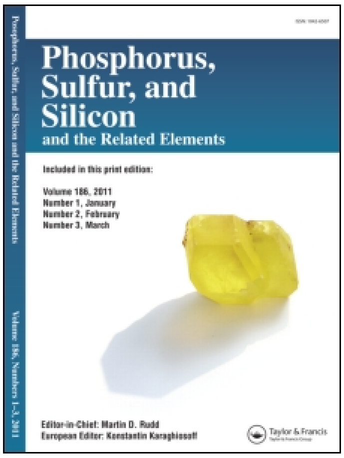

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Organophosphorus Complexones. Efficiency and Selectivity

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ORGANOPHOSPHORUS COMPLEXONES. EFFICIENCY AND SELECTIVITY

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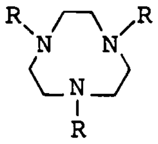
Abstract Organophosphorus chelating agents of a new type, cyclopendant compounds, are characterized by a high efficiency of binding metals to complexes and a high selectivity of their action.

Organophosphorus chelating agents (PCA) were for the first time synthesized by G. Schwarzenbach[1] in 1949. Starting from 1956 we have been concerned with the chemistry of aminophosphonic acids. We have found them to be capable of strongly binding yttrium and ytterbium[2]. This prompted us to undertake a systematic study of PCA which has since been under way[3].

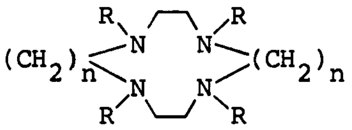
We divide all PCA into three groups such as (i) PCA with flexible chains, (ii) PCA with a limited conformational mobility, and (iii) cyclopendant PCA. Compounds (i) were examined by us in the 1950s to 1970s. They are mostly phosphonic analogues of known chelating agents with carboxylic groups (CC). PCA of this type form strong complexes with many metal atoms, often stronger than those formed by the corresponding CC. The selectivity of PCA is also usually higher than with CC. One more advantage of PCA is their ability to bind cations in a wide range of pH values: from strongly acidic media where they form "hydrogen complexes" to strongly basic ones. They give easily polynuclear complexes.

The efficiency and selectivity of polydentate chelating agents depends on two characteristics: viz. the energy of binding cations by donor atoms and the correspondence of energetically favourable ligand conformations to the geometry of coordination polyhedra. The first characteristic being the same (the same number of donor atoms), the determining role is played by the second one. PCA with flexible chains easily adopt conformations fitting spatial requirements of various cations, and for this reason they are not very selective. Ligand skeleton flexibility can be decreased by introducing substituents, cyclic groups, or other rigid fragments. It has, however, been found that suppressing chain flexibility not always increases selectivity. At the same time natural cyclic polydentate ligands, such as porphin and corrin derivatives etc., are highly selective. Their selectivity is explained by "extracoordination", that is the formation of coordination bonds with additional donor groups present in side chains (pendants). In recent years synthetic chelating agents of this type have been prepared. We call them cyclopendant compounds. Hence the idea of combining the principle of "cyclopendancy" with the presence of pendant groups containing phosphorus. We expected such PCA to be both highly effective and highly selective. And indeed, they proved to be so.

We have studied the following cyclopendant PCA:



(I, II)



I: R = $CH_2PO_3H_2$; II: R = $CH_2CH_2PO_3H_2$; III: n = 2, R = $CH_2PO_3H_2$; IV: n = 2, R = $CH_2CH_2PO_3H_2$; V: n = 3, R = $CH_2PO_3H_2$; VI: n = 3, R = $CH_2CH_2PO_3H_2$.

Alongside experimental studies energetically favourable complexing conformations have been calculated by the method of molecular mechanics with the use of atom-atom potential functions and the "penalty function" and "floating point" techniques[4]. The results are following. Compound I. The lowest-energy complexing conformation is a basket with the macrocycle as bottom and the pendant groups as walls. The basket volume corresponds to cations of a small radius ($r < 0.8$ Å), such as Mg^{++}, Zn^{++}, and Fe^{+++}. The "ladle" conformation with one of the pendant groups tilted as if to produce a ladle handle is somewhat less favourable. The "ladle" can bind cations with radii of about 1 Å. With compound II, the basket volume is larger; nevertheless, cations of small radii are preferable. Compounds III and IV fit well cations of large radii. Chelating agents V and VI show a noticeable structural flexibility and resemble open-chain PCA.

Compounds I to VI were synthesized following a general procedure. First the corresponding macroheterocycles were prepared, and then pendant groups were introduced.

The experimental stability constants of ML agree with calculation results. Chelating agent I: note a high stability of Mg^{++} complex (log $K_{stab.}$ = 11.01) compared with Ca^{++} (6.38): this is unparalleled. Also, the Zn^{++} complex is more stable than the Cd^{++} one (24.90 and 19.70, respectively). Compound II also forms more stable complexes with Mg^{++} (6.10 against <2 for Ca^{++}). The stability of the Co^{++} complex is strikingly high compared with Ni^{++} (13.38 and 9.20, respectively). Compound III. Now calcium forms more stable complexes than magnesium (10.3 and 7.3, respectively). All cations give exceptionally stable complexes, especially large ones (log $K_{stab.}$ = 23 to 25). Chelating agent IV preferably binds heavy metals. IB and IIB Group cations, Cu^{++}, Zn^{++}, Cd^{++}, and Hg^{++}, however, give stronger complexes (log $K_{stab.}$ = 20 to 29) than typical transition metals, Co^{++}, Ni^{++}, and Mn^{++}, (log $K_{stab.}$ = 12 to 15). On the other hand, alkaline earth metals and magnesium give only very unstable complexes. Chelating agents V and VI with a 14-membered macrocycle show properties close to those of open-chain PCA. The only exception is their interaction with Cu^{++} (this also refers to other cyclopendant PCA studied): the cation is bound by four nitrogen atoms in the vertices of a square. One pendant group participates in the formation of a square pyramid so typical of copper. The complex stability is very high (log $K_{stab.}$ = 26.6; for other chelating agents: I, 21.3; II, 21.3; III, 25.4; IV, 27.1).

To sum up, cyclopendant PCA include compounds characterized by both a high efficiency of binding metal cations and a high selectivity of their complexing action. This is a new and very interesting group of PCA and chelating agents in general.

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