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(Borohydrido)(18-crown-6)potassium and (borohydrido)(dibenzo-18-crown-6)(tetrahydrofuran)potassium

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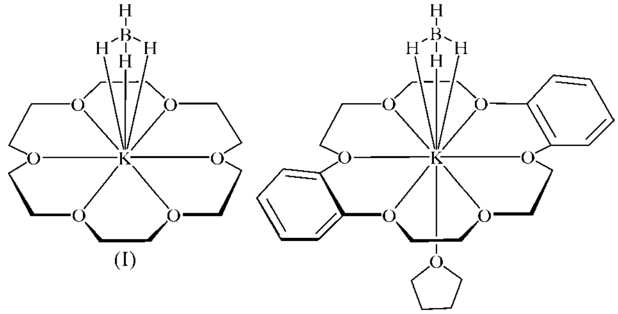
In the two compounds (borohydrido)(1,4,7,10,13,16-hexa-oxacyclooctadecane-κ^6O)potassium, $[K(BH_4)(C_{12}H_{24}O_6)]$, (I), and (borohydrido)(1,4,7,10,13,16-hexaoxa-2,3:11,12-di-benzocyclooctadeca-2,11-diene-κ^6O)(tetrahydrofuran)potassium, $[K(BH_4)(C_4H_8O)(C_{20}H_{24}O_6)]$, (II), the K atom is bound to the six O atoms of the crown ether and to a tridentate borohydride group, with further coordination to a tetrahydrofuran molecule in (II). The alkali metal ion environment is thus distorted hexagonal–pyramidal in (I) and bipyramidal in (II).

Comment

Alkali metal borohydrides are very versatile reagents in organic and coordination chemistry, and the synthesis of their molecular complexes with donor ligands is of major interest for the determination of their structures and the control of their properties. While the crystal structures of some ether and amine adducts of $LiBH_4$ and $NaBH_4$ have been reported (Reger *et al.*, 1997; Giese *et al.*, 1999), no such compound of KBH_4 has been structurally characterized to date. We report here the structures of two adducts of KBH_4 with the crown ethers 18-crown-6 [for compound (I)] and dibenzo-18-crown-6 [for compound (II)].



(I) (II)

Complex (I) presents the characteristic features of compounds containing the [K(18-crown-6)] moiety (Fig. 1). The K^+ ion is located at the centre of the 18-crown-6 ligand and is coordinated by the six O atoms. The K1—O bond lengths are in the range 2.7532 (17)–2.9135 (16) Å [mean value = 2.85 (6) Å] (Table 1). The metal centre is located 0.6416 (8) Å from the O_6 mean plane (r.m.s. deviation = 0.19 Å). The borohydride anion is tridentate, with K1—H bond lengths in the range 2.71–2.84 Å, whereas the K1···B1—H4 angle involving the terminal uncoordinated H atom is nearly linear, with a value of 176°. The K···B distance is significantly shorter in (I) than in KBH_4 (Luck & Schelter, 1999), with values of 2.947 (3) and 3.3640 (9) Å, respectively. The BH_4 moiety in (I) is slightly inclined with respect to the O_6 mean plane, with an angle between the K1···B1 line and the normal to the plane of 12.2°, and B1···K1—O angles of 90.12 (7), 95.44 (7), 95.30 (7)° for atoms O1, O2 and O3, and 112.47 (7), 112.54 (7) and 111.12 (7)° for atoms O4, O5 and O6, respectively. The crown ether moiety presents an usual conformation, with the *gauche* O—C—C—O torsion angles defining the sequence $g^+g^-g^+g^-g^+g^-$ and all the C—O—C—C torsion angles close to *anti* values (distorted D_{3d} symmetry),

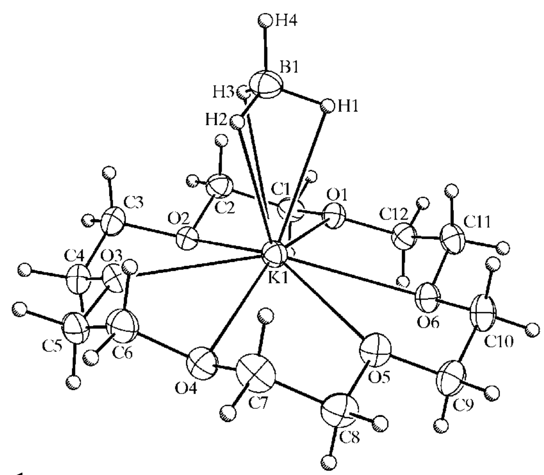


Figure 1
A view of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

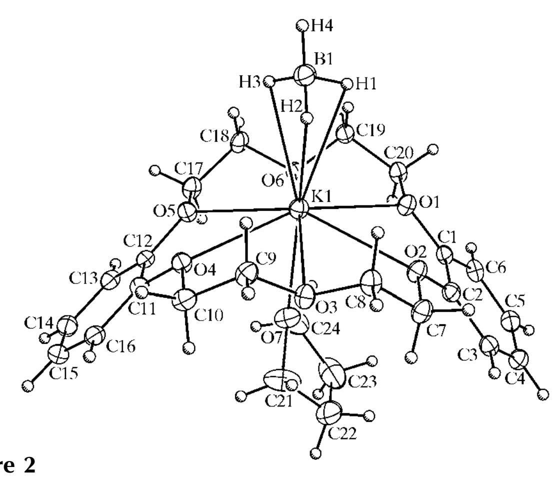


Figure 2
A view of compound (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

which is commonly found in uncomplexed as well as complexed crown ethers (Fyles & Gandour, 1992).

Complex (II) is different from (I) in two respects, namely the conformation of the more rigid dibenzo-18-crown-6 molecule and the presence of an additional tetrahydrofuran (THF) ligand (Fig. 2). The K^+ cation is bound to the six O atoms of the crown ether, with K1—O bond lengths in the range 2.786 (2)–2.829 (2) Å [mean value = 2.806 (17) Å], significantly shorter than in (I) (Table 2). This is probably a result of the different crown ether conformation, which in (II) adopts a curved shape with two orthogonal pseudosymmetry planes perpendicular to the mean O_6 plane (r.m.s. deviation = 0.11 Å), one containing atoms O3 and O6 and the other the centroids of the aromatic rings (approximate C_{2v} point group symmetry). The shortest K1—O bond lengths involve these atoms O3 and O6, indicating a pinching of the macrocycle along the O3···O6 line. The O—C—C—O torsion angles define the sequence $cg^+g^-cg^+g^-$ (*c* is *syn*), with all the C—O—C—C torsion angles close to 180°. This conformation is usual for potassium complexes of dibenzo-18-crown-6, as evidenced by the structures reported in the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002). The K^+ ion is located 0.6189 (11) Å from the O_6 mean plane, on the same side as the borohydride group. The latter is tridentate, with K1—H bond lengths in the range 2.75–2.93 Å, and the K1···B1—H4 angle is 175°. The K1···B1 distance of 2.993 (4) Å is slightly larger than in (I). The angle between the K1···B1 line and the normal to the O_6 mean plane is 0.8°, and the B1···K1—O angles are in the range 99.85 (10)–106.34 (10)°. The THF molecule is located on the concave side of the crown ether, with a K1—O7 bond length of 2.686 (3) Å, in good agreement with the mean value of 2.70 (15) Å for the K—O(THF) bonds in the CSD (221 hits). The O7—K1···B1 angle is 176.96 (11)° and the K^+ cation is thus in a distorted hexagonal–bipyramidal environment, if the BH_4 group is considered as a single donor atom.

The 18-crown-6 and dibenzo-18-crown-6 ethers thus form two stable 1:1 complexes with KBH_4 in refluxing THF, which makes these two ligands effective agents for the solubilization of KBH_4 in THF. Compounds (I) and (II) are new examples of crown ether complexes of alkali metal borohydrides, after [$Li_2(BH_4)_2$(18-crown-6)] (Antsyshkina *et al.*, 1994) and [$Na(BH_4)$(15-crown-5)] (Gorbunov *et al.*, 1985).

Experimental

KBH_4, 18-crown-6 and dibenzo-18-crown-6 were purchased from Aldrich and used without further purification. The ^{1}H NMR spectrum was recorded with a Bruker DPX 200 instrument and referenced internally using the residual protonated solvent resonances relative to tetramethylsilane (δ = 0 p.p.m.). For compound (I), a 50 ml round-bottomed flask was charged with KBH_4 (13.7 mg, 0.25 mmol), 18-crown-6 (66 mg, 0.25 mmol) and THF (2 ml). The mixture was refluxed gently for 48 h and then cooled to room temperature, giving crystals of (I) which were filtered off and dried under a vacuum (78.5 mg, 98% yield). Analysis calculated for $C_{12}H_{28}BKO_6$ (318.25): C 45.29, H 8.87, B 3.40, K 12.29%; found: C 45.47, H 8.75, B 3.43, K 12.40%. ^{1}H NMR (THF-d_8, 200 MHz, 296 K): δ 3.53 (*s*, 24H, CH_2), −0.39 [quartet, 4H, BH_4, $^1J(^{11}B^1H)$ = 81 Hz]. For compound (II), an NMR tube was charged with KBH_4 (2.1 mg, 0.039 mmol), dibenzo-18-crown-6 (14 mg, 0.039 mmol) and THF (0.4 ml). The mixture was refluxed for 22 d, giving crystals of (II) in quantitative yield.

Compound (I)

Crystal data

[$K(BH_4)(C_{12}H_{24}O_6)$]	Z = 4
M_r = 318.25	D_x = 1.198 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 8.2049 (5) Å	μ = 0.32 mm^{-1}
b = 11.9741 (8) Å	T = 100 (2) K
c = 17.9611 (12) Å	Parallelepiped, colourless
V = 1764.6 (2) Å^3	0.30 × 0.30 × 0.25 mm

Data collection

Nonius KappaCCD area-detector diffractometer	3290 independent reflections
φ scan with 2° steps	2858 reflections with $I > 2\sigma(I)$
11824 measured reflections	R_{int} = 0.053
	θ_{max} = 25.7°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.2179P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.035	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.083	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.03	$\Delta\rho_{max}$ = 0.15 e Å^{-3}
3290 reflections	$\Delta\rho_{min}$ = −0.14 e Å^{-3}
181 parameters	Absolute structure: Flack (1983), with 1642 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.03 (4)

Table 1
Selected bond lengths (Å) for (I).

K1—O1	2.8023 (16)	K1—O4	2.8911 (17)
K1—O2	2.9135 (16)	K1—O5	2.8584 (18)
K1—O3	2.7532 (17)	K1—O6	2.8797 (17)

Compound (II)

Crystal data

[$K(BH_4)(C_4H_8O)(C_{20}H_{24}O_6)$]	Z = 4
M_r = 486.44	D_x = 1.290 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 9.5611 (4) Å	μ = 0.25 mm^{-1}
b = 9.9657 (5) Å	T = 100 (2) K
c = 26.2779 (15) Å	Platelet, colourless
V = 2503.8 (2) Å^3	0.22 × 0.22 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer	4737 independent reflections
Two φ and two ω scans with 2° steps	3880 reflections with $I > 2\sigma(I)$
42072 measured reflections	R_{int} = 0.060
	θ_{max} = 25.7°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0789P)^2 + 0.4778P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.048	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.129	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.02	$\Delta\rho_{max}$ = 0.37 e Å^{-3}
4737 reflections	$\Delta\rho_{min}$ = −0.25 e Å^{-3}
298 parameters	Absolute structure: Flack (1983), with 2367 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.08 (6)

Table 2
Selected bond lengths (Å) for (II).

K1—O1	2.829 (2)	K1—O5	2.801 (2)
K1—O2	2.823 (2)	K1—O6	2.787 (2)
K1—O3	2.786 (2)	K1—O7	2.686 (3)
K1—O4	2.812 (2)		

H atoms bound to B atoms were found in difference Fourier maps. The BH_4 group in both compounds was then constrained to an ideal tetrahedral geometry and the H atoms were treated as riding atoms, with B—H bond lengths of 1.15 Å and $U_{iso}(H) = 1.2U_{eq}(B)$. All other H atoms were introduced in calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH) or 0.97 Å (CH_2) and $U_{iso}(H) = 1.2U_{eq}(C)$. Restraints on displacement parameters (ISOR) were applied for two C atoms of the coordinated THF molecule in (II).

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL2000* (Otwinowski & Minor, 1997); data reduction: *HKL2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3011). Services for accessing these data are described at the back of the journal.

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