Csp^3—Csp^3 single bond. The average C—C bond length is also shorter by 0.011 Å than that of uncomplexed 18-crown-6 at 100 K (Maverick *et al.*, 1980) or shorter by 0.014 Å from that of the room-temperature structure of barium(II)bis(trimethylacetate)–18-crown-6 (Rheingold *et al.*, 1993). This so-called macrocyclic C—C shortening effect has been observed in a number of crown-ether structures, and has also been intensively discussed (Shoham *et al.*, 1983).

The conformation of the 18-crown-6 macrocycle in the present complex is that of the typical crown-ether arrangement determined by the torsion angles within the crown ring (Table 1). The usual O—C—C—O and C—O—C—C torsion angles, which are close to +*sc* or −*sc* and *ap* conformations, respectively, were observed, indicating that the rigid 18-crown-6 macrocycle has approximately D_{3d} symmetry.

The packing structure of the title complex is stabilized by intermolecular C—H···O interactions (Table 2). Two of the interactions [C2—H2*B*···O8($\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$) and C6—H6*A*···O8($x, y, 1+z$)] interconnect the molecules into layers stacked along the *b* axis. The C···O distances of the weak interactions are decreased slightly compared with those of the structure at 300 K. Irrespective of almost similar C—H···O angles, the weak interactions are strengthened as the temperature decreases, especially for C6···O4.

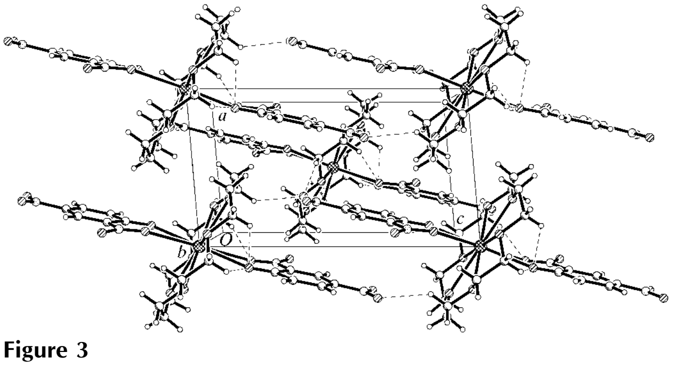

Figure 3
Packing diagram of (I) viewed down the *b* axis. The dashed lines denote the hydrogen bonds.

Experimental

The title complex was prepared by thoroughly mixing 3.16 g (10 mmol) of $Ba(OH)_2 \cdot 8H_2O$, 3.68 g (20 mmol) of 2,4-dinitrophenol and 2.64 g (10 mmol) of 18-crown-6 and then dissolving in 50 ml of ethanol. Distilled water (2 ml) was then added and the mixture was warmed until a solution was obtained. The solution was filtered and left to evaporate slowly in air. Orange single crystals suitable for X-ray data collection were obtained from the solution after a few days.

Crystal data

$[Ba(C_6H_3N_2O_5)_2(C_{12}H_{24}O_6)]$
$M_r = 767.86$
Monoclinic, $P2_1/n$
$a = 7.2679$ (3) Å
$b = 15.0351$ (7) Å
$c = 13.3607$ (6) Å
$\beta = 91.921$ (1)°
$V = 1459.1$ (1) Å^3
$Z = 2$
$D_x = 1.748$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7844 reflections
$\theta = 2.0$–29.5°
$\mu = 1.45$ mm^{-1}
$T = 183$ (2) K
Block, yellow
0.44 × 0.16 × 0.12 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.569$, $T_{max} = 0.846$
7712 measured reflections
2486 independent reflections
2043 reflections with $I > 2\sigma(I)$
$R_{int} = 0.071$
$\theta_{max} = 25°$
$h = -8 \rightarrow 7$
$k = -17 \rightarrow 16$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.121$
$S = 1.04$
2486 reflections
206 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.14$ e Å^{-3}
$\Delta\rho_{min} = -1.32$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0063 (11)

Table 1
Selected geometric parameters (Å, °).

Ba1—O4	2.689 (3)	O2—C4	1.436 (5)
Ba1—O2	2.732 (3)	O3—C5	1.430 (5)
Ba1—O1	2.804 (3)	O3—C6	1.434 (5)
Ba1—O3	2.864 (3)	O4—C7	1.252 (5)
Ba1—O5	2.995 (3)	C1—C6^i	1.514 (6)
N1—O6	1.229 (4)	C2—C3	1.498 (7)
N1—O5	1.242 (4)	C4—C5	1.492 (6)
N1—C12	1.431 (5)	C7—C8	1.448 (6)
N2—O7	1.212 (5)	C7—C12	1.459 (6)
N2—O8	1.218 (5)	C8—C9	1.363 (6)
N2—C10	1.456 (6)	C9—C10	1.407 (6)
O1—C2	1.409 (5)	C10—C11	1.370 (6)
O1—C1	1.432 (5)	C11—C12	1.378 (6)
O2—C3	1.422 (6)		
O4—Ba1—O2	104.35 (9)	O2—Ba1—O3	60.10 (8)
O4—Ba1—O1	72.30 (8)	O2—Ba1—O5	95.86 (10)
O2—Ba1—O1	59.69 (9)	O1—Ba1—O5	114.48 (9)
O4—Ba1—O3	114.19 (8)	O3—Ba1—O5	62.92 (8)
C2—O1—C1—C6^i	179.2 (3)	C3—O2—C4—C5	−166.3 (4)
C1—O1—C2—C3	175.4 (4)	C6—O3—C5—C4	176.8 (3)
C4—O2—C3—C2	172.4 (4)	O2—C4—C5—O3	−61.8 (5)
O1—C2—C3—O2	55.9 (5)	C5—O3—C6—C1^i	−179.4 (3)

Symmetry code: (i) $-x, -y, -z$.

Table 2
Geometries (Å, °) of the hydrogen-bonding interactions.

Data at 300 K are unpublished.

	$D\cdots$H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$A\cdots$O5^{i}				
300 K	0.96	2.55	3.199 (8)	125
183 K	0.96	2.56	3.172 (5)	122
C2—H2$B\cdots$O8^{ii}				
300 K	0.96	2.52	3.275 (7)	136
183 K	0.96	2.55	3.266 (7)	132
C5—H5$A\cdots$O4^{i}				
300 K	0.96	2.62	3.231 (7)	122
183 K	0.96	2.60	3.198 (5)	121
C6—H6$A\cdots$O8^{iii}				
300 K	0.96	2.57	3.468 (7)	155
183 K	0.96	2.57	3.460 (6)	154
C6—H6$B\cdots$O4^{i}				
300 K	0.96	2.56	3.180 (6)	123
183 K	0.96	2.49	3.119 (5)	123

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

All H atoms were fixed geometrically and allowed to ride on their parent C atoms, with C—H = 0.96 Å, and were refined isotropically with fixed displacement parameters, $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1500). Services for accessing these data are described at the back of the journal.

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