

## MS24.P45

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

L. Mariscal B.,<sup>a</sup> J. Hernández A.,<sup>a</sup> E. Camarillo G.,<sup>a</sup> C. Flores J.,<sup>a</sup> H. Murrieta S.,<sup>a</sup> G. Aguilar S.,<sup>b</sup> I. Camarillo G.,<sup>c</sup> <sup>a</sup>*Instituto de Física, Instituto de Investigación en Materiales UNAM A.P.20-364 Del. A. Obregón CP01000, D.F. (México).* <sup>b</sup>*Dpto de Física UAM-Iztapalapa, D.F. (México).* E-mail: mariscal2005@gmail.com

It is known that the Mn<sup>2+</sup> 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 Mn<sup>2+</sup> ion was introduced as a doping element in sodium halides mixtures, containing different amounts of chloride and bromine. The concentrations were as follows NaCl:Mn<sup>2+</sup>, NaCl(95%)Br(5%):Mn<sup>2+</sup>, NaCl(75%)Br(25%):Mn<sup>2+</sup>, NaCl(50%)Br(50%):Mn<sup>2+</sup>, 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:Mn<sup>2+</sup> 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

## MS24.P46

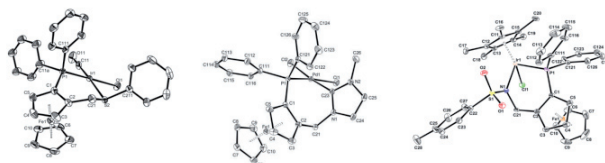
*Acta Cryst.* (2011) A67, C374**P,O; P,S and P,(NHC) ferrocenyl ligands for asymmetric catalysis**

Jean-Claude Daran,<sup>a</sup> Agnès Labande,<sup>a</sup> Catherine Audin,<sup>a</sup> Eric Deydier,<sup>a</sup> Rinaldo Poli,<sup>a,b</sup> Eric Manoury,<sup>a</sup> <sup>a</sup>*Laboratoire de Chimie de Coordination, CNRS UPR 8241, 205 route de Narbonne 31077 Toulouse Cedex 4, (France).* <sup>b</sup>*Institut Universitaire de France, 103 bd Saint-Michel 75005 Paris, (France).* E-mail: jean-claude.daran@lcc-toulouse.dfr

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.



[1] (a) L. Routaboul, S. Vincendeau, J.-C. Daran, E. Manoury, *Tetrahedron Asym.* **2005**, *16*, 2685-2690. (b) R. Malacea, E. Manoury, L. Routaboul, J.-C. Daran, R. Poli, J.P. Dunne, A.C. Withwood, C. Godard, S.B. Duckett, *Eur. J. Inorg. Chem.* **2006**, 1803-1816. (c) L. Routaboul, S. Vincendeau, C.-O. Turrin, A.-C. Caminade, J.-P. Majoral, J.-C. Daran, E. Manoury, *J. Organomet. Chem.*, **2007**, *692*, 1064-1073. (d) R. Malacea, L. Routaboul, E. Manoury, J.-C. Daran, R.J. Poli, *Organomet. Chem.* **2008**, *693(8-9)*, 1469-1477. [2] (a) S. Gülcemal, A. Labande, J.-C. Daran, B. Cetinkaya, R. Poli, *Eur. J. Inorg. Chem.* **2009**, 1806-1815. (b) N. Debono, A. Labande, E. Manoury, J.-C. Daran, R. Poli, *Organometallics*, **2010**, *29*, 1879-1882. [3] E. Le Roux, R. Malacea, E. Manoury, R. Poli, L. Gonsalvi, M. Peruzzini, *Adv. Synth. Catal.* **2007**, *349*, 1064-1073.

**Keywords :** structure, reactivity, catalysis

## MS24.P47

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

Biserka Kojić-Prodić,<sup>a</sup> Krešimir Molčanov,<sup>a</sup> Darko Babić,<sup>a</sup> Damir Pajić,<sup>b</sup> Nikolina Novosel,<sup>b</sup> Krešo Zadro,<sup>b</sup> <sup>a</sup>*Rudjer Bošković Institute, Bijenička c. 54, Zagreb, (Croatia).* <sup>b</sup>*Department of Physics, Faculty of Science, University of Zagreb, Bijenička c. 32, Zagreb, (Croatia).* E-mail: kojic@irb.hr

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  $\pi$ -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].