

Structural Studies on Hybrid Organic-Inorganic Coordination Assemblies

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Introduction

Molecular recognition and engineering of 3D architectures are key features of supramolecular chemistry. Hybrid organic-inorganic coordination assemblies stand for a class of supramolecular compound whose preparation is a very active area in chemical and materials research. The concept of hybrid organic-inorganic materials realizes experimental strategies for customizing physical and chemical properties by influencing dimensionality and devolution pattern of classical inorganic structures within organic matrices. A few of the key research areas under this purview include catalysis and separation science, gas storage media, optical, electronic and magnetic materials etc. [1,2].

Synthetic methodology

We have developed synthetic approaches yielding in novel coordination assemblies where the architecture and dimension of the inorganic regions of the materials is influenced by the functionality and shape of organic ligands. The crystallographic studies investigate structure-directing effects of iminodiacetic acid substituted phenols and naphthol derivatives (L) which react with Fe^{III} salts to give dinuclear complexes with the general formulae $[\text{Fe}_2(\mu\text{-OH})(\mu\text{-CO}_3)\text{L}_2]^{3-}$ and $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CO}_3)\text{L}_2]^{4-6-}$. The counterions of these complexes bind through the carboxylate groups and other O-donors to these negatively charged complexes and are further linked to each other through water molecules forming supramolecular coordination assemblies. Variation of the organic ligand results in structures where the packing of hydrophilic and hydrophobic portions results, for instance, in lamellar arrangements, dense hexagonal arrays or open-framework networks [3].

Structure of $\text{K}_6[\text{Fe}_2(\text{O})(\text{CO}_3)(\text{CHNIDA})_2] \cdot 13.5\text{H}_2\text{O}$ (**1**)

From aqueous systems, we crystallized a rather fascinating example of such hybrid organic-inorganic coordination networks, $\text{K}_6[\text{Fe}_2(\mu\text{-O})(\mu\text{-CO}_3)(\text{CHNIDA})_2] \cdot 13.5\text{H}_2\text{O}$ (**1**) and investigated the structure at BL 18B (Fig. 1). Crystal data: red cuboctahedron 0.2 x 0.2 x 0.2 mm, T = 200 K, rhombohedral, R-3c, $a = 35.475(4)$, $c = 43.4480(4)$ Å, $V = 47354(10)$ Å³, $Z = 36$, $R_1(F) = 12.8$.

The X-ray analysis reveals that the Fe^{III} centres of the dinuclear complex are doubly bridged by a carbonate and an oxo ligand O(1). N- and O-donors of the iminodiacetic acid moiety occupy *facial* positions of the distorted octahedral coordination polyhedra whilst the bridging O-donor and the N-donors coordinate in *trans* positions relative to each other. The dinuclear Fe^{III} complexes in **1** are organized so that the polar O-donors together with the

water-bridged K⁺ ions form a honeycomb structure. The resulting channels, with a cross-sectional diameter of 12nm, run in direction of the crystallographic *c*-axis and are filled with naphthyl moieties of the ligands. The dinuclear Fe^{III} subunits penetrate the honeycomb walls with the Fe-Fe axis nearly perpendicular to the *c*-axis. The naphthalene moieties of each Fe^{III} complex project into neighbouring channels and the naphthalene mean planes form angles of 40.7 and 51.4° to the *c*-axis [3].

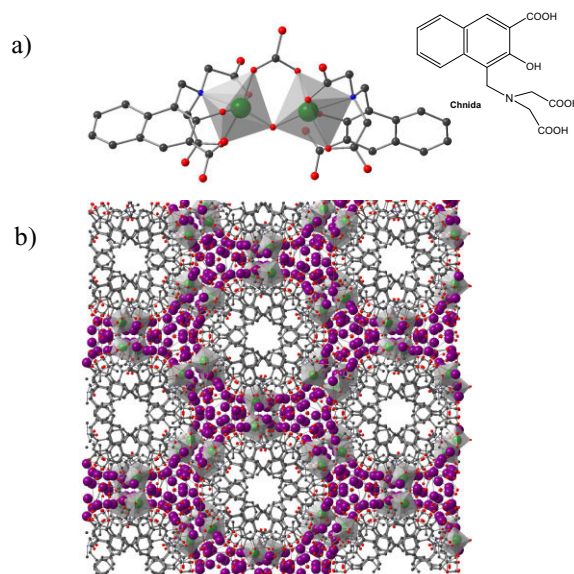


Figure 1. a) $[\text{Fe}_2(\mu\text{-O})(\mu\text{-CO}_3)(\text{CHNIDA})_2]^{6-}$ in **1**. b) Supramolecular structure of **1** viewing in [001]. Colour code: Fe green, O red, N blue, K purple, C dark grey.

Currently we are investigating thermal stability and gas adsorption properties and conductivity of these materials. In addition we use **1** as a template for the production of nanostructured materials.

References

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