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Stoichiometric Reduction of Coordination Polymers by Organometallic Complexes. Mikhail Meilikhov^a, Kirill Yusenko^a, Antonio Torrisi^b, Caroline Mellot-Draznieks^b, Roland A. Fischer^a, ^a*Inorganic Chemistry II - Organometallic and Materials, Ruhr-University Bochum, German*, ^b*Department of Chemistry, University College London, United Kingdom*
E-mail: mikhail.meilikhov@rub.de

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)]_n (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(C₅H₅)₂]_{0.5}@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)]_n which allows large changes of the cell volume of ± 470 Å³ (33 %). However, the crystal structure of **1** also reveals quite a significant contraction of the cell volume by 120 Å³ (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)]_n. [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 V³⁺/V⁴⁺ 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 CO₂ over N₂. This effect can be explained by the possibility of polarization of the CO₂ molecules by the charged framework which causes the adsorption of CO₂ 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.*

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

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X-Ray study of fluorine-graphite intercalation compounds CF_{0.25} and CF_{0.33}. Alexey Alexeyev^{a,b}, Andrey Danilenko^a, Sergey Gromilov^{a,b}, ^aNikolayev *Institute of Inorganic Chemistry, Novosibirsk Russia*, ^b*Novosibirsk State University, Russia*
E-mail: alexeyev@niic.nsc.ru

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_α-radiation, graphite monochromator, CCD-detector). The compounds CF_{0.25} and CF_{0.33} were obtained by the reaction of natural graphite with BrF₃ 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_{0.25} and *a* = 2.448–2.453, *c* = 5.810–5.962 Å for CF_{0.33}, 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 d₁₀₀ upon fluorination indicates the corrugation of the hexagonal carbon layers in the given compounds.

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

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Dynamic and reversible contraction in {Ni₃(H₂O)₃(Bpa)₄}(V₆O₁₈)·8H₂O vanadate. Roberto Fernández de Luis^a, M. Karmele Urriaga^a, José Luis Mesa^b, Teófilo Rojo^b, María Isabel Arriortua^a
^a*Departamento de Mineralogía y Petrología*, ^b*Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco EHU/UPV, Apdo. 644, E-48080, Bilbao, Spain.*
E-mail: roberto.fernandez@ehu.es

The crystal structure of {Ni₃(H₂O)₃(Bpa)₄}(V₆O₁₈)·8H₂O 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