Inorganica Chimica Acta, 14 (1975) 45–48

Alkali Metal Tetraphenylborate Complexes with Some Macrocyclic, ”Crown”, Polyethers

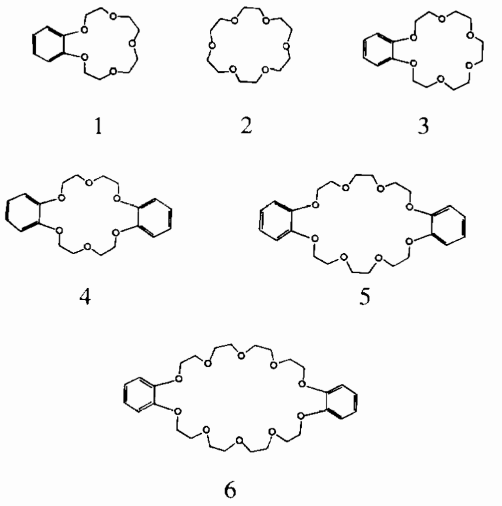
D. G. PARSONS, M. R. TRUTER and J. N. WINGFIELD
Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Hertfordshire, AL5 2JQ, U.K.
Received December 11, 1974

Complexes of sodium, potassium and caesium with a range of cyclic polyethers have been synthesised using tetraphenylborate as the counterion. While some complexes are found to have similar metal co-ordination to compounds studied previously, the non co-ordination of the tetraphenylborate anion enables new products to be obtained when reaction conditions are varied. Thus, the sandwich compound Na(benzo-15-crown-5)$_2$BPh$_4$ crystallises in high yield when appropriate reactant ratios are empoyed, and dibenzo-30-crown-10 is found to co-ordinate either one or two sodium ions depending on the solvent conditions used.

Introduction

Since Pedersen's[1] discovery that cyclic polyethers complex with alkali metal cations, a large number of such complexes have been isolated, and many solution studies have been carried out[2]. Several factors, including the ionic radius and degree of solvation of the complexing cation, and also the anion and solvent used have been found to influence the formation of complexes with these cyclic polyethers.

As part of the systematic study of the co-ordination chemistry of the alkali metals, we have prepared a range of cyclic polyether complexes of sodium, potassium and caesium, using the bulky tetraphenylborate group, which has little tendency to take part in co-ordination as counterion. The structural formulae and systematic names are shown in Figure 1, together with abbreviations used in this paper.


1 2 3

4 5

6

Figure 1. Structural formulae of the macrocyclic ethers. The systematic names and "crown" names are: (1) 2, 3, 5, 6, 8, 9, 11, 12-octahydro-1, 4, 7, 10, 13-benzopentaoxacyclopentadecin (benzo-15-crown-5); (2) 1, 4, 7, 11, 15, 19-hexaoxacyclo-octadecin (18-crown-6); (3) 2, 3, 5, 6, 8, 9, 11, 12, 14, 15-decahydro-1, 4, 7, 10, 13, 16-benzohexaoxacyclo-octadecin (benzo-18-crown-6); (4) 6, 7, 9, 10, 17, 18, 20, 21-octahydrodibenzo[b,k][1, 4, 7, 10, 13, 16]hexaoxacyclo-octadecin (dibenzo-18-crown-6); (5) 6, 7, 9, 10, 12, 13, 20, 21, 23, 24, 26, 27-dodecahydrodibenzo[b,n][1, 4, 7, 10, 13, 16, 19, 22]octaoxacyclotetracosin (dibenzo-24-crown-8); (6) 6, 7, 9, 10, 12, 13, 15, 16, 23, 24, 26, 27, 29, 30, 32, 33-hexadecahydrodibenzo[b,q][1, 4, 7, 10, 13, 16, 19, 22, 25, 28]decaoxacyclotriacontin (dibenzo-30-crown-10).

Results and Discussion

Table I lists the compounds satisfactorily isolated and characterised. In general, reactions were carried out in methanol in beakers open to the air, with no precautions taken to exclude moisture, since several of the crown complexes studied in the past have only been isolated as hydrates. In the present work, some of the hydrated species isolated correspond well with complexes which have previously been obtained and whose structures have been determined. Thus, the co-ordination round the sodium ion in the compound NaBPh$_4$(1)H$_2$O is likely to be similar to that found in the complex NaI(1)H$_2$O[3], there being no sodium–anion interaction. This complex, NaBPh$_4$(1)H$_2$O, is obtained when tetrahydrofuran or aqueous ethanol (80% ethanol) are used as solvent, but the alcoholates NaBPh$_4$(1)ROH (R = Me, Et, isoprop) crystallise from absolute methanol, ethanol and isopropanol re-

TABLE I. Preparations and Analytical Data of Complexes.

Complex	Ratio of Reactants (metal: ligand)	Solvent	Yield (%)	Analyses Found (%)			Calc (%)			M.P. (°C)
				C	H	M	C	H	M	
NaBPh$_4$(1)H$_2$O	1:1	thf:H$_2$O(4:1)	91	72.64	6.77	3.40	72.60	6.75	3.66	162–3[a] dec (softens 94)
NaBPh$_4$(1)CH$_3$OH	1:1	MeOH	72	72.80	6.95		72.89	6.92		162–3[a] dec
NaBPh$_4$(1)C$_2$H$_5$OH	1:1	EtOH	69	73.19	6.93		73.16	7.08		162–3[a] dec
NaBPh$_4$(1)(CH$_3$)$_2$CHOH	1:1	Pr^{i}OH	84	73.48	7.22		73.42	7.23		162–3[a] dec
NaBPh$_4$(1)$_2$	1:2	MeOH	66	71.02	6.93	2.40	71.05	6.89	2.62	122
KBPh$_4$(1)$_2$	1:2	EtOH	90	69.93	6.70		69.78	6.77		171–2
CsBPh$_4$(1)$_2$	1:2	Bu^{n}OH	78	63.15	5.90		63.16	6.13		145 dec
NaBPh$_4$(2)1·5H$_2$O	1:1	EtOH	35	68.42	7.42	3.29	68.23	7.49	3.63	200–220 dec
KBPh$_4$(2)	1:1	MeOH	50	69.54	7.09		69.45	7.12		245[b]
CsBPh$_4$(2)	1:1	EtOH	44	60.93	5.70		60.34	6.20		137 dec
NaBPh$_4$(3)H$_2$O	1:1	EtOH	52	71.53	7.02	2.97	71.42	6.91	3.42	180 dec
NaBPh$_4$(4)2H$_2$O	1:1	MeOH	81	71.71	6.83	2.85	71.54	6.56	3.11	163 dec
KBPh$_4$(4)H$_2$O[d]	1:1	MeOH	60	72.16	6.59		71.72	6.31		181–2 dec
NaBPh$_4$(5)[e]	1:1	MeOH	74	72.95	6.84	3.07	72.90	6.64	2.91	187
KBPh$_4$(5)	1:1	MeOH	43	71.54	6.59		71.44	6.51		143–4 dec
CsBPh$_4$(5)	1:1	MeOH	28	64.03	5.96		64.00	5.83		152–3 dec
NaBPh$_4$(6)	1:1	MeOH[f]	42	70.84	7.00	2.37	71.05	6.89	2.62	108
(NaBPh$_4$)$_2$(6)H$_2$O	2:1[g]	CH$_2$Cl$_2$	95	73.59	6.74	3.86	73.66	6.68	3.71	240 dec
(NaBPh$_4$)$_2$(6)2H$_2$O	2:1[g]	MeOH[h]	50	72.11	6.93		72.60	6.75		240[c] dec
(NaBPh$_4$)$_2$(6)2H$_2$O	2:1[g]	thf	90	72.60	6.81		72.60	6.75		240[c] dec
KBPh$_4$(6)	1:1	MeOH	15	68.96	6.85		69.78	6.77		159–60 dec
CsBPh$_4$(6)	1:1	MeCN	68	62.06	6.38		63.16	6.12		dissoc > 53

[a] M.p. of anhydrous NaBPh$_4$(1). [b] Shows signs of dissociation below this temperature. [c] M.p. of (NaBPh$_4$)$_2$(6)H$_2$O.
[d] Mixture of mainly monohydrate and anhydrous crystals. Hydrate converted to anhydrous form by heating at 160° C for 20 min. [e] Recrystallised from dichloromethane–methanol. [f] Anhydrous methanol carried out under a nitrogen atmosphere.
[g] Slight excess of sodium tetraphenylborate. [h] Analar methanol carried out exposed to atmosphere.

spectively. These crystals are converted to the hydrate on standing in air. Attempted preparation of the complex NaBPh$_4$(1)t-BuOH from t-butanol was not successful, NaBPh$_4$(1)H$_2$O being obtained, presumably because of the larger steric requirements of the bulky t-butanol group.

Nitrogen bases are not able to displace water, or the alcohols in the co-ordination around the sodium ion. Thus, recrystallisation of 1 mol of NaBPh$_4$(1)H$_2$O from ethanol in the presence of 1 mol of pyridine, bipyridyl or ethylene diamine, yields pure NaBPh$_4$(1)EtOH only. This was confirmed by i.r. spectra, and also by ^{1}H n.m.r., where integration showed a ligand to ethanol ratio of 1:1.

Reaction of sodium tetraphenylborate with benzo-15-crown-5 in a ratio of 1 : 2 gives the only anhydrous 1:2 complex known to date for sodium in high yield. In further studies with other anions we were also able to synthesise NaClO$_4$·2(1). Similar products are obtained from potassium and caesium tetraphenylborates although the caesium complex has a tendency to dissociate in methanol, and attempted purification by cyclic extraction methods yielded pure benzo-15-crown-5 and pure caesium tetraphenylborate. No 1:1 complex is observed for potassium or caesium.

Figure 2 illustrates the infrared spectrum of NaBPh$_4$·2(1), KBPh$_4$·2(1) and NaBPh$_4$(1)H$_2$O in the region 1200–900 cm^{-1} where the greatest change is observed for cyclic crown ethers on going from an uncomplexed to a complexed state.

There is a marked similarity between A and B, suggesting similar structures for these two complexes, whereas C is different. This is consistent with the differences observed crystallographically for KI·2(1)[4] and NaI(1)H$_2$O[3], where the former molecule, a sandwich complex, has all methylene carbons on the opposite side of the plane of oxygen atoms to the cation, and the latter molecule has two methylene carbons on the same side of the oxygen plane as the cation. This indicates that the conformation of the ring is variable according to the total co-ordination of the complexed cation.

The crystal structure of NaBr(4)2H$_2$O[5] showed that there were two types of sodium co-ordination in the

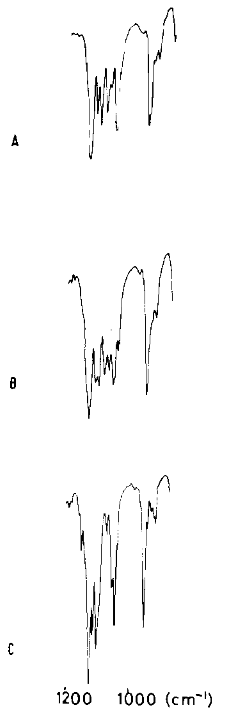


Figure 2. Infrared spectra of benzo-15-crown-5 complexes. A, $KBPh_4(1)_2$: B, $NaBPh_4(1)_2$; C, $NaBPh_4(1)H_2O$, all taken as nujol mulls.

molecule, one of them involving a sodium–bromine interaction. A similar interaction is unlikely for tetraphenylborate anion in the complexes $NaBPh_4(4)2H_2O$, $NaBPh_4(3)H_2O$ and $KBPh_4(4)H_2O$, and the probable co-ordination is six oxygen atoms in a plane around the metal, with water molecules in one or both of the axial positions. This is indicated by the OH i.r. stretching frequencies in these hydrates, where sharp bands are observed, indicating direct bonding of water to the metal. For $NaBPh_4(2)1 \cdot 5H_2O$ the OH band is very broad in the 3550–3400 cm^{-1} region, indicating the presence of water in the lattice as well as directly bonded to the metal.

Previous studies with dibenzo-24-crown-8, (5), have shown that sodium and potassium salts may react to give 2:1 (metal:crown) complexes[6]. In the potassium isothiocyanate complex the nitrogen atoms of the anions bridge two potassium ions[7]. The tetraphenylborate anion is unlikely to take part in this type of bonding, and the compounds of sodium, potassium and caesium cations obtained with dibenzo-24-crown-8 for this anion are anhydrous 1 : 1 complexes. All three complexes have similar i.r. spectra indicating a similar co-ordination for all the metals. Experiments with space-filling molecular models show that the ligand may wrap around the central cation, so that all the ether oxygen atoms are reasonably close for co-ordination, but that the central cation is not completely enclosed.

The compounds $KBPh_4(6)$, $NaBPh_4(6)$ and $CsBPh_4(6)$ likewise have very similar i.r. spectra, and are thought to be "wrap around" complexes with metal ion co-ordination similar to that found for potassium in KI(6)[8]. The ligand can replace a solvent sheath around a metal ion in a stepwise manner, each step having a low energy of activation. The reaction of sodium tetraphenylborate with (6) proceeds in this way in anhydrous methanol under an atmosphere of dry nitrogen, the low melting (108° C), anhydrous 1:1 complex being formed in high yield; in the presence of moisture the 1:1 ratio of reactants gives a mixture of the anhydrous 1:1 complex and a hydrated 2:1 complex. However, if analar methanol is used, and the reaction carried out in a beaker open to the air, with excess sodium tetraphenylborate, then the complex $(NaBPh_4)_2(6)2H_2O$ is obtained in good yield. The monohydrate $(NaBPh_4)_2(6)H_2O$ may be isolated pure by heating the above dihydrate at 220° C for 15 min or by heating at 160° C the dihydrate obtained from sodium tetraphenylborate and dibenzo-30-crown-10 in tetrahydrofuran (see Table II); the final water molecule is not driven off until melting takes place. The existence of two dihydrates suggests a species with water ligands bridging the two sodium ions, as well as a terminal water ligand species, but we are unable to assign definite structures to the products. The monohydrate may be made directly from the reaction of sodium tetraphenylborate with dibenzo-30-crown-10 in dichloromethane, when opaque crystals are obtained.

Stability constant measurements[9] in methanol of the complexes formed by potassium chloride gave the following trend in logK values for several cyclic polyethers: dibenzo-18-crown-6 > dibenzo-30-crown-10 > dibenzo-21-crown-7 > dibenzo-24-crown-8. The relatively high value for the dibenzo-30-crown-10 complex is explained by its ability to wrap around the potassium cation. A smaller cation than potassium will tend to

TABLE II. Infrared OH Frequencies.

$NaBPh_4(1)H_2O$	3650 (m), 3540 (m), 1610 (m)
$NaBPh_4(1)C_2H_5OH$	3535 (m)
$NaBPh_4(1)CH_3OH$	3540 (m), 3520 (sh, m)
$NaBPh_4(2)1 \cdot 5H_2O$	3530 (w), 3500 (w, br), 3410 (v, br)
$NaBPh_4(3)H_2O$	3525 (m)
$NaBPh_4(4)2H_2O$	3600 (w), 3555 (m)
$KBPh_4(4)H_2O$	3635 (w), 3538 (m)
$(NaBPh_4)_2(6)H_2O$	3620 (m), 3520 (m), 1620 (m)
$(NaBPh_4)_2(6)2H_2O$[a]	3615 (m), 3555 (m), 1625 (m)
$(NaBPh_4)_2(6)2H_2O$	3640 (w), 3610 (w), 3580 (w, sh) 3440 (w), 3410 (w), 1615 (br, w)

[a] From tetrahydrofuran.

contract the cavity within the wrapped-around cyclic polyether, and hence increase the intra-ligand repulsions, thus giving a less stable 1 : 1 complex. The reactions of sodium tetraphenylborate with dibenzo-30-crown-10 result from a balance between the energy gained in chelation by a complete wrapping around of the ligand, and the energy required to remove co-ordinated solvent from around the cation, and to overcome any intra-ligand repulsion. Measurements in non-aqueous solvents[9–11] have shown that the stability of the complex ions formed between Na^+ and macrocyclic ethers increases with decreasing dielectric constant of the solvent used, for example, in water–methanol mixtures, stability increases with increasing methanol concentration.

All stability constant measurements have been interpreted on the assumption that the complexes are mononuclear, our present and previous[6] results indicate that binuclear complexes are possible for the larger rings in the presence of water or a co-ordinating anion. We have now shown that with a non co-ordinating anion the solvent sheath of methanol may be readily removed, but in the presence of water hydrated species may be isolated.

The behaviour of caesium tetraphenylborate illustrates the effect of relative solubilities. From methanol a 1 : 1 complex was crystallised with dibenzo-24-crown-8, but, although with dibenzo-30-crown-10 on boiling there was complete dissolution, the unreacted starting materials crystallised on cooling. From methylcyanide the complex $CsBPh_4$(6) could be obtained in good yield. In methanol dibenzo-18-crown-6 did not solubilize caesium tetraphenylborate even on boiling. Solution is, however, obtained when a dilute solution of 18-crown-6 and caesium tetraphenylborate are refluxed in ethanol. If this solution is concentrated by warming, needle crystals of caesium tetraphenylborate are obtained; these redissolve on cooling the solution to room temperature, and the complex $CsBPh_4$(2) slowly crystallises at –3 °C.

Thallium tetraphenylborate gives no visible reaction with dibenzo-18-crown-6, dibenzo-24-crown-8 or dibenzo-30-crown-10 in boiling methanol.

Experimental

General Remarks

Unless stated, analar reagents were used without further purification. The cyclic polyethers were either prepared by published routes, or by modifications which will be published separately[12]. Methanol was dried by distilling over lithium aluminium hydride. I.r. spectra were taken as nujol mulls on a Perkin–Elmer 457 Grating Spectrophotometer, and n.m.r. spectra as pyridine solutions on a Perkin–Elmer R10 Spectrometer. Melting points were determined on a Koffler hot stage melting point apparatus. Sodium analyses were determined with a Gallenkamp FH 500 flame photometer, using sodium tetraphenylborate solutions as standards. Microanalyses were performed in University College, Chemistry Department.

Preparation of Tetraphenylborates

Potassium and caesium tetraphenylborates were obtained as precipitates from mixing methanol solutions of the appropriate metal iodide and sodium tetraphenylborate. Thallous tetraphenylborate was obtained by removal of sodium formate from the precipitate obtained on stirring a methanolic solution of thallous formate and sodium tetraphenylborate.

Preparation of Polycyclic Ether Complexes of the Metal Tetraphenylborates. General Remarks

Complexes were obtained as crystalline deposits from clear solutions of the reactants. However, in certain cases, the product obtained depended on (a) the ratio of reactants used and/or (b) the solvent used. Thus (a) the reaction of $KBPh_4$ with benzo-15-crown-5 always gave the product K(benzo-15-crown-5)$_2$BPh$_4$, whereas both Na(benzo-15-crown-5)(solvent)BPh$_4$ and Na(benzo-15-crown-5)$_2$BPh$_4$ may be obtained depending on the ratio of reactants used: (b) Na(dibenzo-30-crown-10)BPh$_4$ was obtained from dry methanol whereas Na$_2$(dibenzo-30-crown-10)(BPh$_4$)$_2$ 2H$_2$O crystallises from wet methanol. Full details of reaction ratios and solvents used are given in Table I.

References

1 C.J. Pedersen, *J. Am. Chem. Soc., 89,* 7017 (1967).
2 "Structure and Bonding", Vol. 16, Springer-Verlag, New York, 1973 (and references therein).
3 M.A. Bush and M.R. Truter, *J. Chem. Soc. (Perkin II),* 341 (1972).
4 P.R. Mallinson and M.R. Truter, *J. Chem. Soc. (Perkin II),* 1818 (1972).
5 M.A. Bush and M.R. Truter, *J. Chem. Soc. (B),* 1440 (1971).
6 N.S. Poonia and M.R. Truter, *J. Chem. Soc. (Dalton),* 2062 (1973).
7 M. Mercer and M.R. Truter, *J. Chem. Soc. (Dalton),* 2469 (1973).
8 M.A. Bush and M.R. Truter, *J. Chem. Soc. (Perkin II),* 345 (1972).
9 H.K. Frensdorff, *J. Am. Chem. Soc., 93,* 600 (1971).
10 P.B. Chock, *Proc. Nat. Acad. Sci. USA, 69,* 1939 (1972).
11 J.J. Christensen, D.J. Eatough and R.M. Izatt, *Chem. Rev., 74,* 351 (1974).
12 D.G. Parsons, to be published.