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Crystal Structure of Addition Compound of Lithium Iodide with One Enclosed and Four Co-ordinated Molecules of Triphenylphosphine Oxide

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CRYSTALLINE complexes are formed by a variety of organic molecules with alkali-metal halides and some other ionic halides. They include sucrose–sodium bromide (1 : 1, dihydrate),[1] succinimide–tetraethylammonium iodide (2 : 1),[2] and acetamide–sodium bromide (2 : 1).[3] Known interactions with the organic component include hydrogen bonding and ion-dipole effects, and the dispositions of the ions relative to each other and to the rest of the structure are varied. The compounds $MX,5PH_3PO$ ($MX = LiI$, NaI, LiBr, Ph = phenyl)[4] have a higher proportion of organic molecules and the particular 5 : 1 ratio suggests an unusual structural principle.

Crystal observations and data: colourless, m.p. 292°; Orthorhombic, $a = 19{\cdot}426 \pm 0{\cdot}01$, $b = 25{\cdot}716 \pm 0{\cdot}01$, $c = 15{\cdot}414 \pm 0{\cdot}01$ Å, $U = 7702$ Å^3, $D_m = 1{\cdot}320 \pm 0{\cdot}005$ (by flotation), $Z = 4$, $D_c = 1{\cdot}315$. Space group $Pna2_1$ (No. 33) from systematic absences and structure determination. Weissenberg photographs, Cu-K_α radiation.

A variety of standard methods were used to elucidate the structure from 2264 F^2_{hkl} -values. The present R-value, 0·145, is satisfactory for an asymmetric unit of composition $C_{90}H_{75}P_5O_5,LiI$. Iodine and all phosphorus, oxygen, and carbon atoms have been located. The lithium ion, two electrons only, is at this stage inaccurately placed *e.g.*, in difference maps but its position may be independently inferred; the sodium analogue should provide confirmation.

Four oxygen atoms form a tetrahedron of average edge-length 3·17 Å. This can be explained only by the presence of a lithium ion near the centre of the tetrahedron with approximate distances Li–O of 1·97 Å. The associated phosphorus atoms form an outer tetrahedron with lithium-to-phosphorus distances averaging about 3·3 Å and with attached phenyl groups spreading outwards in accordance with normal phosphorus stereochemistry. Four triphenylphosphine oxide molecules may therefore be described as co-ordinated to the lithium ion through oxygen. Iodide ions occupy isolated positions at distances not less than 8·5 Å from lithium.

The fifth phosphorus is over 9Å from the nearest lithium and over 8Å from the nearest iodine. Its associated oxygen is correspondingly distant from these ions. Such large separations show that the fifth triphenylphosphine oxide molecule is not attached to cation or anion. It is also not joined through oxygen or phosphorus to any other triphenylphosphine oxide molecule but is enclosed by the rest of the structure. It is in a geometrically complicated cage roughly central to six iodide and six lithium ions, the inside of the cage being lined with phenyl groups.

The chemical significance is that such a molecule, and neutral ligands in general, may in a sufficiently complex structure play the part of the included component of a clathrate or similar compound. Its stoicheiometric amount cannot in itself be taken as sufficient evidence for a particular co-ordination number. Behaviour of this kind has been inferred from observations on co-ordination complexes of nickel(II) which from empirical formulae might be supposed 7-co-ordinated. Some complexes with methylpyrazine have been explained[5] as octahedral with an additional methylpyrazine molecule "solvating the crystal". Others with certain α-arylalkylamines are similarly explained[6] as six-co-ordinated with one molecule of amine enclosed as in related clathrates.

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