

**Keywords:** X-ray\_diffraction, cobalt, 4-midazole

## MS17.P19

*Acta Cryst.* (2011) **A67**, C320

### Structural Analysis of Hexa-4-methylimidazole nickel(II) 5-aminoisophthalate tetrahydrate.

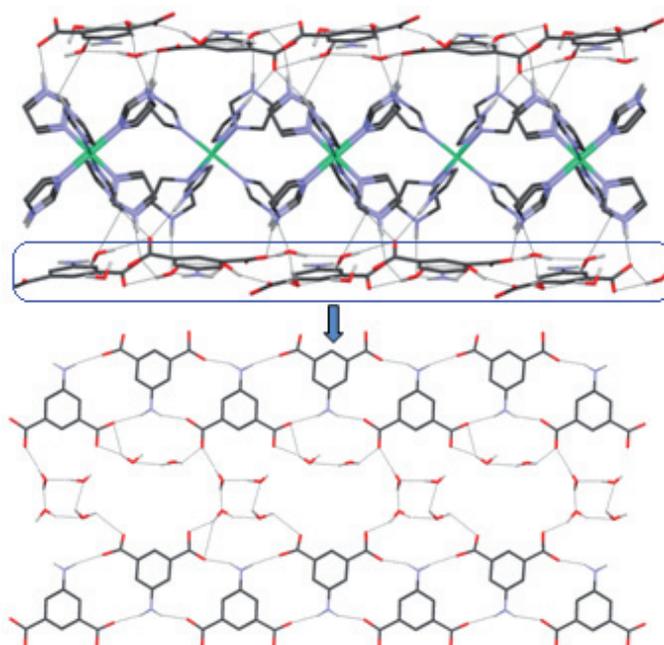
Ersin Temel,<sup>a</sup> Alper Tolga Çolak,<sup>b</sup> Okan Zafer Yeşilel,<sup>c</sup> Handan Günay,<sup>c</sup> Orhan Büyükgüngör,<sup>a</sup> <sup>a</sup>Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139, Kurupelit/Samsun, (Turkey). <sup>b</sup>Department of Chemistry, Faculty of Arts and Sciences, Dumlupınar University, Kütahya, (Turkey). <sup>c</sup>Department of Chemistry, Faculty of Arts and Sciences, Eskişehir Osmangazi University, Eskişehir, (Turkey). E-mail: etemel@omu.edu.tr

The title compound is composed of  $[\text{Ni}(4\text{-methyl imidazole})]^{+2}$  complex cations, 5-amino isophthalato anions and water molecules. Two nickel atoms are located at special positions. Each Ni atom has a slightly distorted octahedral coordination geometry defined by 4-methyl imidazole rings coordinated through N atoms. In the 5-amino isophthalato anions, while aniline parts are planar, carboxylate groups deviates from planarity.

The crystal packing is achieved by strong and moderate hydrogen bonds which play an important role in the formation of the 3D network. These interactions are drawn in Figure.

The packing is formed by periodic repetition of 2D A- and B-layers which are parallel to *ab*-plane. While layer A is composed of only nickel complexes, layer B is composed of the combination of 5-amino isophthalato and water molecules. In the layer A, nickel complexes with each other linked by C-H... $\pi$  interaction. On the other hand, B-layers act as a bridge between nickel complexes along *c*-axis. Layers A and B are linked by N-H...O type hydrogen bonds.

It can be seen from figure that N-H...O and O-H...O hydrogen bonds construct 2D network in layer B. 5-amino isophthalato anions linked to each other by N-H...O type hydrogen bonds, generating adjacent  $R_2^2(14)$  ring motifs along *a*-axis [1]. Tetrameric water clusters connect 5-amino isophthalato anions along *b*-axis. While the cyclic water tetramer is formed by O2W, O3W, O5W and O8W atoms, the dimeric clusters are formed by O1W, O4W and O6W, O7W atoms. Oxygen atoms of carboxylate groups are hydrogen bonded to dimeric and tetrameric clusters.



[1] J. Bernstein, R.E. Davis, L. Shimoni, N.L. Chang, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1555-1573.

**Keywords:** X-ray\_diffraction, nickel, cluster

## MS17.P20

*Acta Cryst.* (2011) **A67**, C320-C321

### When organic and metal-organic molecules cease to crystallize?

Jan Fábry,<sup>a</sup> Radmila Krupková,<sup>a</sup> Miloš Kopecký<sup>a</sup> <sup>a</sup>Inst. Of Physics of the Academy of Sciences of the Czech Republic. Na Slovance 2, 182 21 Praha 8, Czech Republic. . E-mail: fabry@fzu.cz

The dependences of occurrences of the most frequent space-group types  $P\bar{1}$ ,  $P2_1$ ,  $P2_1/c$ ,  $C2/c$ ,  $P2_12_12_1$  and  $Pbca$  on reduced unit-cell volumes up to 8000 Å<sup>3</sup> were investigated for organic and metal-organic compounds with different number of residues, *i.e.* with different number of molecular constituents (1-3). The dependences for these space-group types are similar, single-peaked; their maxima are proportional to the number of asymmetric units, affected by  $Z'$  (number of formula units *per* asymmetric unit) in the pertinent space-group types. The dependences of  $Z' < 1$ ,  $Z' = 1$ ,  $Z' > 1$  within each space group type on reduced unit-cell volumes are also similar in shape. From these dependences it can be inferred that ability for crystallization of organic and metal-organic molecules ceases for the structures with the reduced unit-cell volumes above 8000 Å<sup>3</sup>. This volume corresponds roughly to 450 non-hydrogen atoms in a unit cell, *i.e.* to non-hydrogen 56 atoms *per* molecule [1].

The loosing ability for crystallization for large molecules is also manifested by the deviation from linearity of the Kempster-Lipson [2] rule for the structures composed from C, H, N, O at most. The present analysis has the following implications:

While a broadly shared view that the more symmetric is a molecule the more symmetric is a crystal arrangement seems to be correct [3,4] the opposite conclusion has been shown not to be quite true because the larger organic or metal-organic molecules tend to crystallize in a more symmetric space-group type such as  $Pbca$ . The present analysis shows influence of the molecular size on the symmetry of the crystalline state. It is known that biological macromolecules often contain huge dummy parts the function of which is unclear while active centres are surprisingly small. Can be the size of the biological

molecules assumed as a protection against spontaneous crystallization in organisms? **Acknowledgements:** The support by the Grant Agency of AS CR under grant no. IAA100100915 is gratefully acknowledged.

[1] J. Fábry and R. Krupková *Ferroelectrics* **2008**, *375*, 59-73. [2] C.J. E. Kempster and H. Lipson *Acta Cryst.* **1974**, *B28*, 3674. [3] A. I. Kitajgorodskij *Organic Crystal Chemistry* **1955**, Izdatel'stvo Akademii Nauk SSSR, Moscow. [4] C. P. Brock and J. D. Dunitz *Chem. Mater.* **1994**, *6*, 1118-1127.

**Keywords:** molecular packing, space-group frequencies, crystallization

## MS17.P21

*Acta Cryst.* (2011) **A67**, C321

### Stacking interactions between phenanthroline ligands in square-planar complexes

Dragan B. Ninković,<sup>a,d</sup> Goran V. Janjić,<sup>c</sup> Predrag V. Petrović,<sup>a</sup> Snežana D. Zarić,<sup>b</sup> <sup>a</sup>Innovation center of the Department of Chemistry, Studentski trg 12-16, 11000 Belgrade, (Serbia). <sup>b</sup>Department of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, (Serbia). <sup>c</sup>IHTM, Njegoševa 12, 11000 Belgrade, (Serbia). <sup>d</sup>E-mail: dragannin@yahoo.com

Noncovalent interactions of  $\pi$ -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  $C_6$ -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  $C_6$ -ring and one chelate rings. This planar system has propensity to form stacking interactions with the  $\pi$ -system of various aromatic groups. Tendency for stacking interactions is important for using these complexes in biochemistry, supramolecular 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.

[1] D.N. Sredojević, Z.D. Tomić and S.D. Zarić, *Crystal Growth & Design* **2010**, *10*, 3901-3908. [2] G.V. Janjić, J. Andrić, A. Kapor, Ž.D. Bugarčić, S.D. Zarić, *Cryst EngComm* **2010**, *12*, 3773-3779. [3] G.V. Janjić, P. Petrović, D. Ninković and S.D. Zarić, *J Mol Model* **2010**, DOI 10.1007/s00894-010-0905-3

**Keywords:** Stacking interaction, Intermolecular interaction, Crystal structures

## MS18.P01

*Acta Cryst.* (2011) **A67**, C321

### Structure and magnetic properties of nanoparticles

$Ni_{0.5}Zn_{0.5}Cr_{0.1}Fe_{1.9}O_4$

L. M. Salah, E. Ateia, A. A. H. El-Bassuny, *Physics Department, Faculty of Science, Cairo University, Giza, (Egypt)*. E-mail: lobnasalah2003@yahoo.com

Nanostructure ferrite of composition  $Ni_{0.5}Zn_{0.5}Cr_{0.1}Fe_{1.9}O_4$  was prepared by sol-gel, co-precipitation, citrate-gel, flash and oxalate precursor methods. Structural and micro structural analysis of all the samples were carried out (XRD, IR, TEM, SEM and AFM). The saturation magnetization at room temperature was also studied. Lattice constant and particle size were determined by different methods. The average values of the crystal size for different method were in nanometric range (5 - 75 nm). It was observed that the lattice parameter of cubic spinel was not varied and the positions of the tetrahedral and the octahedral band are not shifted which give the indication that the cation distribution are the same. So, the results of magnetic hysteresis were explained in terms of the relation between grain size and magnetic properties in addition to surface randomizing effect in nanocrystals leading to superparamagnetism state.

**Keywords:** nanocrystals, synthesis, ferrite.

## MS18.P02

*Acta Cryst.* (2011) **A67**, C321-C322

### Identification of single photoswitchable molecules in nanopores of silica xerogels using neutron powder diffraction

Dominik Schaniel,<sup>a</sup> Theo Woike,<sup>b</sup> A. Cervellino,<sup>c</sup> Lukas Keller,<sup>d</sup> Jürg Schefer,<sup>d</sup> <sup>a</sup>Laboratoire de Cristallographie, Résonance Magnétique et Modélisation (CRM2), Institut Jean Barriol, Nancy Université, Nancy (France). <sup>b</sup>Institut fuer Strukturphysik, TU Dresden, Dresden (Germany). <sup>c</sup>Swiss Light Source (SLS), Paul Scherrer Institute, Villigen PSI (Switzerland). <sup>d</sup>Laboratory for Neutron Scattering (LNS), Paul Scherrer Institute, Villigen PSI (Switzerland). E-mail: dominik.schaniel@crm2.uhp-nancy.fr

Single photo-switchable molecules of  $(CN_3H_6)_2[Fe(CN)_5NO]$  (GuNP) are embedded into nanopores of a  $SiO_2$  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 ( $Q < 37 \text{ nm}^{-1}$ ) 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