

MS24.P45

Acta Cryst. (2011) A67, C374**Divalent manganese in alkaline halides mixtures**

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It is known that the Mn²⁺ fluorescence spectrum consists of an emission band that might be found in the green or in the red of the electromagnetic spectrum according to the nearest environment. In order to control this emission in one or the other wavelength the Mn²⁺ ion was introduced as a doping element in sodium halides mixtures, containing different amounts of chloride and bromine. The concentrations were as follows NaCl:Mn²⁺, NaCl(95%)Br(5%):Mn²⁺, NaCl(75%)Br(25%):Mn²⁺, NaCl(50%)Br(50%):Mn²⁺, all with a manganese concentration of 0.3%. The solutions were analyzed by x-ray diffraction and fluorescence. All the analyzed samples correspond to the as grown (AG) crystal. It was observed that the relative emission intensities in the red or in the green changed as a function of the Br ion concentration increasing from NaCl(100%) to a maximum for NaCl(75%)Br(25%) and then presented a decrease. The green band in NaCl:Mn²⁺ has been associated to the Suzuki phase manganese precipitates. As mentioned before the samples were analyzed with x-rays, the main results being that the variation of the lattice parameter does not follow Vegard's rule and that on the other hand the x-ray diffraction pattern shows the presence of some sort of structures around the (200) diffraction plane probably associated to manganese structures embedded in the lattice, these also associated with the increase of bromine ions concentration.

Keywords: manganese, fluorescence, spectrum

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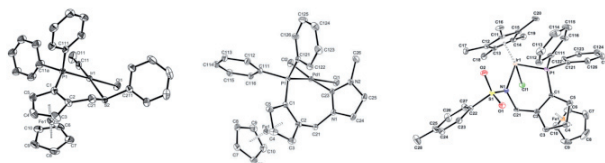
Acta Cryst. (2011) A67, C374**P,O; P,S and P,(NHC) ferrocenyl ligands for asymmetric catalysis**

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We have long been interested in the design and the synthesis of new chiral catalysts for exploring new asymmetric catalytic reactions or for improving existing ones. In this area, chiral phosphines have played a significant role. The possibility to easily modify their electronic and steric properties by a proper choice of their substituents proved to be extremely useful to successfully optimize catalytic reactions. We will present our last results on the development of ferrocenyl phosphines functionalized by an oxygen, a sulfur atom [1], a nitrogen or an N-Heterocyclic Carbene fragment [2] (P,O; P,S; P,N and P,(NHC) ferrocenyl type ligands).

Some of them were prepared in an enantiomerically pure form (planar chirality) and tested in asymmetric catalysis (allylic substitution, ketone hydrogenation [3], Suzuki-Miyaura carbon coupling [2]...).

The X-ray structures of some of these ligands as well as of some of their transition metal complexes will be described together with their use in some catalytic reactions.



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Keywords : structure, reactivity, catalysis

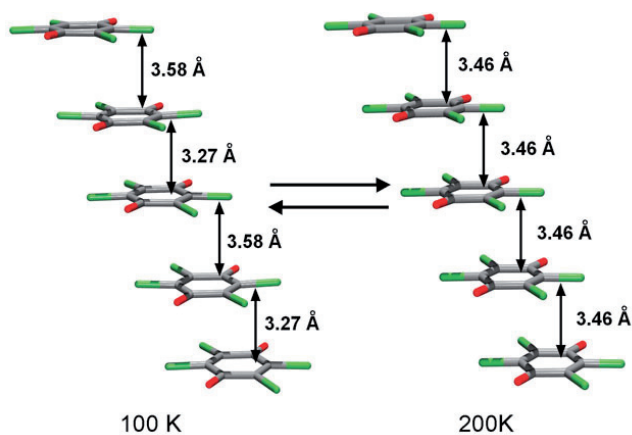
MS24.P47

Acta Cryst. (2011) A67, C374-C375**Magnetic bistability in the salt of organic radical anion-tetrachlorosemiquinone**

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Tetrachlorosemiquinone anion radical salt of potassium was prepared [1] and crystallised as 2-butanone solvate. Its structural and magnetic characteristics were studied by variable-temperature single crystal X-ray diffraction, DFT (wB97XD) and CAS-MP2 calculations, and magnetic susceptibility measurements in the temperature range from 10-340 K. The X-ray structure analysis detected the two polymorphs at 100 K and 200 K which undergo reversible phase transition in the range 120-170 K. The 100 K-structure reveals π -stacked dimers of anion radicals with interplanar separation distance of 3.272 (2) Å and ring centroid distance of 3.631(3) Å with offset of 1.573 Å. The infinite stack of dimers repeated by translation reveals interdimer separation distance of 4.353(3) Å and offset of 2.504 Å. Diamagnetic response of this crystalline phase involves the antiparallel electron-spin coupling between the two contiguous anion radicals. These dimers continuously uncouple their electron-spins with increasing temperature, which leads to an increase of paramagnetic contribution to magnetisation. The continuous phase transition can be monitored by measuring the unit cell parameters in the range 120-170 K, with a step of 5 K; the volume of monoclinic unit cell ($P2_1/c$) of 100 K-polymorph was reduced two times and unit cell reveals pronounced n -glide plane symmetry ($P2_1/n$) in the 200 K-polymorph. The paramagnetic 200 K-structure is characterised by interplanar separation distance of radical anions of 3.467 Å and offset of 2.090 Å.

According to the literature [2] solvates and solvent-free crystals reveal different magnetic behaviour, so crystal engineering approach was introduced; to design crystals of desired magnetic properties one can vary the size and polarisability of the cation, and polarity and size of solvent molecule [3].



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Keywords: spin-coupled biradical anions, magnetic properties, tetrachlorosemiquinone anion radical

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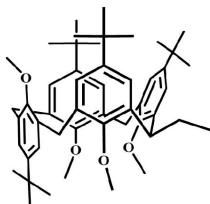
Acta Cryst. (2011) A67, C375

Crystal engineering of Calix[4]arenes. Chemical straightening of guest channels

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Three solvate crystal structures of the laterally ethyl substituted tetra-*tert*-butyltetramethoxycalix[4]arene (**1**) with THF, CHCl₃ and CH₂Cl₂ are compared to the corresponding solvent free structure using single crystal X-ray structure determination, isostructurality and molecular isometricity calculations [1]. To study the effect of the lateral substitution, the laterally non-substituted host with the guest THF is also included to the comparison.



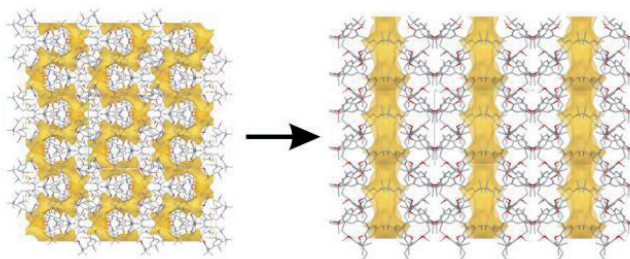
The calixarene molecules due to the absence of any intramolecular hydrogen bonding at the lower rim all adopt a *partial cone* conformation, which has already been calculated to be the lowest energy conformer [2]. The guest molecules are always being positioned interstitially.

The presence of solvent molecules induces the formation of the higher symmetrical orthorhombic crystal structures of the laterally substituted calixarene, being isostructural irrespective of the included guest molecule. The packing arrangement of all structures is controlled by weak intermolecular C-H... π -interactions and van der Waals forces, whereas π ... π interactions are absent.

The introduction of the lateral ethyl substituent expands the total room available for guest molecule inclusion by nearly 30%, being a promising fact for crystal inclusion chemistry.

The serpentine like channels disposable of the solvent guest molecules in the crystal structures straighten as the effect of lateral substitution of the host calix[4]arene. This fact seems to be an

interesting crystal engineering aspect, as the channel geometry of a calixarene lattice can be straightened by the effect of a simple lateral monosubstitution to the host molecule.



[1] C. Fischer, G. Lin, P. Bombicz, W. Seichter, E. Weber, *Struct Chem* **2011**, *22*, 433-439. [2] M. Gruner, C. Fischer, T. Gruber, E. Weber, *Supramol Chem* **2010**, *22*, 256-266.

Keywords: calixarene, crystal engineering, inclusion compounds

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Two reversible thermochromic phase transitions of copper(II) diiminate

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Two thermal reversible first-order phase transitions for solid copper(II) diiminate Cu[-N(H)-C(CF₃)=C(F)-C(CF₃)=N(H)-]₂ (**1**) at 68.6 °C ($\alpha \rightarrow \beta$) and 87.5 °C ($\beta \rightarrow \gamma$) have been found by differential scanning calorimetry. They are accompanied by *green* (α) – *yellow* (β) – *red* (γ) thermochromism.

The α (monoclinic, $P2_1/n$, $Z = 2$), β (tetragonal, $P4_2/n$, $Z = 4$) and γ (monoclinic, $P2_1/n$, $Z = 4$) phases of **1** have been studied by X-ray single-crystal structural analysis and powder diffraction. It has been revealed that the solid phase transitions are related to the transformations of six-membered metallocycle geometry from bent to planar ($\alpha \rightarrow \beta$) and Cu(II) coordination from square-planar to tetrahedral ($\beta \rightarrow \gamma$). Presumably, these transformations are explained by (i) Jahn-Teller effect of Cu(II) (d^9 -system), (ii) the intramolecular repulsion between NH-groups, and (iii) the short intermolecular Cu...F and F...F contacts. The high-temperature β and γ phases exist at room temperature in a metastable state and slowly transform into the stable α phase for some days. However, these processes proceed very fast on further cooling. The crystal densities of the studied phases decrease in the range of α (2.278 g/cm³) > β (2.162 g/cm³) > γ (2.065 g/cm³).

Solid state thermochromic behaviour is of special interest in the design of devices for visual and prompt monitoring of temperature changing. The reversible interconversion in copper(II) diiminate **1** can provide a new class of thermochromic materials.

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Keywords: Cu(II) diiminate, reversible thermochromic phase transitions, X-ray single-crystal and powder diffraction