Crystal Structures of Three Alkali-metal Complexes with a Macrobicyclic Ligand

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Summary The crystal structures of three cryptates are reported, those of sodium and potassium iodide and caesium thiocyanate with a macrobicyclic system containing eight heteroatoms; in all three structures the alkali-metal ion is completely enclosed in the cavity of the ligand.

RECENTLY it has been shown that the macrobicyclic diamino-hexa-ether, $C_{18}H_{36}N_2O_6$, 'the football ligand',[1] forms remarkably stable complexes with various metal cations.[2,3] The crystal structures of two of these, the rubidium and barium cryptates, have been determined.[4,5] In order to provide additional information on the alkali-metal salts of this ligand we have studied the crystal structures of the corresponding sodium, potassium, and caesium compounds.

Complex (A): $C_{18}H_{36}N_2O_6$,NaI crystallizes in the hexagonal system with $a = 8{\cdot}625(3)$, $c = 18{\cdot}582(9)$ and two formula units per cell $D_O = 1{\cdot}45$, $D_C = 1{\cdot}46$ g cm^{-3}. The Laue symmetry of all the crystals examined was invariably $6/m\ mm$; systematic absences of 1 odd for $(hh2\bar{h}l)$ indicate the presence of a c glide plane. Attempts to solve and refine the structure on the basis of one of the apparent space groups defined by the above symmetry requirements ($P\bar{6}2c$, $P6_3mc$, and $P6_3/m\ mc$) were unsuccessful. Instead analysis of the structure was accomplished by the assumption that an incoherent twinning mechanism involving a trigonal single crystal component of symmetry $P31c$ is operative.

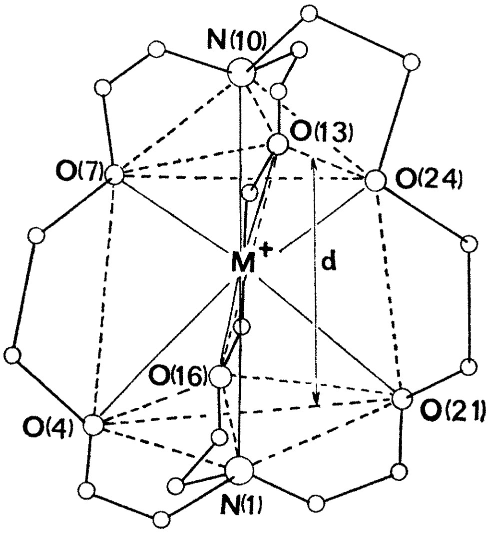

FIGURE 1

The twinning of the reciprocal lattice of this individual crystal of $\bar{3}m$ point group symmetry by an operation such as a reflection across a (100) mirror plane would give rise to a twin composite with the same hexagonal unit cell but with the observed $6/m\ mm$ Laue symmetry.

The structure was solved by the heavy atom method and was refined by full-matrix least-squares using the Wei procedure.[6] R is 0·090 for 795 independent non-zero reflections recorded on a Picker automatic diffractometer. The crystallographic symmetry of the complex cation present in (A) is C_3.

Complex (B): $C_{18}H_{36}N_2O_6$,KI: monoclinic, $a = 14{\cdot}453(5)$, $b = 8{\cdot}553(3)$, $c = 20{\cdot}655(9)$ Å, $\beta = 103{\cdot}77(7)°$, $Z = 4$, space group $C2/c$.

Complex (D): $C_{18}H_{36}N_2O_6$,CsSCN,H_2O: monoclinic, $a = 22{\cdot}681(2)$, $b = 8{\cdot}333(1)$, $c = 14{\cdot}399(3)$ Å, $\beta = 109{\cdot}93(3)°$, $Z = 4$, space group $P2/c$.

The structures of these compounds have been solved by standard methods. R is 0·058 for (B) with 922 independent non-zero reflections measured on a Pailred diffractometer and is 0·061 for (D) with 3578 independent non-zero reflections recorded on a Picker diffractometer.

The crystallographic symmetry of the complex cations present in (B) and (D) is $C2$. Complex (D) is isomorphous with the corresponding rubidium cryptate[4] $C_{18}H_{36}N_2O_6$,Rb-SCN,H_2O (C). Analytical results agree with the formulae given.

In (A), (B), and (D), as in (C), the alkali-metal cation is

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enclosed within the molecular cage. The conformation of the ligand in each case is *in–in*.[7] In all the compounds the polyhedron, defined by the eight heteroatoms, has D_3 symmetry and is intermediate between a bicapped trigonal prism and a bicapped trigonal antiprism. The values of the angle of twist α between the two O_3 triangular faces (see Figure 2) of the bicapped trigonal prisms for (A), (B), (C), and (D), the distance d between the two O_3 triangular faces, the mean values of the metal–oxygen and metal–nitrogen distances, and for comparison the sum of the appropriate ionic radii and the packing radii of nitrogen or oxygen[8] are given in the Table.

TABLE

	(A)	(B)	(C)	(D)
α	45°	21°	15°	15°
d	2·10 Å	2·65 Å	2·81 Å	2·87 Å
$M^+ \ldots O$	2·57(2)	2·789(7)	2·897(5)	2·966(5)
$r_{M^+} + r_O$	2·37	2·73	2·88	3·09
$M^+ \ldots N$	2·77(2)	2·866(6)	3·000(5)	3·029(5)
$r_{M^+} + r_N$	2·47	2·83	2·99	3·19

In these compounds the ligand completely replaces the hydration spheres of the alkali-metal cations. None of these compounds exhibits strong interaction between the metal ion and the anion or water molecules when the latter are present. The corresponding metal–anion and metal–OH_2 distances are all greater than 3·5 Å.

The stability order of the alkali-metal complexes with the 'football ligand' is $K^+ > Rb^+ > Na^+ >> Cs^+$.[3] The relatively low stabilities of the caesium and sodium compounds clearly arise from the influence of the radius ratio effects. Sodium is somewhat too small for effective co-ordination whereas caesium is too large. The repulsive interaction between the caesium ion and the heteroatoms of the ligand must be very large. In the caesium complex, the metal–oxygen and metal–nitrogen distances are not very different from the values found for the same distances in the rubidium compound. However, the analytical results for the caesium compound indicate that no other alkali-metal is present in significant amount.

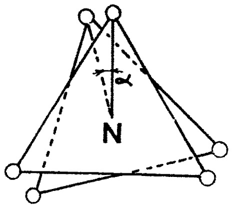

FIGURE 2

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