Stacking interactions between phenanthroline ligands in square-planar complexes

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Noncovalent interactions of π-systems, including stacking interactions, have been extensively studied in recent years. Stacking interactions are generally studied between aromatic organic molecules or fragments. However, it was shown that other planar molecules and fragments can be also involved in stacking interactions.

Stacking interactions between chelate and C aromatic rings were recognized by analyzing the data in crystal structures of square-planar transition metal complexes from the CSD. In the crystal structures there are mutual slipped-parallel orientation of these rings, similar to the orientation of two benzene rings. Recently we showed the existence of chelate-chelate stacking interactions in crystal structures from CSD [1]. Geometrical analysis of stacking interactions with aromatic nitrogen-containing ligands show that nitrogen-containing aromatic rings usually form slipped parallel alignment where most of the ring-plane area overlaps [2].

Phenanthroline (1,10-phenanthroline-N,N') (phen) molecule coordinating to a metal ion forms large planar system of four rings: two pyridine fragments, one C ring and one chelate rings. This planar system has propensity to form stacking interactions with the π-system of various aromatic groups. Tendency for stacking interactions is important for using these complexes in biochemistry, supramolecular chemistry, and medicinal chemistry.

To understand better stacking interactions of phen complexes, here we analyze the geometry of stacking interactions between phen square planar metal complexes in crystal structures from the CSD.

In the Cambridge Structural Database (CSD) 61 structures with 172 stacking interactions of phen square-planar complexes were found [3]. The results of crystallographic analysis show that in most of the structures two interacting ligands are oriented “head-to-tail”, with the large area of phen ligand involved in the overlap. Phen complexes show large range of different overlap geometries in stacking interactions, however, short metal-metal distances were not observed. Stacking interactions of phen square-planar complexes form chains and dimers in crystal structures.

Keywords: molecular packing, space-group frequencies, crystallization

Identification of single photo-switchable molecules in nanopores of silica xerogels using neutron powder diffraction

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Single photo-switchable molecules of (CNH2)6[Fe(CN)6] (GuNP) are embedded into nanopores of a SiO2 xerogel. We show that it is possible to identify the structural motif (fingerprint) of the embedded complex by analyzing neutron powder diffraction data in a limited Q range (Q<37 nm-1) using the Debye approach. The structural study reveals that the pores are occupied by GuNP-monomers with a fill factor of 60-80%. The mutual arrangement of the anion and cation in the GuNP monomer is slightly changed (~1% elongation) while the bond lengths within anion and cation are changed by less than 0.2% with respect to the single crystalline form of GuNP.

This example demonstrates that the structure of single molecules in nanopores and their distance to nearest neighbors of the host network can be analyzed using a standard neutron powder diffractometer with limited Q-range such as DMC@SINQ. From the analysis of the small angle range one obtains an estimate for the average pore size and the fill factor of pores with embedded complexes. The distance between atoms of the host network and the guest complexes can be determined from the intermediate scattering range. Assuming a sufficient scattering contrast between host and guest this method can be extended also to the x-ray case, such that these experiments can be performed on laboratory...