

MS60.P02

Acta Cryst. (2011) **A67**, C602

Structural Complexity for the Series [Ni(H₂O)₂(15C5)](X)₂ (X=BF₄⁻, NO₃⁻, HSO₄⁻)

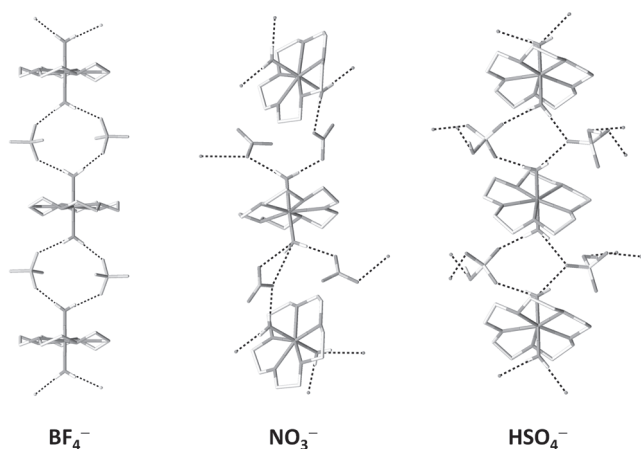
Maxime A. Siegler, *Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, (USA)*. E-mail: msiegler2@jhu.edu

The insertion of the Ni²⁺ center inside the cavity of the 15-crown-5 ligand (15C5) has been successfully conducted for the series of compounds [Ni(H₂O)₂(15C5)](X)₂ (X = BF₄⁻, NO₃⁻, HSO₄⁻) [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 [Ni(H₂O)₂(15C5)]²⁺ ions, but more interestingly, the existence of phase relationships associated with solid-solid phase transitions while cooling/heating the crystals. When X = NO₃⁻ or HSO₄⁻, the transitions are always driven in the direction for which ΔZ' > 0 while cooling the sample; the case for X = BF₄⁻ 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 (BF₄⁻), planar (NO₃⁻), or three-dimensional (HSO₄⁻).

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 Siegler, unpublished results.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

Ivan A. Tumanov,^a Andrey F. Achkasov,^a Elena V. Boldyreva,^{ab} and Vladimir V. Boldyrev,^{ab}. ^aREC-008 Novosibirsk State University, ul. Pirogova, 2, Novosibirsk, (Russia). ^bInstitute of Solid State Chemistry

and Mechanochemistry SB RAS, ul. Kutateladze, 18, Novosibirsk, (Russia). E-mail: i.tumanov.ssc@mail.ru

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.

The study was supported by the Projects of RAS (21.44, 5.6.4), grants from RFBR (09-03-92658, 10-03-00252, 11-03-00684), a BRHE grant from the CRDF (RUX0-008-NO-06) and aFASI (RF) Contract No GK P2529.

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

Marta Demchyna,^a Bohdana Belan,^a Anna Gagor^b ^aFaculty of Chemistry, Ivan Franko National University of Lviv, Ukraine. ^bW. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, (Poland). E-mail: marta.dem.85@gmail.com

Among the systems RE–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 Pr₆Fe₁₃In (ST Nd₆Fe₁₃Si, SG *I4/mcm*, *a* = 8.103 Å, *c* = 23.527 Å) [2] was found in the Pr–Fe–In system. The other RE–Fe–In (RE = Nd, Sm) systems have been investigated in order to find isotypic RE₆Fe₁₃In indides.

The aim of this investigation is construction of the isothermal sections of {Tb, Dy}–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: RE₂In, RE₅In₃, REIn, RE₃In₅, REIn₃, REFe₂, REFe₃, RE₆Fe₂₃, RE₂Fe₁₇ (RE = Tb, Dy).

New compound TbFe_{1.8}In_{0.2} was found in the Tb–Fe–In