

MS29-P17 A Three-Pronged Approach to Strong Halogen Bonds – Crystallographic, Solution and Computational Study of *N*-Halosuccinimide-Pyridine Complexes

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Over the past couple of decades halogen bonds (XB) have transformed from an obscure intermolecular interactions known only to a handful of experts into an indispensable tool of crystal engineering rivaling even to hydrogen bond (HB). However, detailed studies of XB energetics are still quite scarcer than those for HB.

In our study we have used commercially available *N*-iodo-, *N*-bromo- and *N*-chlorosuccinimide (**NIS**, **NBS**, **NCS**) as halogen bond donors, succinimide (**S**) as an equivalent HB donor, and 7 *p*-substituted pyridines as halogen (or hydrogen) bond acceptors. The pyridines have been selected to cover as wide as possible range of Hammett coefficients (-0.88 to 0.66), while avoiding functionalities which could act as hydrogen bond donors. This has ensured a relatively large variability of XB acceptor qualities, while ensuring that the observed XB is the only strong intermolecular interaction. In order to provide a detailed description of the halogen bonding in these systems, *N*-halosuccinimides were crystallised with the pyridines in order to study the formed complexes in the solid state. Simultaneously, microcalorimetric measurements were made to study the formation of halogen bonded complexes in acetonitrile solution, and, extensive computations in order to study the deformation of electron density upon XB formation, as well as the effect of various geometric parameters on the energy of XB.

Solid state studies have shown that **NIS** and **NBS** form strong halogen bonds with all 7 pyridine derivatives. **NIS** is expectedly a better XB donor (*N*...*X* distances 29-32% shorter than the sum of van der Waals radii for **NIS** and 23-29% shorter for **NBS**). In both cases the more nucleophilic pyridine nitrogen atoms were better XB acceptors forming shorter bonds. The scattering of the datapoints was larger in the case of **NBS** indicating wider and more shallow potential well for XB with **NBS**, as confirmed computationally. The differences in the measured bond lengths were mirrored in the stability of the **NIS**-pyridine complexes in the solution - the stability constants were found to vary by over three orders of magnitude from $\log K = 4.003(9)$ for the complex exhibiting the shortest XB to $\log K = 0.825(3)$ for the one with the longest bond. In comparison, **S** was found to produce hydrogen-bonded cocrystals only with the two strongest nucleophiles used, and the corresponding stability constants were nearly four orders of magnitude lower than those for halogen bonded complexes with **NIS**.

Keywords: halogen bond, supramolecular chemistry, *N*-halosuccinimides

MS29-P18 β -diketones and their derivatives in Rh(I) dicarbonyl and phosphine complexes

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This study is concerned with the application of β -diketone derivatives, specifically enamino-ketones and cupferron variants, as ligand systems and the influence of substitution on such ligands with regard to rhodium(I) complex formation. Enamino-ketones contain nitrogen and oxygen donor atoms as well as an alkene functionality, and as such these electron-rich compounds are of interest in various areas, including application as liquid crystals [1], in fluorescence studies [2], the medical field [3,4] and with significant potential in homogeneous catalysis [5].

A range of crystal structures of the $[\text{Rh}^{\text{I}}(\text{Bid})(\text{CO})(\text{PX}_2)]$ (where X is a combination of phenyl and cyclohexyl groups) complexes [6,7] as catalyst precursors will be discussed. Furthermore, the exchange between free and coordinated phosphine as indicated through nuclear magnetic spin transfer techniques will be highlighted.

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