

calculated in order to describe the effect of the small guest molecules on the crystal structure. Also the influence of the replacement of the phenyl substituent to naphthyl and the exchange of the carbinol C to Si on the inclusion properties and on the geometry of the host molecules has been studied.

[1] Csöregi I., Weber E., Skobridis K., Bombicz P., Seichter W., *Silicon Analogues of Triarylmethanol Hosts. Inclusion Properties and Host-Guest Structures – A Comparative Study., in preparation, and references therein.*

**Keywords:** isostructurality, host isometricity, inclusion compounds

#### P.08.10.3

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#### The Many Crystal Forms of $[M(15\text{-crown-5})(\text{H}_2\text{O})_2](\text{NO}_3)_2$

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Five structure types have been found between 90 and 320 K for crystals grown near 295 K from aqueous solutions equimolar in 15-crown-5 and  $M(\text{NO}_3)_2$ ,  $M = \text{Mg, Mn, Fe, Co, Cu, or Zn}$  (12 structures). In the tetragonal form ( $P4_1$ ,  $Z'=2$ ; Mn and Co) water ligands and nitrate ions form a 3-D network of H bonds. The other four structure types have 2-D patterns of H bonds and are best understood as modulated variants of a basic structure. Two 2-D phases have been seen for each metal except Co; the phase pairs are all linked by reversible transitions during which the crystals remain single. The 2-D phases all have  $Z' > 1$ :  $P2_1/c$ ,  $Z'=3$  (Mg, Mn, Fe, Zn);  $P2_1/n$ ,  $Z'=5$  (Cu),  $P2_1$ ,  $Z'=8$  (Mg, Fe, Zn), and  $P-1$ ,  $Z'=2$  (Mn, Cu).

In the 2-D phases, cations adjacent along the direction of the modulation are either essentially superimposable or enantiomeric. In the five transitions, which relate three different pairs of the four phases, the phase found at the higher temperature always has a larger value of  $V/Z$  and a more perfect pattern of enantiomeric alternation.

The values of  $Z' > 1$  are a consequence of a conflict between the spacings of the  $M$  and nitrate ions most favorable for the formation of H bonds and the spacings most favorable for the close packing of the crown ligands. The reversible phase transitions are possible because inversion of the crown ligand does not require large atomic displacements. Analyses of the crystal packings show why 15-crown-5 ligands increase the probability that a structure will be disordered or modulated.

**Keywords:** polymorphs, phase transition, crystal packing

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#### Polymorphs of 4,4-Diphenyl-2,5-cyclohexadienone

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4,4-Diphenyl-2,5-cyclohexadienone **1** exists as a cluster of four conformational polymorphs A, B, C and D [1]. X-ray crystal structures show 19 crystallographic distinct molecular conformations due to rotation of gem-diphenyl rings: form A ( $P2_1$ ,  $Z'=1$ ), form B ( $P-1$ ,  $Z'=4$ ), form C ( $P-1$ ,  $Z'=12$ ) and form D ( $Pbca$ ,  $Z'=2$ ). These crystal structures are analyzed in terms of having different C-H...O hydrogen bonds and phenyl ring conformations. Crystal lattice and molecular conformation energies (Cerius<sup>2</sup>, DFT) suggest that forms A and D are more stable than triclinic forms B, C. The stable form A has molecule **1** in a lower energy conformation whereas molecular conformations in forms D, B and C having increasing  $Z'$  numbers are progressively higher in energy. Variable-temperature PXRD shows transformation of various forms present in the solid to the stable form A upon heating to ca. 70 °C. Further heating of A to 110-120 °C and cooling gives form B, implying that the melt phase is the kinetic form (ca. 2 kcal/mol less stable than form A, Dreding). The monoclinic form A is SHG active (ca. 2 x urea); this morph can be prepared in pure form by heating the mixture of polymorphs to ca. 70 °C. X-ray crystal structures, VT-PXRD measurements, energy computations and phenyl ring conformations of tetramorphic cluster **1** will be discussed.

[1] Kumar V.S.S., Addlagatta A., Nangia A., et al., *Angew. Chem. Int. Ed.*, 2002, **41**, 3848-3851.

**Keywords:** conformational flexibility, polymorphism, powder X-ray diffraction

#### P.08.10.5

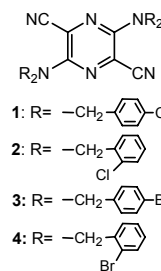
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#### A Series of Polymorphs with Different Colours in Diaminodicyanopyrazine Dyes

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2,5-Diamino-3,6-dicyanopyrazine dyes have been studied as a novel fluorescent dye because of their intense fluorescence in solution as well as in the solid state [1]. These dyes have also been found to have crystal polymorphs with different colours depending on the amino substituents. The colour difference, in the range from yellow through orange to red, of the polymorphs of dyes **1-4** were investigated in terms of intermolecular interactions.

The colour of these polymorphs were found to reflect different molecular conformation in the crystals. The amino nitrogen in the red and orange phases have a trigonal planar geometry; whereas a tetrahedral conformation of the amino groups was found in the yellow phase. Semi-empirical molecular orbital calculations revealed that this structural feature is well related to the calculated absorption band of a molecule in the crystals. Exciton interaction was also estimated and it was found to be about one order of magnitude smaller than the effect of conformational change. The colour difference is thus considered to be mainly attributed to the change in molecular conformation among the polymorphs.



[1] Matsuoka M., *Colorants for Non-textile Applications*, Freeman H.S. and Peters A.T. ed., Elsevier Science, 2000, 339.

**Keywords:** dyes, polymorphism, structure colour relationship

#### P.08.10.6

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#### A New Crystallographic Form of the Layered Weak-Ferromagnet $\text{Fe}[(\text{CH}_3\text{PO}_3)(\text{H}_2\text{O})]$

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A second form of the literature-known layered weak-ferromagnet  $\text{Fe}[(\text{CH}_3\text{PO}_3)(\text{H}_2\text{O})]$  has been isolated. The X-ray single crystal structure of this new form, i.e. form (2), has been carried out at  $T = 300, 200$  and  $130$  K [1]. The latter crystallizes as a needle-like crystals, in the orthorhombic space group  $Pmn2_1$ :  $a = 5.717(1)$ ,  $b = 8.809(2)$ ,  $c = 4.815(1)$  Å, while form (1) crystallizes, as a platelet-like crystals, in the orthorhombic space group  $Pna2_1$ :  $a = 17.58(2)$ ,  $b = 4.814(1)$ ,  $c = 5.719(1)$  Å [2]. The difference between the two forms lies in the ligand arrangement. In the form (2) the methyl groups above and below the inorganic layer are  $\sim 12^\circ$  away from the normal axes of the inorganic layers, keeping the same orientation from layer to layer along the  $b$ -direction. In form (1) the  $a$  parameter is twice larger than the corresponding  $b$  parameter of form (2) due to the alternation of the inclination of the methyl groups in a zig-zag way. This is the first example of dimorphism observed in metal alkylphosphonates.

[1] Léone P., Palvadeau P., Boubekeur K., Meerschaut A., Bellitto C., Bauer E.M., Righini G., *J. Solid State Chem.*, in press. [2] Bellitto C., Federici F., Colapietro M., Portatone G., Caschera D., *Inorg. Chem.*, 2002, **41**, 709.

**Keywords:** polymorphism, organic inorganic hybrid materials, metal phosphonates