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Perchlorate Anion to Metal Coordination in Some Alkali Metal–Cyclic Polyether Complexes

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In earlier papers,[1] we studied the effect of anion and also reaction conditions on the complex formation of cyclic polyethers with alkali and alkaline earth metals. We now wish to report some of the complexes formed between alkali metal perchlorates and cyclic polyethers. The perchlorate anion is now known to take part in coordination frequently, and in the present study, the ClO_4^- asymmetric bending frequency (~ 625 cm^{-1}) is used as a diagnostic test for coordination of the anion.[2] Table I lists the complexes isolated, and their relevant infrared information which is not obscured by ligand vibrations. 1:2 complexes only are formed between $MClO_4$ (M = K, Cs) and benzo-15-crown-5, but sodium perchlorate may yield both 1:1 and 1:2 complexes depending on the conditions employed. Under normal reaction conditions crystals of the 1:1 complex are formed in good yield, but from a very concentrated solution of one mol of sodium perchlorate and two mol of benzo-15-crown-5 in methanol, some well-formed crystals of the 1:2 complex may be isolated, having a very similar infrared spectrum to the $KClO_4 \cdot 2$benzo-15-crown-5 complex.

Other NaX complexes studied (X = Br, I, NCS),[3] with the exception of sodium tetraphenylborate,[1a] form only 1:1 complexes with benzo-15-crown-5, but the lattice energy of sodium perchlorate is quite low,[4] (Table II) and this is likely to be an important factor in the formation of a 1:2 complex. The 1:2 complexes $MClO_4 \cdot 2$benzo-15-crown-5 (M = Na, K, Cs) all show a single asymmetric ClO_4^- bending frequency at ~ 630 cm^{-1}, indicating free "ionic" perchlorate, which is consistent with a proposed sandwich structure. $NaClO_4 \cdot$benzo-15-crown-5, however, shows splitting of this bending frequency, indicating that the perchlorate is bonding to the metal. This 1:1 complex is also unusual in being anhydrous in the isolated crystalline stage, further suggesting that the perchlorate is occupying the vacant coordination position.

$NaClO_4 \cdot$dibenzo-18-crown-6$\cdot H_2O$ has a single asymmetric bending absorption at 628 cm^{-1} suggesting no perchlorate coordination, but the complex is hydrated [3605(s), 3520(m), 3470(m)], the water probably coordinating to the metal. $NaClO_4 \cdot$dibenzo-24-crown-8 is anhydrous and shows only one ClO_4^- asymmetric bending frequency at 628 cm^{-1}. The known structures of dibenzo-24-crown-8 with alkali metals have two metal ions coordinated to one dibenzo-24-crown-8 molecule, and bridged by anions.[5] The apparent presence of ionic perchlorate and also lack of solvent, suggests that the structure of $NaClO_4$ dibenzo-24-crown-8 may be a partial wrap-around structure, as proposed for the analogous sodium tetraphenylborate[1a] and sodium thiocyanate[5a] complexes. Barium perchlorate likewise forms a 1:1 anhydrous crystalline complex with dibenzo-24-crown-8 but the Cl–O bending frequency is split in this case indicating perchlorate bonding to the metal.[1b]

Experimental

Infrared spectra were recorded as nujol mulls or potassium bromide discs on a Perkin–Elmer 457 Grating Spectrophotometer. Melting points were determined on a Koffler hot stage melting point apparatus. Elemental analyses were determined at the Microanalytical Laboratory, U.C.L.

Reactions were in general carried out by dissolving the reactants separately in hot solvents followed by mixing and filtering where necessary. After crystallization had taken place, the products were collected on a sinter, washed with a small amount of reaction solvent, and then dried *in vacuo* at ambient temperatures.

Reaction of Sodium Perchlorate with Benzo-15-crown-5

(a) 1:1

Sodium perchlorate (0.123 g) and benzo-15-crown-5 (0.268 g) were refluxed together in ethanol (15 ml) to give a clear solution, which was filtered hot and set aside to crystallize. The chunky needle crystals of $NaClO_4 \cdot$benzo-15-crown-5 formed were collected on a sinter, washed with ethanol, and dried *in vacuo* (0.2 g, 59%).

(b) 1:2

Sodium perchlorate (1.27 g) and benzo-15-crown-5 (5.36 g) were dissolved in hot methanol (10 ml), and allowed to crystallize. Some chunky crystals of $NaClO_4 \cdot 2$benzo-15-crown-5 were obtained from the mother liquor, and these were carefully extracted, washed with a small amount of methanol, and dried *in vacuo*.

TABLE I. Analytical and Infrared Data.

Compound	Reaction Solvent[a]	Analysis				M.p. °C	ClO_4^- Asym Bending Frequency (cm^{-1})
		Req.		Found			
		C	H	C	H		
$NaClO_4$·benzo-15-crown-5	et	43.02	5.12	43.04	5.10	147–8	638(s), 635(s), 627(s)
$NaClO_4$·2(benzo-15-crown-5)	me	51.02	6.12	51.03	6.15	94	630(s)
$NaClO_4$·4(bromo-benzo-15-crown-5)	et	35.78	4.05	36.39	4.19	168–9 dec	635(s), 625(s), 623(s)
$KClO_4$·2(benzo-15-crown-5)	et	49.81	5.93	49.76	5.91	216–8 dec	625(s)
$KClO_4$·2(4bromo-benzo-15-crown-5)	et	40.36	4.56	40.90	4.74	176–7	628(s)
$CsClO_4$·2(benzo-15-crown-5)	et	43.74	5.23	43.03	5.08	123–4	629(s)
$NaClO_4$·dibenzo-18-crown-6·H_2O	et	47.95	5.19	48.30	5.64	222–3[b]	628(s)
$KClO_4$·dibenzo-18-crown-6[c]	et	48.13	4.81	48.31	5.26	222	630(s, b)
$NaClO_4$·dibenzo-24-crown-8	et	50.48	5.61	50.53	5.72	150–1	628(s)

[a] et = ethanol; me = methanol. [b] Loses solvent at 100 °C. [c] Analysed as amorphous anhydrous product. Crystallises as a hydrate but rapidly goes opaque in air.

TABLE II.[4] Lattice Energies.

Salt	$NaClO_4$	$KClO_4$	$CsClO_4$	NaNCS	NaBr	NaI
Lattice Energy (kcal mol^{-1})	153.8	139.7	128.6	163.4	176.6	164.5

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