

MS60.P02

Acta Cryst. (2011) A67, C602**Structural Complexity for the Series $[\text{Ni}(\text{H}_2\text{O})_2(15\text{C}5)](\text{X})_2$ ($\text{X}=\text{BF}_4^-, \text{NO}_3^-, \text{HSO}_4^-$)**

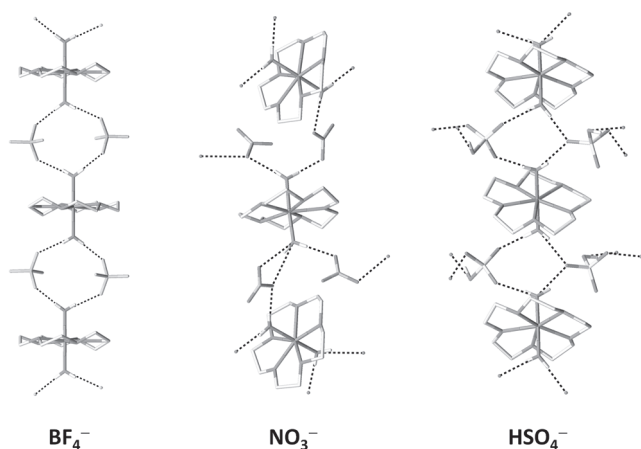
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The insertion of the Ni^{2+} center inside the cavity of the 15-crown-5 ligand (15C5) has been successfully conducted for the series of compounds $[\text{Ni}(\text{H}_2\text{O})_2(15\text{C}5)](\text{X})_2$ ($\text{X} = \text{BF}_4^-, \text{NO}_3^-, \text{HSO}_4^-$) [1-4] by using a synthetic route aimed at limiting the amount of water. All three compounds exhibit variable degrees of complexity in their respective solid-state structures.

Some structural similarities are found among this family, namely a characteristic coordination sphere of the Ni centers in the $[\text{Ni}(\text{H}_2\text{O})_2(15\text{C}5)]^{2+}$ ions, but more interestingly, the existence of phase relationships associated with solid-solid phase transitions while cooling/heating the crystals. When $\text{X} = \text{NO}_3^-$ or HSO_4^- , the transitions are always driven in the direction for which $\Delta Z' > 0$ while cooling the sample; the case for $\text{X} = \text{BF}_4^-$ remains obscure.

Differences in structural features among this family are inherently governed by some strong hydrogen bonding interactions, which may vary depending on the nature of the counterion. Complexity in the hydrogen bonding rises while the H-bonded donor and acceptor ratio D:A (D=donor, A=acceptor) gets closer to 1:1. Hydrogen bond networks are best described as being columnar (BF_4^-), planar (NO_3^-), or three-dimensional (HSO_4^-).

Reasons for which structural complexity may occur for this series of compounds are discussed.



[1] M.A. Siegler, S. Parkin, J.P. Selegue, C.P. Brock *Acta Cryst.* **2008**, B64, 725-737. [2] M.A. Siegler, X. Hao, S. Parkin, C.P. Brock *Acta Cryst.* **2008**, B64, 738-749. [3] M.A. Siegler and E. Stavitski *Acta Cryst.* **2010**, B66, 430-440. [4] M. Siegler, unpublished results.

Keywords: Ni coordination, phase transition, hydrogen bonding

MS60.P03

Acta Cryst. (2011) A67, C602**Controlled mechanochemical synthesis. Relating chemistry to crystal structures**

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Mechanochemistry is widely [1] used to obtain various organic compounds and materials, in particular, molecular complexes, salts and co-crystals. If a ball mill, or a mortar are used for mechanical treatment, it is difficult to study the mechanism of the mechanochemical reactions, to estimate the amount of energy required to complete the process, to study intermediate products of the transformations. We present a method for studying the mechanochemical processes step by step with a special mechanical device, which enables one to treat a reaction mixture by individual mechanical pulses of controllable and variable energy. It allows to observe the system at the different steps of the transformation, and detect the intermediate products of the reaction.

To illustrate the possibilities of detecting the intermediate products in the mechanochemical reactions, we have used the “glycine – oxalic acid dihydrate” system. We have studied the mechanochemical reaction between glycine and oxalic acid (1:1 molar ratio). Treating the reaction mixture by controlled pulses of certain energy we could detect the intermediate products of the reaction. A comparison of the crystal structures of the initial reagents with those of the intermediate and final products made it possible to interpret the sequence of stages of the mechanochemical synthesis. The results of co-grinding were considered in relation to rapid antisolvent crystallization and to the crystallization by slow evaporation from aqueous solution.

[1]. I. Tumanov, A. Achkasov, E. Boldyreva, V. Boldyrev, *CrystEngComm*, **2011**, DOI: 10.1039/C0CE00869A.

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Keywords: co-crystals, intermediate products, mechanochemistry

MS60.P04

Acta Cryst. (2011) A67, C602-C603**Interaction of the components in {Tb,Dy}-Fe-In systems at 600°C**

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Among the systems $RE\text{-Fe-In}$ (RE – rare earths) the isothermal sections are built only for the Er-Fe-In [1] and partially for the Pr-Fe-In systems. The indide $\text{Pr}_6\text{Fe}_{13}\text{In}$ (ST $\text{Nd}_6\text{Fe}_{13}\text{Si}$, SG $I4/mcm$, $a = 8.103 \text{ \AA}$, $c = 23.527 \text{ \AA}$) [2] was found in the Pr-Fe-In system. The other $RE\text{-Fe-In}$ ($RE = \text{Nd, Sm}$) systems have been investigated in order to find isotypic $RE_6\text{Fe}_{13}\text{In}$ indides.

The aim of this investigation is construction of the isothermal sections of $\{\text{Tb, Dy}\}\text{-Fe-In}$ systems at 600°C and study crystal structure of the ternary compounds which are forming. Samples for investigation were prepared by arc-melting of pure metals under an argon atmosphere. Homogeneous annealing was performed at a temperature 600 °C during 720 hour and after that the alloys were quenched in cold water.

We confirmed the existence of all binary compounds which limit the investigated ternary systems: $RE_2\text{In}$, $RE_5\text{In}_3$, $RE\text{In}$, $RE_3\text{In}_5$, $RE\text{In}_3$, $RE\text{Fe}_2$, $RE\text{Fe}_3$, $RE_6\text{Fe}_{23}$, $RE_2\text{Fe}_{17}$ ($RE = \text{Tb, Dy}$).

New compound $\text{TbFe}_{1.8}\text{In}_{0.2}$ was found in the Tb-Fe-In

system. The crystal structure was determined by single crystal X-ray diffraction (Xcalibur diffractometer, CCD detector, Mo $K\alpha$ radiation). The structure belongs to $TbFe_2$ structure type (space group $R\bar{3}m$, $a = 5.5900(8)$ Å, $c = 13.684(3)$ Å), which is deformed variant of $MgCu_2$ structure type.

[1] M.V. Dzvevenko *PhD thesis*, Ivan Franko National University of Lviv, 2006. [2] F. Weitzer, P. Rogl. *Journal of the Less-Common Metals*, 1990, 167, 135-142.

Keywords: intermetallic, crystal structure, rare-earth

MS60.P05

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Preliminary neutron powder diffraction analysis of a meta-stable colored form in photochromic crystal using iMATERIA in J-PARC

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N-Salicylideneanilines, Schiff bases synthesized from salicylaldehydes and anilines, are well known to exhibit photochromism both in solution and in the solid state. The photochromic salicylideneanilines usually take “enol forms” with pale-yellow color in crystals, change to meta-stable photoproducts “trans-keto forms” with red color by irradiation of ultraviolet light (Fig 1). The red color erases by irradiation with visible light or by thermal fading in the dark. The structure of the photoinduced colored species, of *N*-3,5-di-*tert*-butylsalicylidene-3-nitroaniline (**1**), as shown in Fig. 2, was analyzed by X-ray using two-photon excitation, and showed pedal-like structural change around the $C=N$ bond during the reaction.^[1] This reaction begins with a hydrogen atom transfer from hydroxyl group to the nitrogen of the imine, and followed to the pedal motion. Previous X-ray study cannot find the hydrogen atom of the trans-keto form because the population of the photoproduct is only 10% in the single crystal. However, such a hydrogen atom or proton transfer is one of the important phenomena in chemical reactions and is a key role to make clear the whole reaction mechanism. To observe the hydrogen atom transfer clearly, we chose powdered sample with more surface area for light irradiation, and carried out the neutron diffraction measurement at iMATERIA (Ibaraki Materials Design Diffractometer), a time-of-flight neutron powder diffractometer, at BL20 in Materials and Life science Experimental Facility of J-PARC. We prepared a long-lifetime derivative, *N*-3,5-di-*tert*-butylsalicylidene-3-carboxyaniline (**2**) with irradiated using high pressure mercury lamp at -10 deg., and sealed into the vanadium cell. The neutron powder diffraction measurement conditions are as follow: the accelerator beam power is about 220 kW, the pulse repetition is 25 Hz, the range of wavelengths is about 0.2~7 Å, the measurement temperature is 173 K. We will present the detailed data statistics of the preliminary powder neutron diffraction analysis including the data processing and the structural refinement.

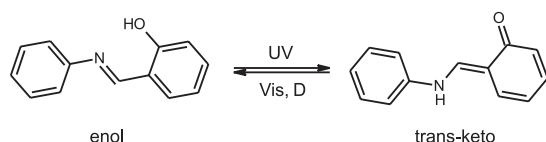


Fig. 1 Reaction mechanism of the photochromism of *N*-Salicylideneaniline

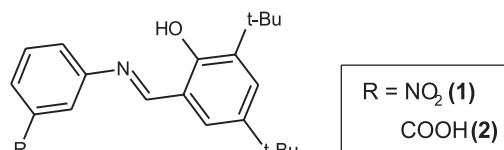


Fig. 2 Structures of *N*-Salicylideneaniline derivatives (**1**) and (**2**).

[1] J. Harada, H. Uekusa, Y. Ohashi, *J. Am. Chem. Soc.*, 1999, 121, 5809-5810.

[2] K. Johmoto, A. Sekine, H. Uekusa, Y. Ohashi, *Bull. Chem. Soc. Jpn.*, 2009, 82, 50-57.

Keywords: photochromism, neutron diffraction, J-PARC

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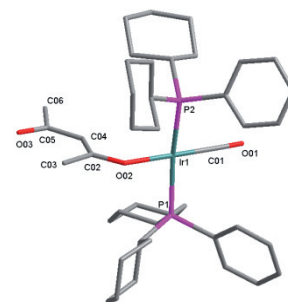
Model iridium phosphine compounds for use in olefin hydroformylation

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The functionalisation of olefins from petroleum sources to aldehydes through the process of Hydroformylation is of great industrial importance. High selectivity for the desired isomer of the aldehyde can be kinetically manipulated by variation of the ligands and process conditions. In rhodium systems, it is known that the presence of phosphine ligands give way to more active, highly selective catalysts reacting under milder reaction conditions [1].

Iridium compounds are often used as model complexes, since Ir(I) and Ir(III) complexes with similar ligand sets to those proposed in rhodium chemistry, tend to behave in the same way and are isolated more readily than the rhodium analogues. Ligand effects in model iridium systems containing tertiary phosphine and diphosphinoamine ligands are investigated to determine the importance of electronic factors and steric crowding from the phosphine based ligands for manipulating the reactivity of the Ir(I) centre [2].

In the present investigation, characterisation and structural evaluation of different complexes and intermediates [beta-diketonato ring opened example shown below], will be presented.



[1] J.A. Osborn, G. Wilkinson, J.F. Young, *Chem. Commun.* 1965, 17. [2] A. Roodt, G.J.J. Steyn, *Journal of Organomet. Chem.* 1997, 536-537, 197-205.

Keywords: iridium, hydroformylation, phosphine

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Structural studies of $SrTcO_3$, $CaTcO_3$ and $Pb_2Tc_2O_{7-d}$

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