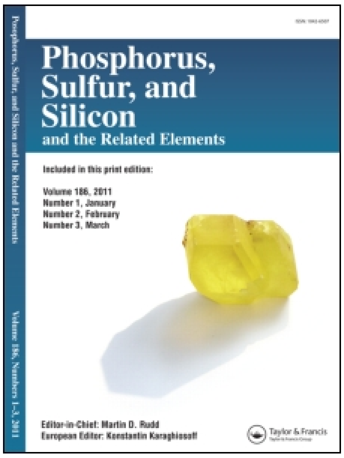

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COORDINATION COMPOUNDS OF ALKALI METAL IONS WITH LIGANDS CONTAINING PHOSPHORYL GROUPS

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Ligands containing phosphoryl groups form coordination compounds with different metals. The coordination compounds of such ligands with alkali metal ions are considered. The effective charge of phosphorus atom in phosphoryl group is approximately +1, and oxygen atom effective charge is approximately -1. Phosphorus and oxygen atoms effective charges depend on the nature of the substituents at phosphorus.

Ions formed by metals of Ia group of the periodic system possess the electronic structure of the preceding inert gase atoms (He, Ne, Ar, Kr, Xe) and are unicharged. These ions belong to the hard acids group and therefore can form rather strong bonds with oxygen atoms of phosphoryl group. Ionic radii of the Ia group metals increase with their atomic number. The number of the virtual orbitals increases in the same order.

Li^+-ion has 4 virtual orbitals ($2sp^3$). Na^+ ion possesses in addition far situated 3d-orbitals ($3sp^3d^5$). Potassium cation has rather close situated $3d^5 4s4p^3$ virtual orbitals. The same set of virtual orbitals is typical for Rb^+ ($4d^5 5s5p^3$). This accounts for high resemblence in the chemical and biochemical behaviour of K^+ and Rb^+. Cs^+ differs essentially from these ions in the set of virtual orbitals ($4f^7 5d^5 6s6p^3$). The energy values of virtual orbitals can be evaluated from ionization potentials found from spectral data.

The coordination numbers of Ia group elements increase from Li^+ to Cs^+ with the increase of radii and number of virtual orbitals. The coordination polyhedrons of the corresponding complexes become more complicated in the same order.

In the solutions of alkali metals coordination compounds following equilibria can be observed:

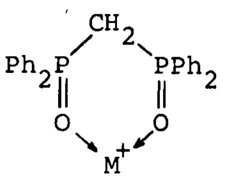
$$\begin{tikzcd}
MX + L \arrow[r, shift left, "K_A"] \arrow[d, shift right] & MLX \arrow[l, shift left] \arrow[d, shift right] \\
M^+ + X^- + L \arrow[u, shift right, "K_D"'] \arrow[r, shift left, "\beta"] & ML^+ + X^- \arrow[l, shift left] \arrow[u, shift right, "K'_D"']
\end{tikzcd}$$

$$\beta = K_A \frac{K'_D}{K_D}$$

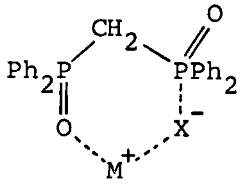
β is stability constant of compound ML^+, K_A - association constant of MLX, K_D and K'_D are dissociation constants of ionic pairs MX and MLX respectively. As a rule the ratio K'_D/K_D exceeds 1, and therefore stability constant of ML^+ is greater than association constant characterizing the formation of complexes MLX from MX and ligand L. However, when specific interaction between the ligand and anion X occurs (addition of X to positive charged ligand atom, hydrophobic interaction, the stacking adduct formation etc.) the ratio K'_D/K_D becomes smaller than 1 and $\beta < K_A$.

The influence of virtual orbitals is most pronounced in interaction of metal ions with polydentate ligand, because the spacial arrangement of donor atoms requires a definite set of virtual orbitals. Thus, the coordination compounds of calcium are less stable than the corresponding complexes of magnesium in case of low dentate ligands (2 or 1), but if polydentate (3 and more) ligands are concerned, stability of calcium and magnesium coordination compounds is the opposite.

The same relations can be observed in case of coordination compounds formed by alkali metal ions. Monodentate ligand Ph_3PO forms stable compounds only with lithium cation. Bidentate phosphoryl containing ligands form coordination compounds with Li^+ (scheme I) and with other alkali metal ions according to both schemes I and II (in the last case ionic pair MX is included in the chelate cycle):



Scheme I



Scheme II

Ligands containing phosphoryl groups, connected by ether bridge fragments (so called "podands") are of great interest, because they form rather stable coordination compounds with different alkali metal ions. Stability of these compounds decreases from Li^+ to Cs^+ if the bridge between phosphoryl groups consists of a few ether units. In case of long polyether chain the stability of podand complexes increases from Li^+ to Cs^+ or passes through maximum at Na^+ or K^+. The stability constant values of such compounds usually vary in a rather narrow interval (10^2 - 10^4) and depend on the solvent nature.

Rather stable coordination compounds of alkali metal ions form also when phosphoryl groups are included into the macrocycles or pseudomacrocycles. Pseudomacrocycles are open chain compounds containing ether fragments and phosphoryl groups and forming the macrocycles as a result of noncovalent interaction between the terminal groups. The stability constant values of phosphoryl-containing macrocycle coordination compounds with alkali metal ions vary in the interval 10 - 10^4. The character of the stability constant variation depends on the cavity dimension and on the conformation lability of macrocycle.

Ligands wich contain phosphoryl groups together with imino groups were found to form rather stable coordination compounds with alkali metal ions. Ligand $Ph_2P(O)CH_2NHC_2H_4NHCH_2P(O)Ph_2$ can be considered as an example. Logarithms of the stability constants (lg β) of coordination compounds with Li^+, Na^+, K^+, Cs^+ are equal to 4,7; 3,7; 2,8; 2,4 respectively.

Stability of alkali metal complexes with cyclopendant ligands such as triaza and tetraaza macrocycles, containing $-CH_2P(O)Ph_2$ and $-CH_2CH_2P(O)Ph_2$ substituents at nitrogen atoms, is much higher. The stability constant values of these compounds in mixed tetrahydrofuran-chloroform solvent are of order $10^3 - 10^6$.

Therefore, the phosphoryl-containing ligand ability to form coordination compounds with alkali metal ions depends on the number and steric position of phosphoryl groups. Ligands with single phosphoryl group form coordination compounds only with lithium ion. The presence of two P = O groups gives rise to complex forming ability of such compounds. Especially strong complexants are ligands containing other groups (ether oxygen or imino group) in combination with phosphoryl one. The maximal ability to form the coordination compounds with alkali metal ions have cyclopendant ligands with polyaza macrocyclic framework.