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A ternary complex of aqua(18-crown-6)bis(*o*-nitrophenolato)barium(II), the triaqua(18-crown-6)(*o*-nitrophenolato)barium(II) cation and the *o*-nitrophenolate anion

Suchada Chantrapromma,[a] Anwar Usman[b] and Hoong-Kun Fun[b]*

[a]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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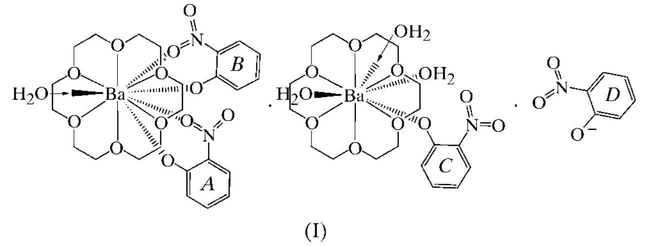
In the title compound [systematic name: triaqua(1,4,7,10,13,16-hexaoxacyclooctadecane-κ^6O)(2-nitrophenolato-κO)barium(II)–aqua(1,4,7,10,13,16-hexaoxacyclooctadecane-κ^6O)bis(2-nitrophenolato-κ^2O,O')barium(II)–2-nitrophenolate (1/1/1)], $[Ba(C_{12}H_{24}O_6)(C_6H_4NO_3)(H_2O)_3][Ba(C_{12}H_{24}O_6)(C_6H_4NO_3)_2(H_2O)](C_6H_4NO_3)$, the two Ba^{II} atoms encapsulated by the 18-crown-6 rings have different coordinations. Although both Ba^{II} atoms are coordinated to the six O atoms of the crowns, in the neutral moiety, the Ba^{II} atom is coordinated to one terminal O atom from a water molecule, two phenolate O atoms and two nitro-group O atoms, while in the cationic moiety, the Ba^{II} atom is coordinated to three terminal O atoms from water molecules and one phenolate O atom. Both the crowns are eclipsed and translated along the *b* direction. In the asymmetric unit, the three components are interconnected by four O—H···O interactions. The packing is stabilized by two intermolecular C—H···O interactions and by one O—H···O interaction.

Comment

Several complexes of barium with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) have been reported (Wei *et al.*, 1988; Rheingold *et al.*, 1993; Usman *et al.*, 2002). In these papers, analyses of the structures of the complexes and the temperature-dependent crystal cell parameters were the main points of interest. As part of our systematic studies of the temperature-dependent crystal cell parameters of 18-crown-6 complexed with barium(II) phenolate derivatives, we have prepared the ternary title complex, (I). However, the cell parameters are almost constant in the temperature range from 300 to 183 K. An X-ray crystal structure determination of (I) was undertaken at 300 K, and the results are reported here. Compound (I) is a ternary complex of neutral aqua(18-crown-6)bis(*o*-nitrophenolato)barium(II), a triaqua(18-crown-6)(*o*-nitrophenolato)barium(II) cation and an *o*-nitrophenolate anion.



(I)

In the neutral moiety, the Ba^{2+} cation is 11-coordinate, which is rare for Ba in 18-crown-6–barium(II) complexes, to the six O atoms of the crown (average $Ba—O_{crown}$ = 2.970 Å), the water O atom on one side [$Ba—O_{water}$ = 2.836 (4) Å], and the O atoms of the phenolate and nitro groups of two *o*-nitrophenolate ligands on the opposite side (average $Ba—O_{phenolate}$ = 2.700 Å and $Ba—O_{nitro}$ = 2.989 Å). These average Ba—O bond lengths are slightly elongated when compared with those in related structures [$Ba—O_{crown}$ = 2.823 (Rheingold *et al.*, 1993) and 2.794 Å (Usman *et al.*, 2002), and $Ba—O_{phenolate}$ = 2.689 Å and $Ba—O_{nitro}$ = 2.995 Å (Usman *et al.*, 2002)].

The rigid 18-crown-6, as is usually observed, has approximate D_{3d} symmetry, with average C—O and C—C bond distances of 1.434 and 1.479 Å, respectively, and O—C—C—O and C—O—C—C torsion angles close to +*sc* or −*sc* and *ap*. The O atoms of the crown form a regular hexagon, with nonbonded O···O distances in the range 2.771 (5)–2.871 (5) Å, and, together with atoms Ba1 and O7, they form a distorted

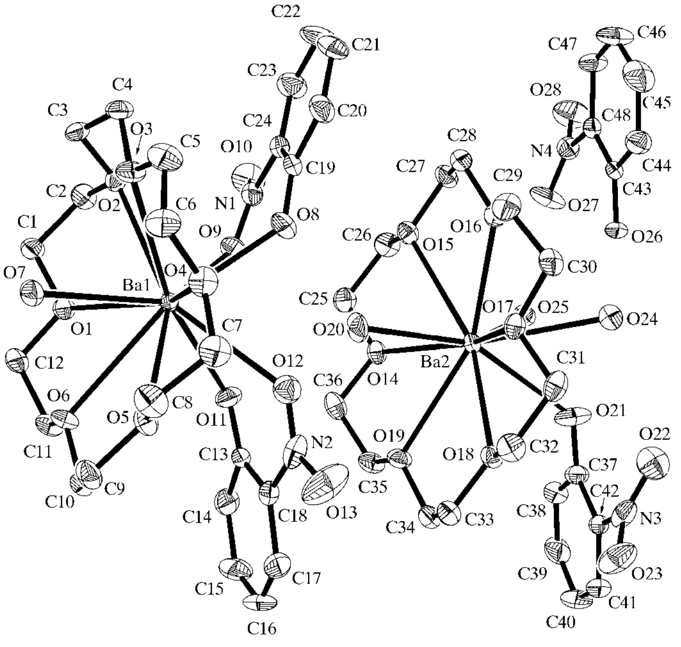


Figure 1
The structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. For the sake of clarity, all H atoms have been omitted.

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hexagonal bipyramid. The apices Ba1 and O7 are displaced by 1.055 (1) and 1.775 (1) Å, respectively, from the basal hexagon. The aromatic rings, *A* and *B* (see *Scheme*), of the two phenolates and the crown plane make dihedral angles of 12.8 (2) and 14.9 (2)°, respectively. The nitro groups (N1/O9/O10 and N2/O12/O13) are both twisted by an angle of 7.1 (3)° from their attached aromatic rings.

In the cationic moiety, the Ba^{2+} cation is ten-coordinate, as is usually observed in 18-crown-6–barium(II) complexes (Wei *et al.*, 1988; Rheingold *et al.*, 1993; Usman *et al.*, 2002), to the six O atoms of the crown [average $Ba—O_{crown}$ = 2.857 (16) Å], the three water O molecules [average $Ba—O_{water}$ = 2.83 (8) Å] and the phenolate O atom [$Ba—O_{phenolate}$ = 2.982 (5) Å]. For comparison, in the neutral complex, the average $Ba—O_{crown}$ distance is 2.97 (6) Å, the $Ba—O_{water}$ distance is 2.836 (4) Å and the average $Ba—O_{phenolate}$ distance is 2.70 (2) Å.

The crown ether of this moiety also adopts approximate D_{3d} symmetry. The average C—O and C—C bond distances (1.430 and 1.484 Å, respectively), the O—C—C and C—O—C angles (average O—C—C = 109.3° and C—O—C = 112.2°), and the O—C—C—O and C—O—C—C torsion angles are all comparable with those in the neutral moiety. The hexagonal bipyramid formed by the regular hexagon of the O atoms of the crown ether is also similar, with atoms Ba2 and O20 as the apices. The O···O distances of the hexagon are in the range 2.778 (5)–2.826 (6) Å, and atoms Ba2 and O20 are displaced by 0.656 and 2.056 Å, respectively. The aromatic ring *C* (see *Scheme*) of the phenolate and the crown-ether plane make a dihedral angle of 19.9 (2)°, and the nitro group (N3/O22/O23) is twisted by an angle of 31.7 (3)° from the aromatic ring.

In the phenolate counter-anion, *D* (see *Scheme*), the nitro group (N4/O27/O28) is twisted by an angle of 25.8 (3)° from the aromatic ring. This ring is coplanar with aromatic ring *C*, the corresponding angle between these two planes being 0.6 (2)°. The closest atom to Ba2 is atom O26, with a Ba2···O26 distance of 4.277 (5) Å.

It should be noted that both crown-ring systems (neutral and cationic moieties) are eclipsed and coplanar with each other, with an average $O_{crown}—Ba1\cdots Ba2—O_{crown}$ torsion angle of 1.0° and a dihedral angle between the crown ring systems of 1.7 (1)°. The crown fragment of the neutral moiety is translated by 6.766 Å from the crown of the cationic moiety, approximately along the *b* direction. However, the two pairs of phenolates, *viz.* *A*/*B* and *C*/*D*, have slightly different orientations towards their crown rings due to the different $Ba—O_{nitro}$ bonds. The twisted angles of the nitro groups of phenolates *A* and *B* are also much smaller compared with those in phenolates *C* and *D*.

In the asymmetric unit of (I), the three components are interconnected *via* intermolecular O20—H12*W*···O11, O20—H12*W*···O12, O20—H22*W*···O8 and O25—H24*W*···O27 interactions (Table 2). The symmetry-related neutral and cationic moieties are linked *via* a C3—H3*A*···O26^{i} intermolecular bond into molecular columns along the *b* direction, and these molecular columns are interconnected by C36—H36*A*···O27^{ii} and O7—H21*W*···O26^{ii} interactions (Fig. 2) [symmetry codes: (i) $x, y-1, z$; (ii) $2-x, 1-y, 1-z$].

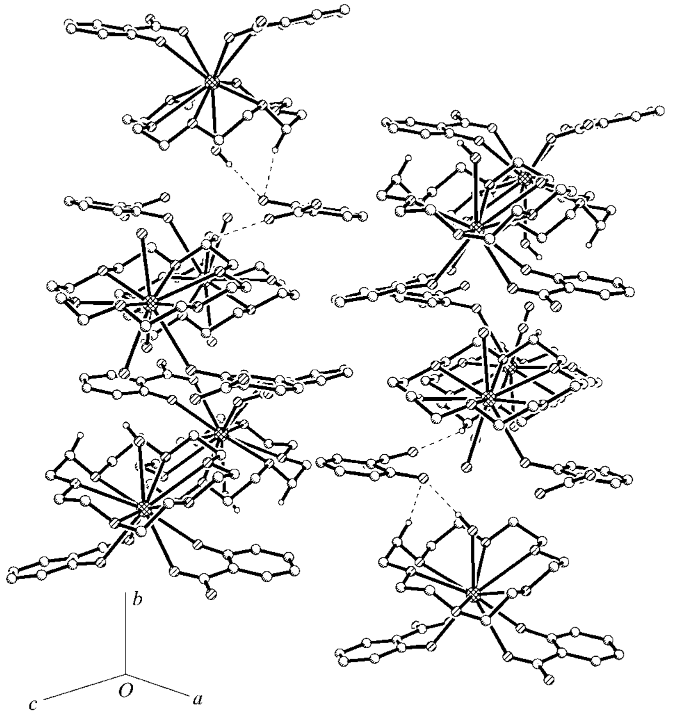

Figure 2
A packing diagram for (I). Dashed lines denote intermolecular C—H···O and O—H···O interactions. All H atoms, except those involved in intermolecular interactions, have been omitted.

Experimental

The ternary title complex was prepared by thoroughly mixing $Ba(OH)_2\cdot 8H_2O$ (1.58 g, 5 mmol), 2-nitrophenol (1.39 g, 10 mmol) and 18-crown-6 (1.32 g, 5 mmol) in ethanol (50 ml). Distilled water (2 ml) was then added and the mixture warmed until all the solid had dissolved. The solution was filtered and left to evaporate slowly in air. Orange block-shaped single crystals of (I) suitable for X-ray analysis were obtained after a few days.

Crystal data

$[Ba(C_{12}H_{24}O_6)(C_6H_4NO_3)(H_2O)_3]$-$[Ba(C_{12}H_{24}O_6)(C_6H_4NO_3)_2$-$(H_2O)](C_6H_4NO_3)$
M_r = 1427.78
Triclinic, $P\overline{1}$
a = 13.7492 (3) Å
b = 14.9672 (3) Å
c = 16.8669 (3) Å
α = 97.9362 (2)°
β = 109.7546 (7)°
γ = 108.8642 (7)°
V = 2969.6 (1) Å^3
Z = 2
D_x = 1.597 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7466 reflections
θ = 2.5–28.3°
μ = 1.41 mm^{-1}
T = 293 (2) K
Block, orange
0.24 × 0.22 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.729, T_{max} = 0.766
17 916 measured reflections
13 455 independent reflections
10 337 reflections with $I > 2\sigma(I)$
R_{int} = 0.081
θ_{max} = 28.3°
$h = -11 \rightarrow 18$
$k = -19 \rightarrow 19$
$l = -22 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.171$
$S = 0.96$
13 455 reflections
692 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 2.47$ e Å^{-3}
$\Delta\rho_{\min} = -2.90$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.0175 (7)

Table 1
Selected geometric parameters (Å, °).

O2—C2	1.434 (7)	C1—C2	1.495 (8)
O1—C1—C2	108.2 (5)	O2—C2—C1	114.0 (5)
O1—C1—C2—O2	−61.2 (7)		

Table 2
Hydrogen-bonding and short-contact geometry (Å,°).

D—H···A	D—H	H···A	D···A	D—H···A
O7—H21W···O26$^{\rm i}$	0.90	2.04	2.838 (7)	147
O20—H12W···O11	0.90	2.23	2.953 (6)	138
O20—H12W···O12	0.90	2.38	2.998 (6)	126
O20—H22W···O8	0.90	2.09	2.880 (7)	146
O25—H24W···O27	0.90	2.27	3.012 (7)	139
C3—H3A···O26$^{\rm i}$	0.97	2.59	3.485 (7)	154
C36—H36A···O27$^{\rm ii}$	0.97	2.50	3.296 (10)	139

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x, 1 - y, 1 - z$

Rigid regular phenyl groups were fitted for all the phenolate aromatic rings. All H atoms were fixed geometrically with ideal bond lengths and angles, and were treated as riding atoms with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C, N})$. The completeness of less than 0.92 is due to the poor quality of the crystal. The highest residual peak and deepest hole are 0.05 Å from Ba2 and 0.94 Å from Ba1, respectively.

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: AV1117). Services for accessing these data are described at the back of the journal.

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