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Potassium Complexes Containing both Crown Ether and Tertiary Phosphine Oxide Ligands

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Treatment of dichloromethane solutions containing 18-crown-6, KX, and PPh_3O, in a 1:1:1 ratio, with pentane leads to quantitative precipitation of the complexes $[(18\text{-crown-}6)K(OPPh_3)X]$ (X: I, **1**; Br, **2**; NCS, **3**). Complexes **1**–**3** are stable in the solid state but dissociate readily in solution. The structure of **1** is established by a single-crystal X-ray diffraction study. Crystallographic data for **1**: space group $R3m$, a = 14.432 (6) Å, c = 13.690 (2) Å, V = 2469.5 (11) Å^3, Z = 3, R = 0.028, R_w = 0.019.

The coordination chemistry of alkali metals is an important, growing branch of inorganic and organometallic chemistry.[1,2] Hundreds of alkali metal cation complexes of macrocyclic polyethers (crown ethers) and related ligands have been synthesized and thoroughly investigated over the last two decades.[1-5] Tertiary phosphine oxides represent another important class of ligands capable of coordinating with alkali metals.[1,2,6] The so-called organophosphorus cyclopendant ligands[7] containing a crown (or aza-crown) macrocycle with phosphoryl groups in its side chains represent a new class of highly important and useful complexones with unique coordination abilities. An excellent review on such cyclopendant ligands was very recently published by Bel'skii et al.[8] The combination of a crown macrocycle and a tertiary phosphine oxide can be quite successfully used for extraction of alkali metals. For instance, a noticeable synergistic effect was observed in the extraction of some alkali metal cations with crown ethers in conjunction with trioctylphosphine oxide.[9] At the same time, it was found that the potassium complex of dibenzo-18-crown-6 with four $CH_2P(O)Ph_2$ groups attached to the benzene rings is *less* stable than that of unsubstituted dibenzo-18-crown-6.[10] Thus, synthesis and investigation of alkali cation complexes containing both crown ether and tertiary phosphine oxide ligands is of particular interest. Only one such complex, $[(15\text{-crown-}5)Na(OPMe_3)]^+[(CO)_3Fe(\mu_2\text{-}t\text{-}Bu_2P)Rh(CO)(PMe_3)]^-$, was isolated (25–29% yield) and structurally characterized.[11] We now wish to report the first examples of similar potassium complexes with simple inorganic counterions, namely 18-crown-6(triphenylphosphine oxide)potassium iodide (**1**), bromide (**2**), and thiocyanate (**3**).

Treatment of a concentrated dichloromethane solution containing 18-crown-6, Ph_3PO, and KX (X = I, Br, SCN) in a 1:1:1 ratio, with pentane leads to immediate precipitation of compounds **1**–**3**, respectively. Complexes **1**–**3** (Table I) are stable, high-melting, snow-white crystalline solids soluble in chloroform and dichloromethane, sparingly soluble in acetone and benzene, and insoluble in petroleum ether and water. The structure of complex **1** was established by a single-crystal X-ray diffraction study (Figure 1, Table II).

The coordination polyhedron (Figure 1) is a hexagonal bipyramid, its basic plane consisting of six oxygen atoms surrounding the potassium cation. The molecule occupies sites of crystallographic symmetry. The atoms K, I, P, and O(3) are on a special position ($3m1$), giving three molecules per cell. Only one phenyl moiety was found per asymmetric unit, with all the carbons on a special position again (m) with a multiplicity of 9. The two other phenyls of the Ph_3PO are generated by the symmetry. The 18-crown-6 has $3m$ symmetry with the oxygen atoms O(1) and O(2) on the plane of symmetry (m). Here again, the asymmetric unit shows just one-third of the crown, the rest being generated by symmetry. The macrocyclic ligand's six ligating oxygens are alternately about 0.50 Å above and below the mean plane. Located inside the crown framework, the potassium atom is 0.293 Å from the plane which is perpendicular to both the K–I bond and the K–O–P linear fragment. Unlike the latter, the Na–O–P angle in $[(15\text{-crown-}5)Na(OPMe_3)]^+$ was found to be 152 (2)°. Both the C–C (1.510 Å) and C–O (1.425 Å) bonds in the macrocyclic ligand of **1** are only slightly elongated in comparison with those of the free 18-crown-6 (1.507 and 1.411 Å, respectively).[5] An insignificant difference (1.3 and 2.3°) was also found between the C–O–C and C–C–O bond angles in **1** and in the uncomplexed hexaether.[12] The potassium–oxygen (crown) bond distances (2.823 Å) are close to those observed in the structures of various (18-crown-6)- or (dibenzo-18-crown-6)potassium complexes.[1,4] The distance between the potassium atom and the phosphine oxide oxygen (2.733 Å) lies in the range of the $K\text{–}OH_2$ bond lengths in different crown–potassium–aqua complexes[4] and is noticeably shorter than the K–O ($P(OPh)_3$) bonding distance (2.829 Å) in $[(18\text{-crown-}6)K][Rh(CO)_2(P(OPh)_3)_2]$.[13] A substantial difference in the K–I bond lengths of **1** (3.74 Å) and of the complexes of KI with dibenzo-18-crown-6 (3.52–3.57 Å)[1,14,15] is indicative of an ionic rather than a covalent bonding interaction between the potassium cation and the iodide anion in **1**.

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Table I. Analytical Data for [(18-crown-6)(Ph_3PO)KX] (**1–3**)

				anal., %									
				C		H		Hal		P		N	
X	yield, %	mp, °C	formula	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
I	99	244–246	$C_{30}H_{39}IKO_7P$	50.85	50.61	5.55	5.89	17.91	18.17	4.37	4.41		
Br	97	167–170	$C_{30}H_{39}BrKO_7P$	54.46	54.18	5.94	6.02	12.08	11.99				
SCN	98	218–220	$C_{31}H_{39}KNO_7PS$	58.20	57.87	6.14	6.19					2.19	2.08

Table II. Crystallographic Data for [(18-crown-6)K($OPPh_3$)I] (**1**)

formula	$C_{30}H_{39}IKO_7P$	Z	3
fw	708.60	V, Å^3	2469.5 (11)
cryst shape	cube	d_{calc}, g/cm^3	1.429
cryst dimens, mm	0.2 × 0.2 × 0.2	T, K	295
cryst system	trigonal	radiation	Mo Kα
lattice params, Å	a = 14.432 (6)	(λ, Å)	(0.709 30)
	c = 13.690 (2)	μ, mm^{-1}	2.63
space group	$R3m$	R (R_w), %	2.8 (1.9)

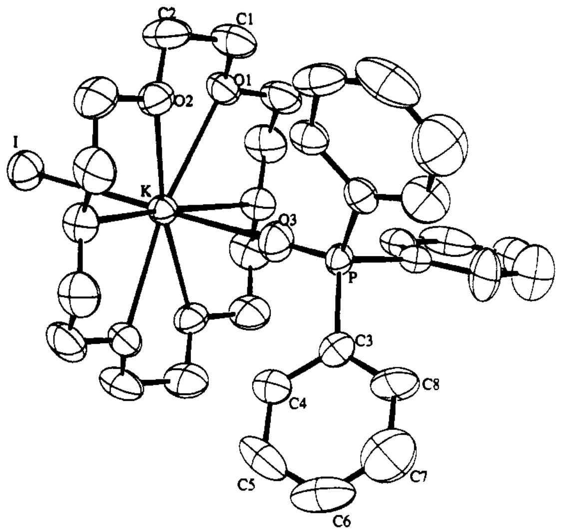

Figure 1. Structure of [(18-crown-6)K($OPPh_3$I] (**1**) showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

Complexes **2** and **3** are likely to possess similar structures in the solid state. A very strong band at 2057 cm^{-1} observed in the IR spectrum of **3** (Nujol mull) indicates that the ambidentate SCN ligand is coordinated with the potassium atom in an "isothiocyanate", rather than a "thiocyanate", fashion. This type of coordination between the harder basic center (N) of the SCN^- anion and such hard acids as alkali metal cations is quite common. For instance, the fragment M—N=C=S (M = K, Rb, Cs) was observed in the crystal structures of the complexes of 18-crown-6 with alkali thiocyanates.[16,17]

The ^1H NMR spectra of **1–3** ($CDCl_3$) contain two groups of signals: a singlet at 3.6 ppm (24 H; aliphatic protons) and a multiplet at 7.3–7.7 ppm (15 H; aromatic protons). A singlet at +29 ppm was observed in the $^{31}P\{^1H\}$ NMR spectra of the complexes. This pattern did not change when triphenylphosphine oxide (1 equiv) was added to a solution of **2** in dichloromethane and the ^{31}P NMR spectra were recorded in the temperature interval of +20 to −85 °C. Hence, in solution the equilibrium (eq 1) is likely to be almost entirely shifted to the right.

$$[(18\text{-crown-6})KX(OPPh_3)] \rightleftarrows [(18\text{-crown-6})KX] + OPPh_3 \qquad (1)$$

$$X = I, Br, NCS$$

Replacement of 18-crown-6 for **2** did not affect the phase-transfer-catalyzed reactions (eqs 2 and 3). Both processes experienced neither a synergistic effect[18] nor inhibition when triphenylphosphine oxide or trioctylphosphine oxide was added

$$PhCH_2CH_2Br \xrightarrow[\text{18-crown-6}]{\text{benzene–50\% KOH}} PhCH{=}CH_2 \qquad (2)$$

$$n\text{-}C_4H_9Br + n\text{-}C_4H_9OH \xrightarrow[\text{18-crown-6}]{\text{benzene–50\% KOH}} (n\text{-}C_4H_9)_2O \qquad (3)$$

to the reaction mixtures containing 18-crown-6 as the phase-transfer catalyst. These data represent another argument in favor of facile elimination of the phosphine oxide ligand from **1–3** in solution.

Experimental Section

Physical measurements were carried using the following equipment: Varian XL 300 (^1H and ^{31}P NMR), Bomem MB-100 (FT-IR), Rigaku AFC6S (X-ray diffraction), and Fisher-Johns apparatus (melting points). Tertiary phosphine oxides, 18-crown-6, and other chemicals were purchased from Aldrich Chemical Co. and used as received.

Synthesis. A clear solution of 18-crown-6 (0.22 g; 0.83 mmol) and KI (0.13 g; 0.78 mmol) in dichloromethane (5 mL) was added to a solution of Ph_3PO (0.22 g; 0.79 mmol) in dichloromethane (5 mL). The resulting colorless solution was concentrated to ca. 3 mL and treated with pentane (10 mL). The snow-white crystals were isolated, washed with pentane, and dried under vacuum. The yield of **1** was 0.55 g (99%). Complexes **2** and **3** were prepared in a similar manner.

X-ray Diffraction. A crystal of **1** having approximate dimensions of 0.2 × 0.2 × 0.2 mm was mounted on a glass capillary. All the measurements were made on a Rigaku diffractometer with Mo Kα radiation. Cell constants and an orientation matrix for data collection, obtained from least-squares refinement, using the setting angles of 25 reflections in the range $40 < 2\theta < 47°$, corresponded to a trigonal crystal with dimensions a = 14.432 (6) and c = 13.690 (2) Å. For Z = 3 and fw = 708.60, the calculated density is 1.429 g/cm^3. On the basis of the systematic absences, the space group was determined to be $R3m$. The data were collected at 22 °C using the ω–2θ scan technique to a maximum 2θ value of 47°.

A total of 915 reflections were collected. The unique set contained only 487 reflections. The standards were measured after every 150 reflections. No crystal decay was noticed. The data were corrected for Lorentz and polarization effects.[19] An absorption correction was made with minimum and maximum transmission factors of 0.847 and 0.993. The structure was solved by direct methods. All the atoms were refined anisotropically except the hydrogens. The hydrogen atoms were calculated, with a bonding distance of 1.04 Å. The final cycle of full-matrix least-squares refinement was based on 462 observed reflections ($I > 2.5\sigma(I)$) and 79 variable parameters. Weights based on counting statistics were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.310 and −0.380 e/Å^3, respectively. All the calculations were performed using the NRCVAX crystallographic software package.[20]

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Supplementary Material Available: Full textual and tabular details of the structure solution, additional structural diagrams, and tables of atomic coordinates, bond lengths and angles, torsion angles, and thermal parameters for complex **1** (8 pages). Ordering information is given on any current masthead page.

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