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Casa Convalescència
ALBA Synchrotron

7-10 June 2016
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BOOK OF ABSTRACTS

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Halogenide Anion Complexes with a Tetrazine-based Ligand

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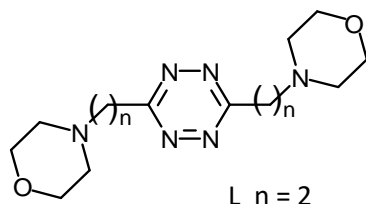
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Anion coordination chemistry has sparked considerable interest in recent years due to the ubiquitous presence of anions in biological and environmental systems, the roles they play in various biochemical processes, and their involvement in many technological areas. The design of receptors for the binding of anions in solution, in particular in water, can be very challenging as the non-covalent interactions employed to anchor anions to the receptor are weak, they must prevail over the competing anion-solvent interactions, and structural features that provide them are often difficult to build into the receptor framework. Fortunately, while individual non-covalent interactions are weak, collectively they could be made sufficiently powerful to afford polyfunctional receptors capable of strong and selective anion binding [1].

Anion- π interactions are among the most recently recognized non-covalent forces [2]. Their importance has long been underappreciated by the scientific community as it is counterintuitive to expect that an attraction may arise between a negatively charged species and common aromatic rings characterised by negative quadrupole moments. However, upon insertion of strongly electron-withdrawing substituents, these quadrupole moments can be inverted, turning parent aromatic systems into π -acids able to attract anions.

We present here preliminary thermodynamic and crystallographic results on the interaction of the tetrazine-based ligand L and halogenide anions. Tetrazines are strong π -acids and, thus, amenable to anion π interactions, but usually they have low water solubility. Functionalization with two morpholine groups makes them sufficiently soluble in water to be studied by means of pH-metric methods.



Potentiometric (pH-metric) titrations performed in aqueous solution showed that both mono- and diprotonated forms of L bind F^- , Cl^- , Br^- and I^- anions forming rather stable complexes. The stability of these complexes is poorly affected by the ligand charge and by the

anion ability to form hydrogen bonds, suggesting that other forces must furnish a significant contribution. The crystal structures of $(H_2L)F_2 \cdot 3H_2O \cdot MeOH$, $(H_2L)Cl_2$, $(H_2L)Br_2$ and $(H_2L)I_2 \cdot H_2O$ (Figure 1) showed that, in the solid state, all complexes are stabilized by an interplay of different weak forces, among which, anion- π interactions are invariably present and prominent. Reasonably, such anion- π interactions are also operative in solution and characterize the particular behaviour of these anion binding equilibria.

Density functional theory (DFT) calculations are in progress to further analyse these binding processes.

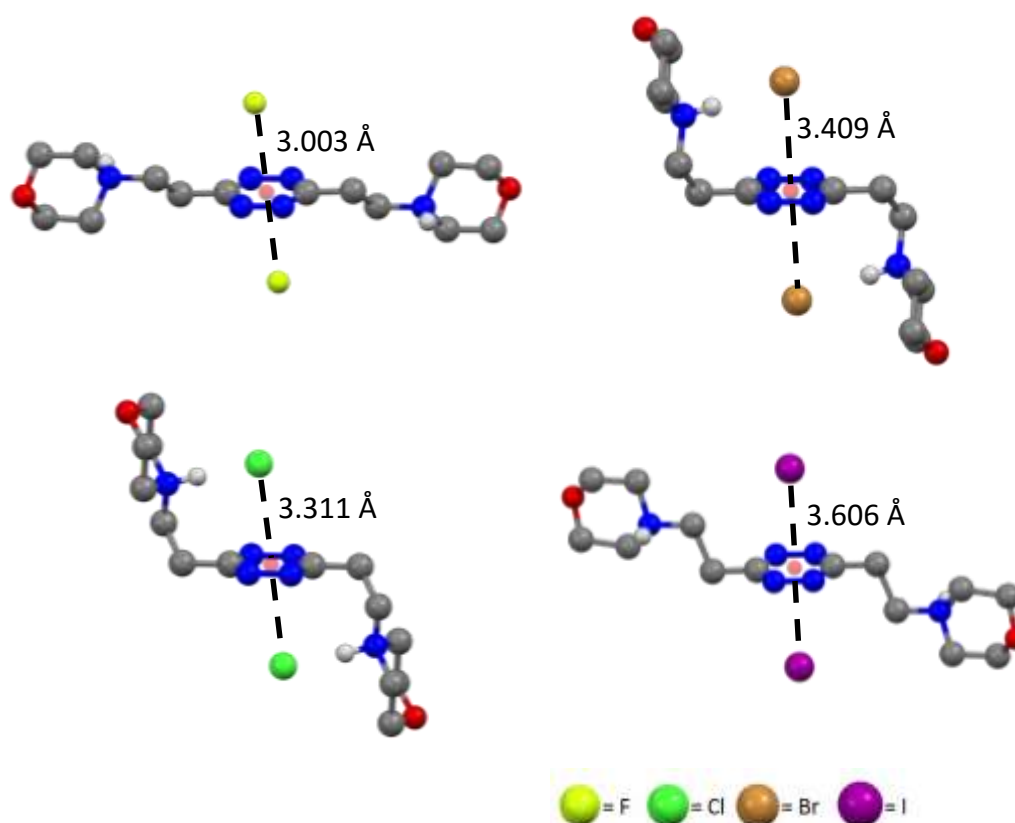


Figure 1. Crystal structures of $(H_2L)F_2 \cdot 3H_2O \cdot MeOH$, $(H_2L)Cl_2$, $(H_2L)Br_2$ and $(H_2L)I_2 \cdot H_2O$

References:

- [1] Bowman-James, K.; Bianchi, A.; Garcia-España, E., *Anion Coordination Chemistry*; Eds. Wiley-VCH: New York, **2012**.
- [2] Quiñero, D.; Garau, C.; Rotger, C.; Frontera, A.; Ballester, P.; Costa, A.; Deyà, P. M., Anion- π Interactions: Do They Exist?. *Angew. Chem., Int. Ed.* **2002**, 41, 3389–3392

Novel bridging μ_2 -N7,O6-acyclovir mode in a tetranuclear complex having a cubane-like core $[Ni^{II}_4(\mu_3\text{-methanolato})_4]^{4+}$