



Both compounds have been used as *ordered building blocks* for open chain cation ligands [4] obtained by alkylation of the phenolic OH with different binding groups [I, R' = CH₃, CH₃CO-, -(CH₂CH₂O)_n-CH₃].

The alkylation of II and III destroys the cup-like structure of the starting compounds, which is mainly determined by intramolecular hydrogen bonds, giving products with different geometries and complexing abilities toward cations. Derivatives of the tetrameric oligomer (II) are a mixture of stereoisomers which do not interconvert at ambient temperature and have non convergent binding groups. Their complexation toward Li⁺, Na⁺, K⁺, NH₄⁺, [C(NH₂)₃]⁺ picrates is very poor, these salts being not extracted by the ligands from water to CDCl₃ and CH₂Cl₂.

Derivatives of the octamer (III) have chains which easily pass through the central hole and are able to wrap the cations as the *octopus* molecules [4]. Methyl and acetyl derivatives of III do not complex any tested cation, while compounds with even short polyethers chains [I, R' = -CH₂CH₂OCH₃, -(CH₂-CH₂O)₂CH₃] are able to extract picrates from water to CH₂Cl₂ and CDCl₃.

A remarkable strong complexation of the latter compounds is observed toward guanidinium cation whose tetraphenylborate is dissolved in CDCl₃ up to a ratio [salt]/[ligand] = 1.3–1.5 and picrate extracted from H₂O to CH₂Cl₂ with an extraction constant K_e ≈ 2 × 10⁴ M⁻².

Results obtained with other ligands built on cyclic oligomers derived from *p*-cresol and *p*-octylphenol will be also reported.

References

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Solvent Effects upon Dielectric, Spectroscopic and Thermodynamical Manifestations of EDA Interaction between Iodine and Pyridines

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Dipole moments and the contributions of the dative structure (F_N) in the ground state of pyridine and γ -picoline complexes with I₂ in non-polar and weakly polar solvents were determined. The results thus obtained were compared with those arising from the solvent effect on the spectroscopic behaviour of the amine-I₂ adducts. Correlations were found between the solvent induced enhancement of the dative structure contribution determined from dipole moment measurements and calculated from the force constants of $\nu(I-I)$ and $\nu(N-I)$ vibrations. A similar correlation of F_N was found with respect to the solvent shift of the transition energy ${}^3\pi_{ou}^+ \leftarrow {}^1\Sigma_g^+$ in the I₂ molecule bounded to amines. Solvent effects were also discussed using formation enthalpies ΔH_{AD} for pyridine-I₂ complex on the basis of the thermodynamic cycle. The dependence of F_N and complex stability upon the solvation type were analysed in terms of the Onsager reaction field theory and also through correlations with empirical parameters of solvent activities, such as k_M and E_T.

Solution Chemistry of [PNP]⁺-Salts in Water and Methanol

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The [PNP]⁺-cation [1] has been shown to be a valuable alternative to the usually employed onium cations for studies of anions in alcohols and various aprotic solvents [2].

[PNP]⁺Cl⁻, which serves as the starting material, is simple to synthesize in high yield and is fairly cheap. Due to the considerable solubility of this salt in warm water, other salts can be easily prepared by precipitation. These salts are generally easy to purify, are very soluble in most alcohols and dipolar aprotic solvents and are non-hygroscopic.