

## FA4-MS29-P01

**Stoichiometric Reduction of Coordination Polymers by Organometallic Complexes.** Mikhail Meilikhov<sup>a</sup>, Kirill Yusenko<sup>a</sup>, Antonio Torrisi<sup>b</sup>, Caroline Mellot-Draznieks<sup>b</sup>, Roland A. Fischer<sup>a</sup>, *<sup>a</sup>Inorganic Chemistry II - Organometallic and Materials, Ruhr-University Bochum, German, <sup>b</sup>Department of Chemistry, University College London, United Kingdom*  
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One of the most challenging topics of the metal-organic frameworks (MOFs) is the probing and fine tuning of physical and chemical properties of MOFs.[1] The host-guest chemistry of MOFs with redox-active framework and the formation of charge-transfer complexes between the framework and the adsorbed molecules represents a new and very promising area. Within this work, the research was focused on the chemical functionalization of the inorganic backbone of MOFs which leads to new electrochemical active frameworks with novel physical and chemical behaviour. One of the presented examples is the first known stoichiometric reduction of the inorganic backbone of a neutral framework [V(O)(bdc)]<sub>n</sub> (MIL-47(V) with bdc = 1,4-terephthalic acid) caused by the gas-phase incorporation of the organometallic reducing agent (OMR) cobaltocene.[2] The resulting mixed-valence material [Co(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sub>0.5</sub>@MIL-47(V) (**1**) exhibits a negatively charged inorganic backbone with one-dimensional chains of positively charged cations which are chemically inert and do not interfere with the coordination chemistry of the MIL-47(V). The MIL-47(V) framework is known to be very rigid in contrast to the breathing, isostructural [Al(OH)(bdc)]<sub>n</sub> which allows large changes of the cell volume of ± 470 Å<sup>3</sup> (33 %). However, the crystal structure of **1** also reveals quite a significant contraction of the cell volume by 120 Å<sup>3</sup> (9%) in comparison to the guest-free, activated MIL-47(V). This observation can be explained by the unusually strong host-guest interactions due to electrostatic forces between the negatively charged framework and cobaltocenium cations. The orientation of the cobaltocenium cations inside the channels of MIL-47(V) only slightly differs from the structure of ferrocene@[Al(OH)(bdc)]<sub>n</sub>. [3] The occupancy of the cobaltocenium positions in **1** is 50%, this means that every second V(IV)-center is reduced. This leads to a mixed valence compound with a 1:1 V<sup>3+</sup>/V<sup>4+</sup> ratio. To our knowledge, this is the first known example for a mixed valence MOF compound. In order to understand the electronic spin state and magnetic behaviour of vanadium centers DFT single point energy calculations were performed. The derived data indicate that the anti-ferromagnetic configuration is the thermodynamically most favourable one. The obtained results are in good accordance with the ESR and magnetic susceptibility data. The channels of the MOF are not completely filled with cobaltocenium cations and exhibit free space between the adsorbed guest molecules. The adsorption studies show that the material selectively adsorbs CO<sub>2</sub> over N<sub>2</sub>. This effect can be explained by the possibility of polarization of the CO<sub>2</sub> molecules by the charged framework which causes the adsorption of CO<sub>2</sub> in the free space in between the pre-adsorbed cobaltocenium molecules.

[1] Meilikhov, M., Yusenko, K., Fischer, R.A., *J. Am. Chem. Soc.*, 2009, 131, 9644. [2] Meilikhov, M., Yusenko, K., Torrisi, A., Jee, B., Mellot-Draznieks, C., Poepl, A., Fischer, R.A., *Angew. Chem. Int.*

*Ed.*, 2010, in press. [3] Meilikhov, M., Yusenko, K., Fischer, R.A., *Dalton Trans.*, 2009, 600.

**Keywords:** porous coordination polymers, charge-transfer complexes, powder structure determination

## FA4-MS29-P02

**X-Ray study of fluorine-graphite intercalation compounds CF<sub>0.25</sub> and CF<sub>0.33</sub>.** Alexey Alexeyev<sup>a,b</sup>, Andrey Danilenko<sup>a</sup>, Sergey Gromilov<sup>a,b</sup>, <sup>a</sup>Nikolayev *Institute of Inorganic Chemistry, Novosibirsk Russia, <sup>b</sup>Novosibirsk State University, Russia*  
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An interest to fluorine-graphite intercalation compounds (F-GIC) was provoked by their possible usability as the components of lithium current sources. Those compounds are known over more than sixty years but some problems remain unresolved concerning the interrelation between their chemical composition and the structure. The exact determination of the structure is complicated since it is unfeasible to prepare perfect single crystals suitable for X-ray structure analysis. The usage of X-ray diffraction study of polycrystals to solve the F-GIC structure is hampered because of the strong preferred orientation. This work reports a new approach to study F-GIC not as polycrystal samples but as imperfect single crystals on a Bruker X8 APEX diffractometer (MoK<sub>α</sub>-radiation, graphite monochromator, CCD-detector). The compounds CF<sub>0.25</sub> and CF<sub>0.33</sub> were obtained by the reaction of natural graphite with BrF<sub>3</sub> in anhydrous HF medium at 273 K. Ten grains were selected from each of the both batches. A study showed a wide parameters spread, *a* = 2.451–2.460, *c* = 5.721–5.876 Å for CF<sub>0.25</sub> and *a* = 2.448–2.453, *c* = 5.810–5.962 Å for CF<sub>0.33</sub>, respectively. A peculiarity observed to some extent in all X-ray powder diffraction patterns is the (1 0 0) peak asymmetry with the profile diffused in the direction of the smaller interplanar distances. A decrease in the graphite d<sub>100</sub> upon fluorination indicates the corrugation of the hexagonal carbon layers in the given compounds.

**Keywords:** intercalation compounds, Debye-Scherrer method, CCD-detectors

## FA4-MS29-P03

**Dynamic and reversible contraction in {Ni<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>(Bpa)<sub>4</sub>}(V<sub>6</sub>O<sub>18</sub>)·8H<sub>2</sub>O vanadate.** Roberto Fernández de Luis<sup>a</sup>, M. Karmele Urriaga<sup>a</sup>, José Luis Mesa<sup>b</sup>, Teófilo Rojo<sup>b</sup>, María Isabel Arriortua<sup>a</sup>  
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The crystal structure of {Ni<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>(Bpa)<sub>4</sub>}(V<sub>6</sub>O<sub>18</sub>)·8H<sub>2</sub>O is a 3D framework constructed from three interpenetrated metal organic subnets, corner linked to the vanadium oxide subunit. This connectivity generates a crystal structure that combines both a 3D metal-organic and inorganic frameworks. The metal-organic subnet consists of three interpenetrating

3D “mot” (4, 4)-c two nodal nets. The interpenetration vector is [0,1,0], Class Ia.

The metal organic nets are constructed from a tetrameric unit and single octahedra linked through the Bpa ligand. The tetrameric unit consists of an edge shared octahedra forming a dimeric unit linked to single octahedra through two Bpa ligand in “Gauche” conformation. Each tetrameric unit is linked to four octahedra via trans-Bpa ligands. This connectivity generates a three dimensional 2 nodal (4,4) connected net with  $\{6^4.8^2\}_2\{6^6\}$  point symbol.

The vanadium oxide subunit consists of twelve corner linked  $\text{VO}_4$  tetrahedra, giving rise to isolated  $\text{V}_{12}\text{O}_{36}$  centrosymmetric cycles. The dimmers of the tetrameric units lie inside the  $\text{V}_{12}\text{O}_{36}$  cycle and the octahedra acts as a linker between adjacent  $\text{V}_{12}\text{O}_{36}$  cycles, generating inorganic-organic chains along the [100] direction. As far as we are concerned, this is the first vanadate in which the  $\text{V}_{12}\text{O}_{36}$  cycle has been isolated in solid state.

The interpenetrating metal organic nets are connected through the vanadium oxide subunit. This way, the  $\text{V}_{12}\text{O}_{36}$  cycle of one of the nets, is corner linked to four octahedra, two of each adjacent nets. The crystal structure possess channels along the [100] direction, in which are located the disordered crystallization water molecules.

The thermal removal of crystallization water molecules (25-85°C) gives rise to a 3% contraction of the crystal structure. Surprisingly, at higher temperatures (85°C – 155°C) the crystal structure presents a continuous structural contraction of 6% without weight loss. The process is totally reversible up to 155°C. However at higher temperatures (200°C) the loss of coordinated water molecules generates an irreversible structural transformation with loss of crystallinity. Finally the structure collapses due to the calcination of the organic ligands.

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**Keywords:** Vanadates, third generation materials, self-catenation

#### FA4-MS29-P04

**Synthesis and characterization of  $\text{B}(\text{OH})_4\text{-H}_2\text{O}$  enclathred gallogermanate sodalite** I. Poltz<sup>a</sup>, L. Robben<sup>a</sup>, J.- Ch. Buhl<sup>a</sup>, <sup>a</sup>*Institut für Mineralogie, Leibniz Universität Hannover, Germany*  
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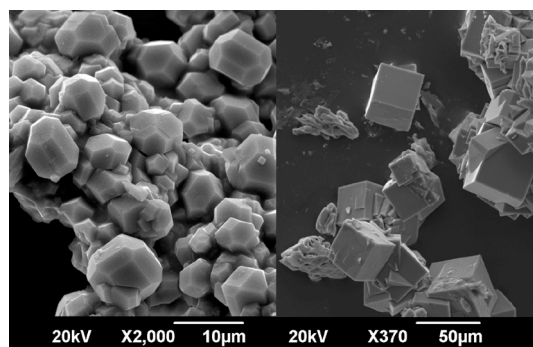
Tetrahydroxoborate and water enclathred sodalite with a gallogermanate host framework was prepared by means of hydrothermal synthesis and characterized by X-ray powder diffraction, IR-spectroscopy, temperature-dependent-IR-(TDIR) spectroscopy as well as scanning electron microscopy

(SEM) and energy dispersive X-ray (EDX)-analysis. The hydrothermal synthesis was performed under mild conditions (i.e. at 393 K) with the beryllonite analogous phase  $\text{NaGaGeO}_4$  as the source of Ga and Ge. Synthesis and crystal structure of the beryllonite type  $\text{NaGaGeO}_4$  are described in detail in [1].

The mild hydrothermal synthesis was carried out in a Teflon coated steel autoclave filled with layers of 1 g of  $\text{NaBH}_4$ -granulate and 1 g of pulverized  $\text{NaGaGeO}_4$ , before 5 ml 1 M sodium hydroxide solution was added. After a reaction time of 24 h the sample was washed with deionized water and dried at 353 K for 12 h.

X-ray powder diffraction shows a mixture of two phases: One is the  $\text{NaGaGeO}_4$  starting material, the other is a typical sodalite phase, which can be indexed in space group P-43n with lattice parameter  $a = 8.995 \text{ \AA}$ . The IR-absorption spectra show typical bands of  $\text{H}_2\text{O}$  at  $1665 \text{ cm}^{-1}$  as well as typical bands of  $\text{OH}^-$  from the  $\text{B}(\text{OH})_4^-$  group at  $3568 \text{ cm}^{-1}$  in good agreement with Pietsch et al. [2]. Furthermore, the presence of the enclathred  $\text{B}(\text{OH})_4^-$  species is confirmed by arising bands in the TDIR- spectra, since  $\text{B}(\text{OH})_4^-$  reacts to  $\text{BO}(\text{OH})_2^-$  at approx. 473 K and subsequently to  $\text{BO}_2^-$  at approx. 873 K by dehydration with increasing temperatures as described by Pietsch et al. [2]. The SEM- investigations show the presence of two different morphologies within the reaction product. As shown in the SEM-images, there are crystallites with rhombic dodecahedral as well as cubic morphology. EDX-analysis shows that the crystallites with cubic morphology tend to have higher Ga/Ge- ratios (average: 1.02) than the crystallites with rhombic dodecahedral morphology (average: 0.86).

Further investigations will aim at controlling the morphology by variation of synthesis parameters and subsequent structural specifications of the two different morphologies as well as studying the behavior of the cage-filling anions.



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**Keywords:** sodalites, synthesis, germinates

#### FA4-MS29-P05

**Robust Alkaline-earth arenedisulfonate Metal-Organic Frameworks materials.** Ana E. Platero-Prats, Natalia Snejko, Angeles Monge, Enrique Gutiérrez-Puebla, *Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC)*.

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