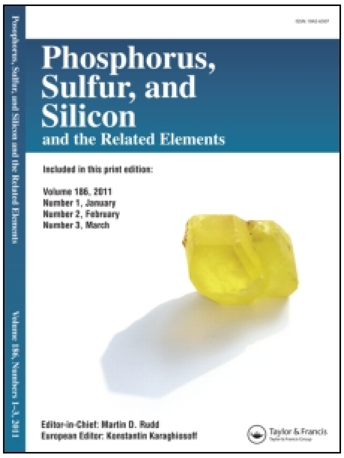

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New Okgano-Phosphorus Cyclopendant Complexons

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NEW ORGANO-PHOSPHORUS CYCLOPENDANT COMPLEXONS.

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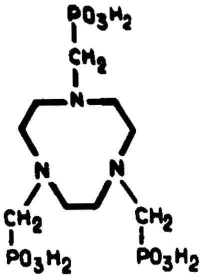
Abstract The organo-phosphorus complexons of new cyclopendant type are studied. It was shown that both high efficiency and high selectivity can be achieved simultaneously.

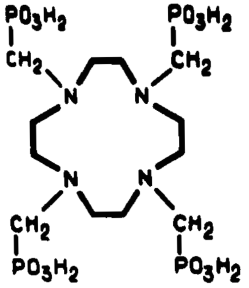
Organo-phosphorus complexons, which are simple or complex analogues of EDTA, differ from their carboxyl prototypes by high selectivity of complex formation. There are numerous highly effective and selective complexons among macroheterocycles. Among those are polyaza-cycloalkane-polyacetic acids.[1,2]

A simple idea of our study consisted in the substitution of carboxyl groups in these cyclopendants by phosphonic groups in order to refine both activity and selectivity.

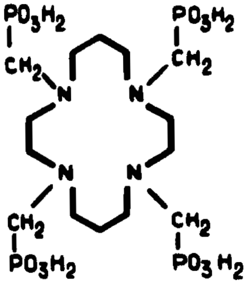
It was suggested that owing to a larger extent of the dihydroxyphosphoryl group, as compared with the carboxyl one, such complexons could form the conformation of a "basket", as shown in Fig. 1 for complexon (I). The basket bottom is formed by the nitrogenous heterocycle, the methylene groups form the walls, and the cap is formed by the phosphoryl oxygen atoms. The metal ion polyhedron should occupy the basket cavity, and when the polyhedron fits the cavity in size and form the complex of considerable strength should be formed.



(I)



(II)



(III)

The study was carried out along both theoretical and experimental pathways. Theoretical calculations were carried out within the framework of molecular mechanics. The calculations showed that the most stable conformation for the triazacyclononane complexon (I) is that with pendants directed sideways. However, there is the second stable conformation, actually a basket

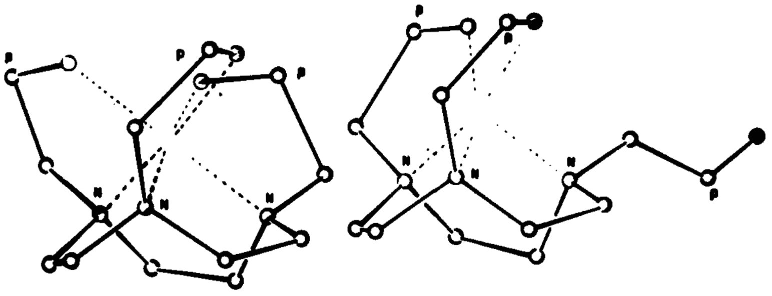


FIGURE 1 Conformations of complexon (I): the basket (left), the dipper (right).

which cavity may fit small metal ions with ionic radius less than 0.8 Å, such as Mg^{++}, Zn^{++}, Fe^{+++},... . This basket cannot accomodate metal ions of greater radius. Still, for the latter case triazacyclononane complexon (I) has one more feasible conformation of low energy, namely a dipper (Fig. 1), with one of pendants directed sideways and forming the handle of the dipper. The dipper can accomodate Ca^{++}, Cd^{++} and other large metal ions and also Cu^{++} which requires the square coordination.

Tetrazacyclododecane complexon (II) is incapable of octic coordination. However, for this ligand there are several penta- and hexadentant conformations of almost equal low energy.

For the complexon (III) the calculations showed that, despite the cycle is larger, this complexon has less number of complexing conformations of low energy than the first two. The complexon (III) is well adapted to accomodate only the copper ion.

The synthesis of the complexons considered was carried out along the general scheme: first the polynitrogenous heterocycle was synthesized, and then the dioxyphosphorylmethyl pendants were attached to the nitrogen atoms.

Stability constants for complexes with metal ions were determined from the potentiometry measurements. The stability constants obtained are presented elsewhere.[3-5]

For triazacyclononane complexon (I)[3] it is noteworthy that its complex with Mg^{++} has considerable strength. Magnesium, having rather small ionic radius, fits well the basket, while only the dipper can accomodate calcium having larger ionic radius. On the whole, complexon (I) yields complexes of very high strength. The selectivity of complex-forming is in this case very high too.

Complexon (II)[4] forms very strong complexes with all heavy metals, surpassing in strength the complexes of its carboxyl analogue and EDTA. Its selectivity is also rather high.

Complexon (III)[5] forms less stable complexes than the former two. Still, the pentadentant complex with Cu^{++} is very strong.

The nature of the complexing conformations was established by the X-ray analysis. The close agreement between the calculated and observed structures is obtained.[6]

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