

**Figure 1.** A view of the tetranuclear  $[\text{Cr}_2(\text{bpy})_4(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4]$  molecule in 1. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms on the aromatic rings are omitted for clarity.

**Keywords:** heterometallic complex, oxalate ligand, oxo bridges, molecular precursor-to-material conversion, chromium niobate

## MS30-P27 Isoquinoline-based Werner clathrates with xylene isomers: Aromatic interactions vs. molecular flexibility

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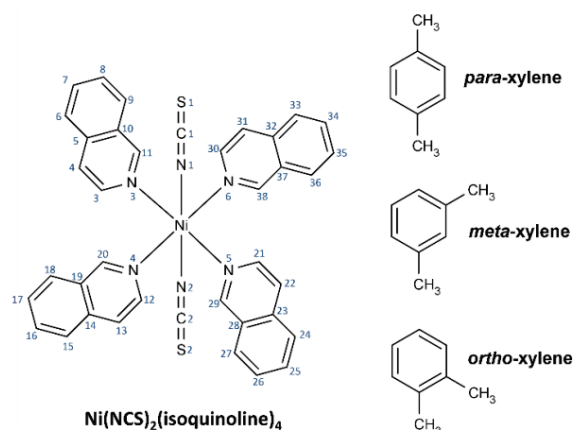
Werner clathrates are inclusion compounds of general formula  $\text{MX}_2\text{L}_4 \cdot n\text{G}$ , where M is a divalent metal cation (typically Ni(II), Co(II), Fe(II), Cu(II) and Mn(II)), X is an anionic ligand ( $\text{NCS}^-$ ,  $\text{NCO}^-$ ,  $\text{CN}^-$ ,  $\text{NO}_3^-$  or halide), L is a substituted pyridine or  $\alpha$ -arylalkylamine, and G is a Guest, usually an organic aromatic compound. The separation of isomers, with similar boiling points, melting points and other physical properties, is difficult to accomplish by classical separation methods. In pursuit of a Werner clathrate which would provide a better system of aromatic interaction between the host and the guest, but simultaneously be selective for xylene isomers,<sup>1</sup> an isoquinoline-based clathrate was made.

The crystal structures of the Werner clathrates  $\text{Ni}(\text{NCS})_2(\text{isoquinoline})_4$  (**H**) with *para*-xylene (**px**), *meta*-xylene (**mx**) and *ortho*-xylene (**ox**) have been elucidated. The kinetics of thermal decomposition of the three inclusion compounds were performed. Selectivity of **H** for the xylene isomers was determined by headspace gas chromatography for both the liquid and vapour phase binary mixtures of the xylenes.<sup>2</sup> Hirshfeld surfaces and fingerprint plots of **H** with the three guests were projected to illustrate the interactions between the host and guest. The chosen ligand has two fused rings which give it a larger aromatic system to improve the possible  $\pi$  interactions between **H** and the selected guests. The rigidity of the isoquinoline ligand, however, causes its lack of selectivity compared to a related Werner complex containing torsional flexibility of the phenyl moieties in the 4-phenylpyridine ligands.<sup>3</sup>

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**Figure 1.** Scheme 1 Structural line diagrams and atomic numbering scheme of the host, Ni(NCS)<sub>2</sub>(isoquinoline)<sub>4</sub>, and the xylene isomers

**Keywords:** Werner clathrate, selectivity, torsional flexibility

## MS30-P28 Interactions in rare-earth coordinated complexes grown from ionic liquids: application to the extraction and separation of rare earths

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Extracting and separating the rare earths is a high demanding process due to their similar chemical properties. The topic to recycle and separate mixtures of rare earths from scrap has been a major research topic over the last few years [1] due to the diminishing of the rare earth reserves and safekeeping of own stock. Since 1970, industry uses a liquid-liquid solvent extraction mechanism by coordinating the mixtures of rare earths with an extracting agent. Each entity is distributed over the aqueous and organic phase, with each consecutive extraction improving the separation and purity of the elements. Our research focuses on improving this process by using ionic liquids as extracting agents and looking at the formed entities at a structural level as current research is solely based on calculating thermodynamical parameters of the extraction/separation process. When dissolving a rare-earth salt into an ionic liquid, the elements are coordinated by the anionic entities of the ionic liquid to form an anionic complex. The organic cation of the ionic liquid neutralizes this and migrates the rare earth to the organic phase. Disturbances in interactions between the anion and cation can change the level of migration. By studying these key interactions, we try to relate them to the overall extraction process.

Different rare-earth salts were dissolved in ionic liquids containing  $\beta$ -diketonate anions and large organic cations such as 1-alkyl-3-methylimidazolium or tetraalkylammonium. After extraction, crystals were grown from the organic phase and measured. Current research results show that a non-classical hydrogen bond is persistent across the different molecules, whilst C-H...F interactions between the cation side chain and halogens on the  $\beta$ -diketonate add extra stability to the crystal structure. When comparing these side chain interactions with solubility data we noticed that these have a major impact on the stability and therefore extractability in the organic phase. Structures formed with 2-thenolytrifluoroacetylacetonate anions have little to no intention to form side chain interactions, leaving the alkyl chains of the cation disordered, whilst structures formed with hexafluoroacetylacetonate have strong side chain interactions, which leads to a better packing and crystal stability.

[1] Dupont, D.; Binnemans K., *Green Chemistry*, 2015, 17, 856-868

**Keywords:** Rare-earths, Ionic liquids, interactions