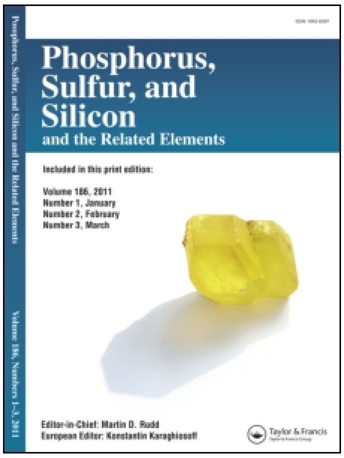

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Synthesis, Structure and Solution Properties of Tetra-Azacycles with Pendant Methylene(Phenylphospinic) Groups

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Synthesis, Structure and Solution Properties of Tetra-Azacycles with Pendant Methylene(Phenylphospinic) Groups

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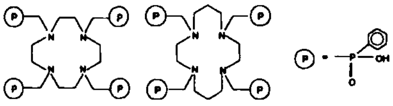
A large number of macrocycles is derived from 12- or 14-membered tetraazamacrocycles *i.e.* "cyclen" and "cyclam", respectively. Here, we report synthesis, structure and solution properties of two polyazamacrocycle ligands, 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl-tetra-methylene-tetrakis-(phenylphoshinic acid) **I**. and 1,4,8,11-tetraazacyclotetra-decane-1,4,8,11-tetrayl-tetra-methylene-tetrakis(phenylphoshinic acid) **II**.



I.

II.

Synthesis - Compounds I and II were synthesised by Mannich reaction of 1,4,7,10-tetraazacyclododecane and 1,4,8,11-tetraazacyclotetradecane tetrahydro-chlorides with paraformaldehyde and phenylphosphinic acid in aqueous HCl. The reaction conditions, *i.e.* concentration of HCl, speed of addition of paraformaldehyde and temperature in the range 50-110 °C were optimised for both the synthesis.

Structure - Crystal structure of II.$4H_2O$ and its bis(adamantylamonium) salt $(AdNH_3)_2$(II).$6H_2O$ was determined by X-ray analysis. The ring conformation is virtually the same for both the structures and is stabilised by hydrogen bonds N2-H2...O11 (2.67 A) in II.$4H_2O$ and N2-H2...O12 2.70 A in $(AdNH_3)_2$II.$6H_2O$. The bond distances of N2...N1 are 2.88 A and 2.89 A respectively, that would point to additional hydrogen bonds, however, the angles N2-H2...N1 are about 110° and thus, we assume only a weak interaction.

Potenciometry - Protonation constants log β were determined pH-metrically at 25 °C and at an ionic strength of 0.1 mol dm^{-3} (KNO_3). The constants determined (for **I** 11.35(1), 18.56(2), 21.26(2), 22.75(2) and for **II** 9.70(2), 19.62(1), 21.75(2), 22.75(2)) correspond to the expected electron withdrawing ability of -$P(Ph)O_2H$ moiety except pK_1 for I which is relatively high. We assume that tha last proton is trapped into a hydrophobic cavity formed by the ring and phenyl groups.

NMR spectroscopy - Contrary to our expectation, the extremely broad signals in ^1H NMR spectra of both the compounds and several signals in the ^{31}P NMR spectra, which roughly correspond to the spectra of the compounds in solid state, were found. We explain the effect by stabilisation of the conformations by hydrogen bonds and hydrophobic interactions of phenyl groups.