

**FA2-MS16-P50**

**Crystal Structures of  $[M^A(NH_3)Cl]M^BO_4$  ( $M^A = Co, Rh, Ir$ ;  $M^B = Mo, W$ ).** Elena Shusharina<sup>a,b</sup>, Svetlana Khramenko<sup>b</sup>, Pavel Plusnin<sup>b</sup>, Sergey Gromilov<sup>b</sup>.

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Double complex salts can be used as precursors for the preparation of bimetallic alloys of high-melting metals upon temperatures less than 600 °C. The crystals of the title compounds have been synthesized by mixing together the aqueous solutions of complex salts containing  $[M^A(NH_3)Cl]^{2+}$  ( $M^A = Co, Rh, Ir$ ) cations and  $MoO_4^{2-}$  or  $WO_4^{2-}$  anions. Single crystal X-ray diffraction analysis was carried out on a Bruker X8 APEX CCD-based diffractometer with  $MoK\alpha$ -radiation at 150 K. All involved complex salts are isostructural and crystallize in the orthorhombic space group  $Pnma$  ( $Z = 4$ ). The compounds have the island crystal structures with the isolated ions. Thermal decomposition in the reducing atmosphere of the double complex salts occurs at temperatures 100–600° K. The XRD analysis of the thermolysis products was performed on an ARL X'TRA diffractometer with  $CuK\alpha$ -radiation and shows the solid solutions formation of title metals with particle sizes less than 50 nm. The final products phase composition is shown to depend on phase diagrams of the respective bimetallic systems. Owing to the fact that those complex salts are isostructural it is possible to prepare the solid solutions and the triple and quadruple alloys after their decomposition.

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**Keywords:** crystal structure analysis, X-ray phase determination, thermal decomposition.

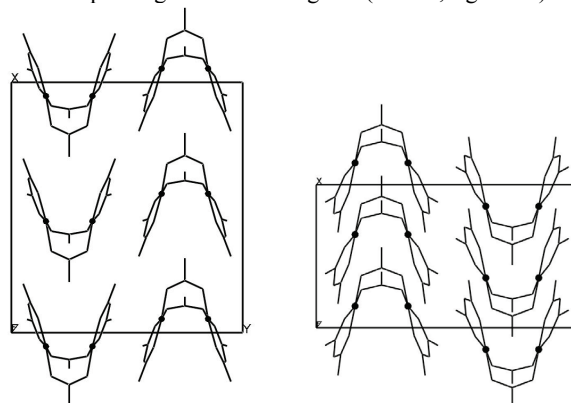
**FA2-MS16-P51**

**Two modifications of  $Pd_2(\mu-CH_3COO)_2(CH(CH_3CO)_2)_2$**  Elena Shusharina<sup>a,b</sup>, Svetlana Khramenko<sup>b</sup>, Sergey Gromilov<sup>a,b</sup>. <sup>a</sup>Novosibirsk State University, Russia. <sup>b</sup>Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia.

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The reaction of  $Pd_3(CH_3COO)_3NO_2$  with acetylacetone (1:3) dissolved in chloroform gives the  $Pd_2(\mu-CH_3COO)_2(CH(CH_3CO)_2)_2$  solution. Upon crystallization of the solution with a small amount of acetic acid the mixture of 3 crystalline phases was formed, two modifications of  $Pd_2(\mu-CH_3COO)_2(CH(CH_3CO)_2)_2$  and a small impurity of  $Pd(CH(CH_3CO)_2)_2$ . X-ray data were collected on a Bruker X8APEX automated diffractometer ( $MoK\alpha$ -radiation, graphite monochromator, CCD-detector) at 150(2) K and at the ambient temperature. Crystallographic data for modification I, T= 150(2) K:  $a = 15.6585(5)$ ,  $b = 14.4689(4)$ ,  $c = 8.0876(3)$  Å, space group  $Pnma$ ,  $V = 1832.3(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{calc} = 1.918$  g/cm<sup>3</sup>; for modification II, T= 150(2) K:  $a = 8.0285(3)$ ,  $b = 14.4785(5)$ ,  $c = 15.2092(5)$  Å, space group  $Pnma$ ,  $V = 1767.9(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{calc} = 1.988$  g/cm<sup>3</sup>. The structures were solved by standard direct methods and refined in an anisotropic (isotropic for H atoms) approximation. All calculations were performed using the SHELX-97 program

package [1]. The H atoms were located experimentally. The Pd...Pd distances are 2.9040(2) (I) and 2.9316(3) Å (II). The molecule packing is shown in Figures (left – I, right – II).



No significant changes in the crystal structures at the ambient temperature have been observed. Series of four unit cell measurements (through 50 K from 147 to 297 K) have shown no phase transitions.

[1] Sheldrick, G.M., *Acta Crystallogr.* 2008, A64, 112.

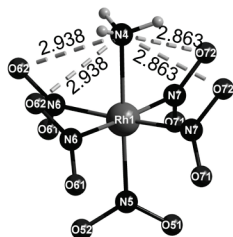
**Keywords:** crystal structure analysis, X-ray phase determination, palladium compounds.

**FA2-MS16-P52**

**First Example of Crystal Structure Containing  $[RhNH_3(NO_2)_5]^{2-}$  Anion.** Elena Shusharina<sup>a,b</sup>, Aleksandra Rybinskaya<sup>a,b</sup>, Pavel Plusnin<sup>a,b</sup>, Sergey Korenev<sup>a,b</sup>, Sergey Gromilov<sup>a,b</sup>. <sup>a</sup>Novosibirsk State University, Russia. <sup>b</sup>Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia.

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The crystal structure of complex salts containing  $[Rh(NO_2)_6]^{3-}$  and  $[Rh(NO_2)_4(NH_3)_2]^{2-}$  anions can be found in literature. The current work covers the crystal structure of a double complex salt containing the  $[RhNH_3(NO_2)_5]^{2-}$  anion. The synthesis of the  $[Pd(NH_3)_4][RhNH_3(NO_2)_5]$  salt can be summarized in the following scheme:  $Na_3[RhCl_6] \rightarrow (NH_4)_2[RhNH_3Cl_5] \rightarrow K_2[RhNH_3Cl_5] \rightarrow K_2[RhNH_3(NO_2)_5] \rightarrow [Pd(NH_3)_4][RhNH_3(NO_2)_5]$ . The crystal structure of the latter compound has been determined by X-ray diffraction. The data from a transparent crystal of the compound was collected on a Bruker X8APEX automated diffractometer ( $MoK\alpha$ -radiation, graphite monochromator, CCD-detector) in the  $\theta$  range of 2.83° to 30.52° at 150(2) K. Crystallographic data for H15N10O10PdRh:  $a = 7.6458(5)$ ,  $b = 9.8813(6)$ ,  $c = 9.5788(7)$  Å,  $\beta = 109.469(2)^\circ$ , space group  $P2_1/m$ ,  $V = 682.30(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{calc} = 2.553$  g/cm<sup>3</sup>. The structure was solved by standard direct methods and refined anisotropically using the SHELX-97 program package [1]. All hydrogen atoms were located geometrically. The Rh-N( $NO_2$ ) distances range from 2.020(4) to 2.060(3) Å, which are similar to that in  $Na(NH_4)_2[Rh(NO_2)_6]$  (2.051(2) Å). The Rh-N( $NH_3$ ) distance is 2.074(4) Å. The shortest intermolecular distances  $N(NH_3)...O(NO_2)$  are shown in Figure.



Upon complex thermolysis in hydrogen the nanoalloy  $\text{Pd}_{0.5}\text{Rh}_{0.5}$  is formed ( $Fm\text{-}3m$  space group,  $a = 3.847 \text{ \AA}$ ). The thermolysis final temperature is  $400 \text{ }^\circ\text{C}$ , the average particle size is  $20 \text{ nm}$ .

The work has been supported by RFBR Grant 08-03-00603, Presidium SB RAS interdisciplinary project No 112 and State contract № P960 of Federal target program «Scientific, Research And Teaching Specialists In Russia» 2009–2013.

[1] Sheldrick, G.M., *Acta Crystallogr.* 2008, A64, 112

**Keywords:** crystal structure analysis, X-ray phase determination, thermal decomposition.

#### FA2-MS16-P53

**High resolution X-ray diffraction experiments for selected minerals.** Marcin Stachowicz<sup>a</sup>, Maura Malinska<sup>a</sup>, Jan Parafiniuk<sup>b</sup> Krzysztof Woźniak<sup>a</sup>.

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Jarosite is used as a by-product of the metal-processing industry as well as a common supergene mineral in ore deposits, and is associated with acid-mine waste. Jarosite is thought to exist on Mars, and its presence suggests that water existed on Mars in the past [1]. Celestine is the most abundant strontium mineral and is the principal commercial source of strontium [2].

The high resolution X-ray diffraction experiments have been carried out for series of natural minerals. Natrojarosite  $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$  had been mined in Greece and celestine  $\text{SrSO}_4$  in Poland. These compounds crystallize in the trigonal R-3m and orthorhombic Pnma space groups, respectively.

The multipole model within the Hansen-Coppens formalism [3] is applied for crystals containing disorder and heavy atoms. In American Mineralogist Crystal Structure Database are four structures of Celestine [2,4-6] all ordered, however fitting of the multipole models of electron density leads to identification of small degree of disorder. Several multipole model refinement strategies have been applied and compared to find the most suitable one. Topological analysis of electron densities estimated from multipole models gives opportunity for better understanding intermolecular interactions and bonding properties in these minerals.

[1] Basciano L.C., Peterson R.C., *American Mineralogist*, 2008, 93, 853. [2] Jacobsen S.D., Smyth J.R., Swope R. J., Downs R.T., *The Canadian Mineralogist*, 1998, 36, 1053. [3] Hansen N.K., Coppens P., *Acta Cryst.*, 1978, A34, 909. [4] Miyake M., Minato I., Morikawa H., Iwai S.I., *American Mineralogist*, 1978, 63, 506. [5] Hawthorne F.C., Ferguson R.B., *The Canadian Mineralogist*, 1975, 13, 181. [6] Garske D., Peacor D.R., *Zeitschrift für Kristallographie*, 1965, 121,204

**Keywords:** X-ray crystallography of minerals, charge density inorganic materials

#### FA2-MS16-P54

**Structural investigations of  $\text{Li}_3\text{Ti}(\text{MoO}_4)_3$ .** A. Thomas<sup>a</sup>, D. Mikhailova<sup>a,b</sup>, H. Ehrenberg<sup>a</sup>

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Complex molybdates with 3d transition metals crystallizing in a NASICON-type structure are promising materials for Li-storage during Li-insertion and deinsertion. Recently, a new molybdate with V(III),  $\text{Li}_3\text{V}(\text{MoO}_4)_3$ , was prepared and characterized. It was shown that Li-ions can be reversibly intercalated and deinserted with formation of  $\text{Li}_2\text{V}(\text{MoO}_4)_3$  and  $\text{Li}_4\text{V}(\text{MoO}_4)_3$  [1]. In the related system Li-Ti-Mo-O, only the composition  $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$  with Ti(IV) and the same crystal structure type is known [2]. There are no examples in the literature for the coexistence of molybdenum(VI) and titanium(III) in one phase. Every stable product which contains titanium and molybdenum was synthesized from titanium(IV) and molybdenum(IV/VI) compositions, for example  $(\text{Ti}_x\text{Mo}_{1-x})_5\text{O}_{14}$  [3] and  $\text{TiMo}_2\text{O}_8$  [4]. If titanium (III) and molybdenum(IV) were used as educts, molybdenum(IV) was reduced to metal and titanium(III) was oxidized to titanium(IV) [5].

A new phase with the composition  $\text{Li}_3\text{Ti}(\text{MoO}_4)_3$  was synthesized by solid state reaction. It crystallizes in the space group *Pnma* and is isostructural to  $\text{Li}_3\text{V}(\text{MoO}_4)_3$ . Similar electrochemical properties as for  $\text{Li}_3\text{V}(\text{MoO}_4)_3$  are expected [1]. The material shows the same plateau at ca.  $1.8 \text{ V}$  during galvanostatic cycling against a Li-anode, which indicates the same two-phase mechanism during first Li-insertion. The similarity of  $\text{Li}^+$  and  $\text{Ti}^{3+}$  radii for octahedral oxygen coordination leads to mixed cation occupancy in the structure, which can be varied by different synthesis conditions. A difference in the lattice parameters for two samples, prepared at different temperatures, between  $a = 5.05876(8) \text{ \AA}$ ,  $b = 10.4833(1) \text{ \AA}$  and  $c = 17.5653(2) \text{ \AA}$  to  $a = 5.0715(1) \text{ \AA}$ ,  $b = 10.5096(2) \text{ \AA}$  and  $c = 17.6050(3) \text{ \AA}$  confirms this assumption. In comparison the lattice parameters of  $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$  are:  $a = 5.0467(12)$ ,  $b = 10.454(3)$  and  $c = 17.538(4)$  [2].

[1] Mikhailova, D.; Sarapulova, A.; Voss, A.; Thomas, A.; Oswald, S.; Gruner, W.; Trots, D. M.; Bramnik, N. N.; Ehrenberg, H.; *Chem. Mat.* (in press). [2] Smit, J. P.; McDonald, T. M.; Poeppelmeier, K. R.; *Solid State Sci.* 10 (2008) 396. [3] Ekström, T.; *Acta Chem. Scand.*; 26 (1972) 1843. [4] Krishnamurty, R.; Chincholkar, V. S.; *Current Sci. [India]* 41 (1972) 36. [5] Kirshenbaum, A. D.; Beardell, A. J.; *Thermochimica Acta*, 4 (1972) 239.

**Keywords:** NASICON-type structure, Li-insertion, cation mixed occupancy

#### FA2-MS16-P55

**Synthesis and structural studies of ammonium-cobalt-nickel phosphates,  $\text{NH}_4[\text{Co}_{1-x}\text{Ni}_x\text{PO}_4]\cdot\text{H}_2\text{O}$ .**

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