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# ISMEC 2017

International Symposium on Metal Complexes

Acta of the International Symposia on Metal Complexes



Université de Bourgogne – Franche-Comté (France)

# ISMEC 2017

## International Symposium on Metal Complexes

**Acta of the International Symposia on Metal Complexes**



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## Effects of the stereoelectronic properties of organic anions on the stability of their anion- $\pi$ complexes in aqueous solution

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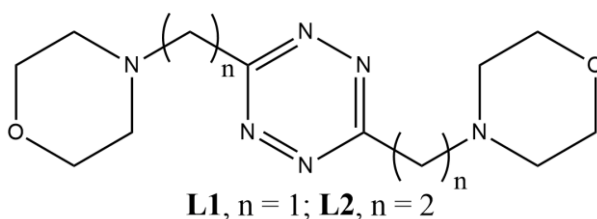
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The binding of anions in solution generally revolves around a combination of weak forces, properly selected incorporating the required structural features in the receptor in its design stage: although individually weak, such interactions can collectively furnish enough stabilization to afford polyfunctional ligands capable of strong and selective anion binding [1].

Among the shortlist of supramolecular forces at our disposal, the most prominent were promptly recognized and investigated in detail (e.g. hydrogen bonding), while others, among which the anion- $\pi$  interaction, required more time to be properly recognized by the scientific community. Alongside with the deeper appreciation of supramolecular forces, also the role of the solvent and its effects on complexation equilibria became more manifest: this is especially true for structured solvents like water, which on one hand compete strongly for charged species, while on the other are capable of promoting the association of poorly solvated species, mostly due to entropic effects, favoring, in some cases, otherwise limited associations.

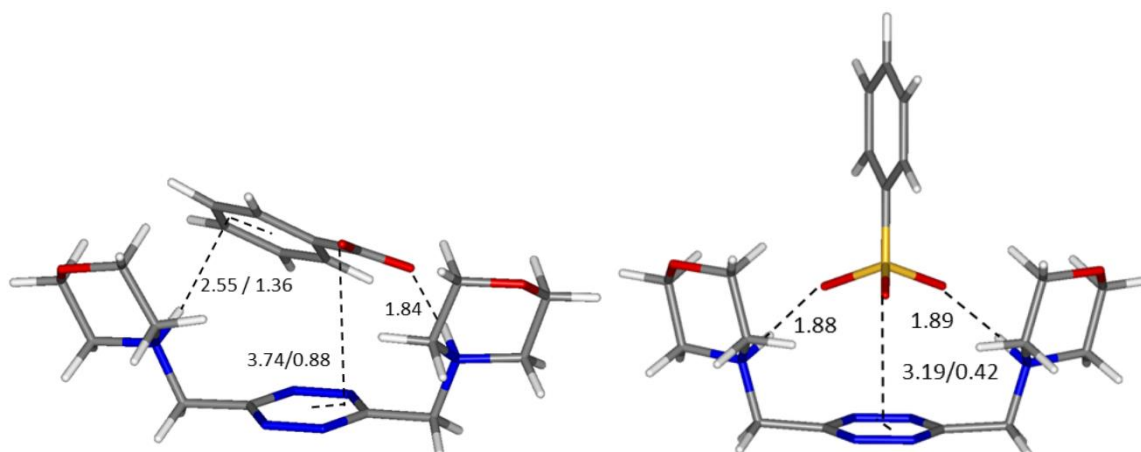
We present our ongoing study on the interplay of different supramolecular forces in the binding in aqueous solution of different organic anions by our tetrazine-based receptors. Such molecules were devised as good model systems for the study of anion- $\pi$  interactions in aqueous solution, conjugating a heterocycle with high positive  $Q_{zz}$  quadrupole moment with morpholine pendants to ensure water solubility without introducing very strong salt bridge donors. A primary study, concerning inorganic anions, demonstrated the correctness of such prediction, indicating a modest contribution of electrostatic forces, while the anion- $\pi$  interaction, corroborated by important desolvation phenomena, was found to be a central feature of such complexes both in solution and in the solid state [2].



Potentiometric (pH-metric) titrations in water environment and *in silico* simulations were employed to evaluate L1 and L2 coordination properties towards a new set of anions presenting selected stereochemical features.

First, the effect of the basicity of the anion, or its tendency to accept a salt-bridge, was inspected comparing acetate with methanesulfonate. In second instance, their simplest aromatic analogues, benzoate and benzenesulfonate, were taken into consideration, as they added to the mix the possibility of  $\pi$ - $\pi$  stacking interactions while enhancing the hydrophobic effect. Lastly, the effect of the insertion of a second charged group was examined studying phthalate and isophthalate anions, allowing to draw a parallel between the stability of the complexes of the two regioisomers. Influence of the mutual size of host and guest was indirectly taken into account due to the different length of the aliphatic spacers in the two ligands.

Needless to say, a complicated picture emerged, demanding further analyses and demonstrating, once again, how shedding light on the subtleties of the interplay of so many different effects, even within the framework of simplified model systems, still remains an ambitious task.



**Figure 1.** Calculated conformations for the adducts of  $H_2L1^{2+}$  with benzoate and benzenesulfonate anions.

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