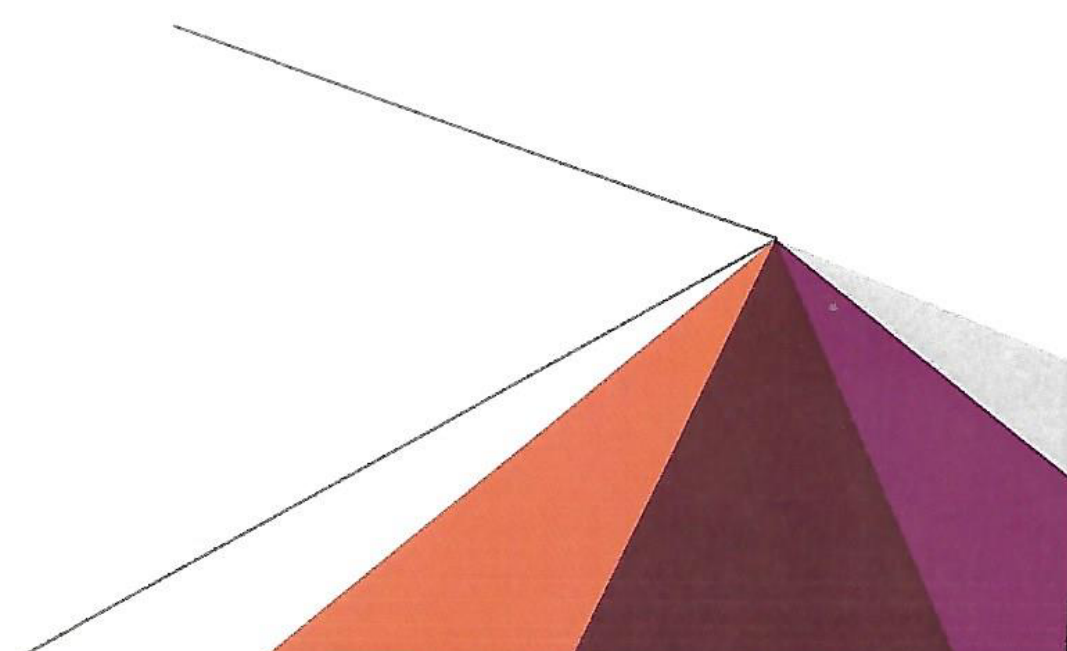




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Complexes of Organic Anions with Tetrazine-based Ligands in Water or How Multifaceted Equilibria Can Arise from Apparently Simple Systems

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Features and nature of any complex species are the result of the interplay of the interactions keeping it together. Yet, at least for classic (cation) coordination chemistry, such interplay is bound to be dominated by the strength of coordination bonds, which generally far exceeds the sum of the contributions from non-covalent forces. [1]

When designed to do so, anion complexes offer the opportunity to “level the playfield”, offering the chance to observe what happens when different types of supramolecular forces (H-bonds, π - π stacking, anion- π , solvent effect, etc.), all falling within a similar energy range, dialogue among themselves to determine the stability and structure of a complex. [1,2]

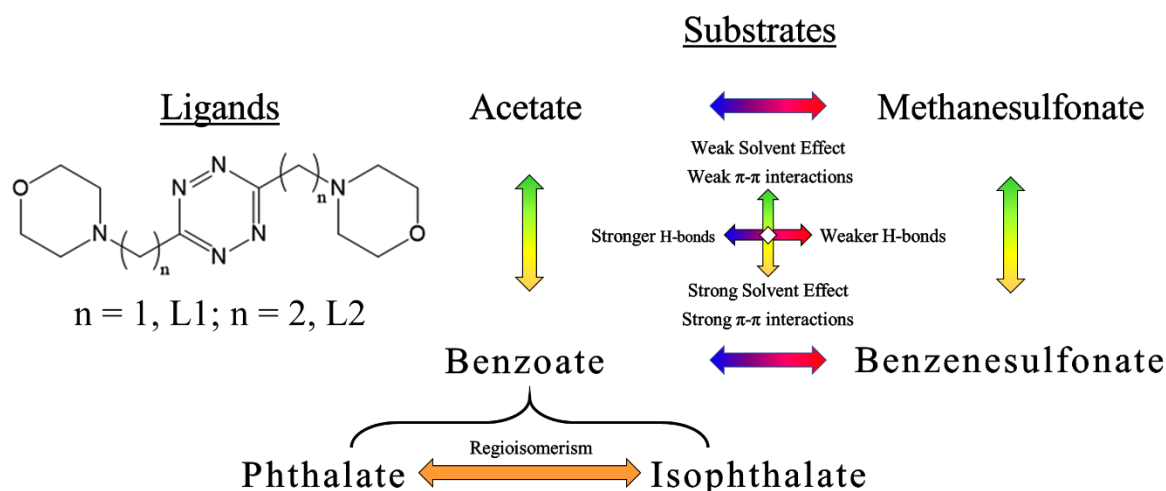
Disentangling the contribution of each type of interactions to the resulting complex and understanding their fine game is hardly practicable for single complexes. However, a rational experimental design featuring homologous molecules as ligands and analogous organic anions as substrates, allowed in our case the achievement of a superior understanding of the forces in play.

Homologous tetrazine-based L1 and L2 ligands, [3] both amenable to anion- π , π - π stacking and H-bonding interactions, but differing in size, were studied with a series of selected and structurally related organic anions in water, as illustrated in Scheme 1. “Basic” carboxylate anions were compared to “non-basic” sulfonate analogues, deeply influencing the intrinsic strength of H-bond interactions, while benzenic vs. methylenic derivatives were used as prototypes for aliphatic and aromatic substrates, fostering the possibility of π - π interactions and increasing the magnitude of hydrophobic effect. Dicarboxylate anions were also considered to account for the presence of a second charged groups, and phthalate regioisomers were investigated to show the effect of substituent position on the interaction modes. [4]

Initially, for monovalent anions, expectable stability trends were found for complex stability (carboxylate > sulfonates, aromatic > aliphatic), which could potentially (and mistakenly) be rationalized in terms of strength of H-bonds, possibility of π - π stacking and increased contribution from solvent effect to complex stability. However, complete speciation data, which required the potentiometric determination of over 40 equilibrium constants, NMR evidences, DFT simulation and solution of 3 crystal structures, revealed a much more

complicated picture, where the geometry of the anion and the size of the receptors are crucial factors in play. [4]

Addition of a second charged group to the substrates brings forth additional effects to be taken into account, adding further depth to the study. It is worth mentioning that the pH dependent selective recognition of phthalate or isophthalate regioisomer is possible in aqueous solution for both ligands. [4] This feature is not generally easily obtained and adds to the fact that detailed understanding of the interplay of different supramolecular forces and its impact on complexes stability, beyond academic interest, has the potential to meet pragmatic scopes, as it foreshadows applications in separation processes.



Scheme 1. General outlook of the ligand/substrate systems considered within present study.

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