

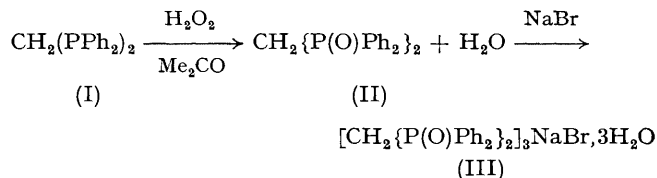
Trigonal Prismatic Co-ordination of Sodium by Oxygen: the Crystal Structure of Tris[bis(diphenylphosphinyl)methane]sodium Bromide Hydrate

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Summary In the crystal of the complex $[\{\text{Ph}_2\text{P}(\text{O})\cdot\text{CH}_2\text{-P}(\text{O})\text{Ph}_2\}_3\text{Na}]\text{Br}\cdot 3\text{H}_2\text{O}$ the cation consists of three molecules of the bis(phosphine oxide) chelating a sodium ion by a trigonal prismatic arrangement of six oxygens. RECENTLY there has been a resurgence of interest in alkali-

metal complexes.¹⁻¹² Methylenebis(phosphine oxides),^{1,2} $R_2P(O)\cdot CH_2\cdot P(O)R_2$ ($R = \text{alkyl or aryl}$), and their arsenic analogues¹ form particularly stable complexes with the halides of the alkali^{1,2} and alkaline-earth¹ metals. Oxidation of the diphosphine (I) in the presence of sodium bromide gave the dioxide (II) (m.p. 184°) and the hydrated complex (III), m.p. 235–240°, which was obtained as well-defined crystals from undried acetone.



The presence of water in the crystals was shown by the i.r. spectrum and confirmed by elemental and thermogravimetric analysis. The 1200 cm^{-1} region of the spectrum was virtually identical with that of the free phosphine oxide (II), there being no apparent shift in the $\nu(\text{P}=\text{O})$ band. Most of the phosphine oxide complexes gave negligible or very small shifts with Group I and II metals; triphenylphosphine oxide behaves similarly with HCl .¹³

Crystal data: $\text{C}_{75}\text{H}_{66}\text{O}_6\text{P}_6\text{BrNa}\cdot 3\text{H}_2\text{O}$ (III), hexagonal, $a = 13.90$, $c = 21.33$ Å, $U = 3569$ Å³, $D_m = 1.35$ g cm^{-3} , $Z = 2$, $D_c = 1.31$ g cm^{-3} , space group $P6_3/m$, Picker diffractometer data, Mo- K_α radiation.

The solution of the crystal structure shows that the water molecules lie on or near to sites of high symmetry within the crystal and are probably disordered. The final choice of space group was dependent on satisfactory refinement of the suggested structure. The present R value for 822 independent reflections, calculated with isotropic parameters for the carbon and hydrogen atoms and anisotropic parameters for the others, is 0.057.

The co-ordination arrangement around the sodium ion is illustrated in Figure 1; the complex cation, $[\text{Na}\{\text{Ph}_2\text{P}(\text{O})\cdot\text{CH}_2\cdot\text{P}(\text{O})\text{Ph}_2\}_3]^+$, has crystallographic $3/m$ symmetry (C_{3h}) with the oxygens of the ligand forming a trigonal prismatic arrangement around the alkali-metal atom. The molecular geometry of the 6-membered chair-shaped chelate ring ($-\text{Na}-\text{O}-\text{P}-\text{C}-\text{P}-\text{O}-$) is given in Figure 2; the Na–O distance, 2.45 Å, is similar to those observed in other crystal structures of sodium salts in which the cation is co-ordinated by oxygen (*e.g.* refs 4 and 5).

The bromide ions lie on the same three-fold axis as sodium, >5 Å away. The nearest approach of a water-molecule oxygen to the sodium atom is 3.8 Å. Consequently there are no contacts, other than those depicted, between possible ligating atoms and the Na^+ ions.

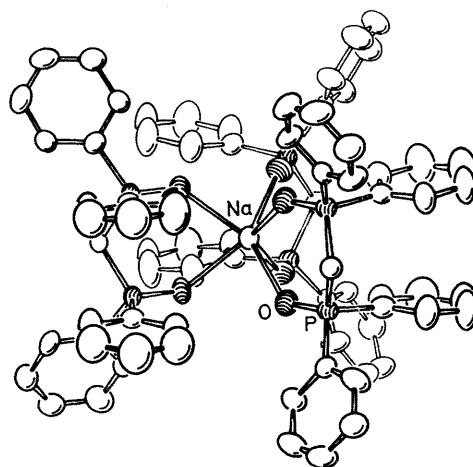


FIGURE 1. The structure of the cation $[\text{Na}\{\text{Ph}_2\text{P}(\text{O})\cdot\text{CH}_2\cdot\text{P}(\text{O})\text{Ph}_2\}_3]^+$

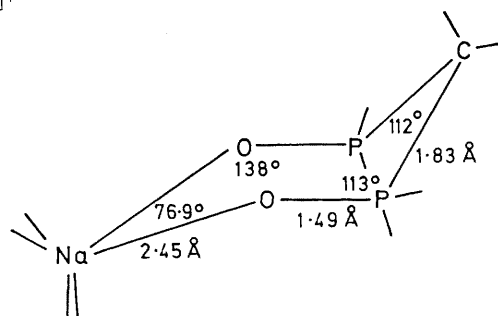


FIGURE 2. Molecular geometry of the six-membered chelate ring—a crystallographic mirror plane passes through the sodium and carbon atoms bisecting the O–Na–O and P–C–P angles.

The bonding between sodium and oxygen is presumably electrostatic and this could give rise to the observed i.r. spectrum in the $\nu(\text{P}=\text{O})$ region. The reason for trigonal-prismatic co-ordination (as opposed to octahedral) may be that it corresponds to the geometrical arrangement that is electrostatically most favourable of 12 lone pairs of electrons from 6 oxygen atoms around the positive charge. The nature of the packing with interlocking phenyl rings may also be important.

The present structure is related to another alkali-metal phosphine oxide complex whose structure has been reported, $\text{LiI}\cdot 5\text{Ph}_3\text{PO}$,³ containing the small lithium cation surrounded tetrahedrally by four oxygen atoms, one from each of four ligand molecules (the fifth phosphine oxide molecule is held in the lattice).

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