

at 800°C) was established by the Lacorre et al [1]. There is no such a compound in the  $\text{Nd}_2\text{O}_3$  -  $\text{MoO}_3$  system, but there is one with the fluorite-like structure near the  $\text{Nd}_2\text{MoO}_6$  [2], [3], [4]. Chemical composition and crystal structure of the  $\text{Nd}_5\text{Mo}_3\text{O}_{16}$  compound were studied before on polycrystals [4] as well as similar structure of  $\text{Pr}_5\text{Mo}_3\text{O}_{16}$  [5]. It was found that the  $\text{Pr}_5\text{Mo}_3\text{O}_{16}$  crystals have a fluorite-like superstructure in Pn-3n sp. gr. There are Pr1 at 12e position, Pr2 at 8c, Mo at 16f, and two kinds of oxygen atoms O1 at 48i and O2 at 16f. Overrated thermal parameters are given in [5] for the Pr2 ( $B_{\text{eq}}=1.32(16) \text{ \AA}^2$ ) and Mo ( $B_{\text{eq}}=0.98(7) \text{ \AA}^2$ ) atoms, while  $B_{\text{eq}}=0.71(4) \text{ \AA}^2$  for the O2 atom.

Single-crystal structure refinement of  $\text{Nd}_5\text{Mo}_3\text{O}_{16}$  and study of the physical properties have been performed. Dark-violet cubical  $\text{Nd}_5\text{Mo}_3\text{O}_{16}$  single crystals were grown by spontaneous flux crystallization. The conductivity of the compound is hypothetically anionic and reaches approximately  $10^{-2} \text{ S/cm}$  at 800°C.

The structure of  $\text{Nd}_5\text{Mo}_3\text{O}_{16}$  single crystal was studied by the X-ray techniques (XCalibur S CCD-diffractometer,  $T=293 \text{ K}$ ). The unit cell was found to be cubic with  $a=11.028(1) \text{ \AA}$ , which relates to that of fluorite  $\text{CaF}_2$  as  $a \approx 2a_f$ . The structure was solved using the Pn-3n symmetry group. It was found that the Nd1 and Mo atoms are shifted from their positions on the 4-fold axis with the formation of 4 positions (0.25 occupation) around it. The Nd2 atoms are not disordered; they are located on the 3-fold axis and are surrounded by oxygens with 6 Nd2-O2 distances equal to 2.597 Å and 2 distances Nd2-O1 equal to 2.294 Å (coordination polyhedron of Nd2 – slightly distorted cube). Inclusion of Mo atoms into  $\text{Nd}_5\text{Mo}_3\text{O}_{16}$  structure, which are surrounded by O2 atoms (Mo-O2 distances from 1.695 to 1.892 Å) lead to the strong distortion of the Nd1 – polyhedron and to the deviation of the structure framework from the fluorite-like. Some shift of the Nd1 and Mo atoms from the axis appears as a result, which was established in the present work ( $R=3.6\%$ ,  $R_w=3.27\%$ ,  $S=1.99$ ,  $B_{\text{eq}}=0.24(1) \text{ \AA}^2$  for the Pr2 atom).

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**Keywords:** Nd5Mo3O16, crystal structure, oxide-ion conductivity

## MS81.P34

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### Synthesis and structure of new vanadium(IV) complex based on isonicotinic hydrazide

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Although the biological significance of vanadium was recognized long ago, the coordination chemistry of this element continues to attract the attention of researchers, not least because of the discovery that vanadium is present at the active site of several enzymes, such as some peroxidases, as models for bromoperoxidase, nitrogenases and other biological systems.

The crystalline coordination compound  $\text{VO}_2\text{L}\cdot 2\text{H}_2\text{O}$  has been obtained as the result of interaction of 2,4-pentanedione isonicotinic hydrazone (HL) with  $\text{VOSO}_4\cdot 3\text{H}_2\text{O}$ . This compound is soluble in

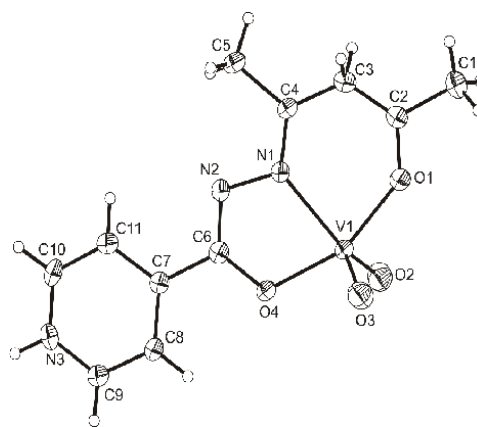
chloroform, dimethylformamide, less soluble in EtOH and MeOH.

The product  $\text{VO}_2\text{L}\cdot 2\text{H}_2\text{O}$  is characterized using IR spectroscopy, elemental analysis and X-ray method.

The disappearance of the band at  $1624 \text{ cm}^{-1}$  ( $\nu(\text{C}=\text{O})$ ) and the absence of oscillations bands of N-H, as well as the appearance of absorbance in the regions  $2700\text{-}2500$  and  $2250\text{-}2000 \text{ cm}^{-1}$  attributed to vibrations of  $=\text{C}=\text{NH}^+$  in the spectrum of  $\text{VO}_2\text{L}\cdot 2\text{H}_2\text{O}$  as compared to that of the uncoordinated ligand, indicates upon the coordination L in enolic form with proton migration (from NH) to the heterocyclic nitrogen. The presence of a narrow band of moderate intensity at  $1636 \text{ cm}^{-1}$  confirms the formation  $=\text{C}=\text{N}-\text{N}=\text{C}$ . The new band at  $1520 \text{ cm}^{-1}$  may be attributed to the oscillations of coordinated  $\nu(\text{C}=\text{O})_{\text{acac}}$ .

The crystallization water molecules are associated ( $\nu(\text{OH})=3215 \text{ cm}^{-1}$ ), forming three hydrogen bonds. The oscillations  $\nu(\text{V}=\text{O})$  are manifested at  $908 \text{ cm}^{-1}$  and is the most intensive band in the spectrum.

According to the x-ray single crystal study, the isolated compound  $\text{VO}_2\text{L}\cdot 2\text{H}_2\text{O}$  has a molecular structure composed by neutral  $[\text{VO}_2\text{L}]$  complexes and solvate water molecules in 1:2 ration. Vanadium atom adopts a  $\text{NO}_4$  trigonal-bipyramidal environment, being coordinated by two oxygen atoms and one tridentate Schiff-base ligand L.



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**Keywords:** coordination compounds, vanadium, Schiff-base

## MS81.P35

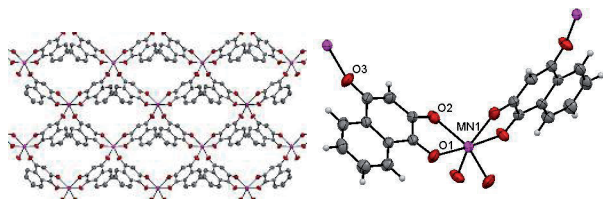
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### X-Ray studies in a manganese lawsonate coordination polymer

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Lawsonate (2-hydroxy-1,4-naphthoquinone) is a natural spin carrier in metal complexes molecules. The redox properties of quinones and their complexes have been explored for applications such as the development of new drugs for cancer [1] and switches for molecular electronics [2]. Here, we describe the synthesis and the characterization of  $[\text{Mn}(\text{C}_{10}\text{H}_5\text{O}_3)_2]_n$  by infrared and ultraviolet spectroscopy, thermogravimetric analysis and single-crystal X-ray diffraction. X-ray data shows the formation of a coordination polymer with the manganese atom in a center of a fully distorted octahedron (C2/c). The carbonyl and the phenoxy oxygens (O1 and O2, respectively) chelate to the manganese, and the other carbonyl oxygen (O3) bridges to another metal center forming a 2D arrangement. Temperature dependent X-ray studies (225K and 110K) shows a significantly variation in bond distances around the metal center, which indicates change in the bond

character. A similar behavior reported early for an analogue complex with lapachol suggest an electron transfer process between the metal center and the naphthoquinone [3].



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**Keywords:** coordination polymer, lawsone, manganese complex

### MS81.P36

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#### Synthesis and investigation of double complex salts involving [AuHal<sub>4</sub>]<sup>-</sup> anions

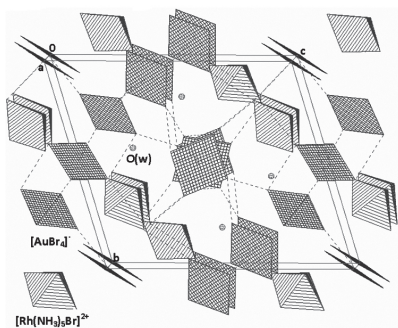
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Double complex salts (DCS) are promising single-source precursors for preparation of ultrafine metal systems. The composition of a DCS can be represented with the general formula [ML<sub>x</sub>]<sub>m</sub>[M'L'<sub>y</sub>]<sub>n</sub>, where M, M' – a transition metal, L, L' – a neutral or charged ligand. Thermal decomposition of such compounds, occurring at relatively low temperatures, allows targeted preparation of metallic systems with composition strictly pre-determined by the stoichiometry of the original DCS [1].

DCS's [M(NH<sub>3</sub>)<sub>5</sub>Hal][AuCl<sub>4</sub>]Cl·nH<sub>2</sub>O (Hal = Cl, Br) and [M(NH<sub>3</sub>)<sub>5</sub>Hal][AuBr<sub>4</sub>]<sub>2</sub>·nH<sub>2</sub>O (M = Ir, Rh; n = 0–1) have been synthesized and characterized with a number of physical chemical techniques. Crystal structures have been determined for all compounds. Single crystal X-ray diffraction analysis was carried out on a Bruker X8 APEX CCD-based diffractometer with MoK $\alpha$ -radiation at 150 K. The structures were solved by standard direct methods and refined anisotropically using the SHELX-97 program package [2]. All hydrogen atoms were located geometrically.

[M(NH<sub>3</sub>)<sub>5</sub> Hal][AuCl<sub>4</sub>]Cl·nH<sub>2</sub>O are monoclinic, sp. gr. C2/m, [M(NH<sub>3</sub>)<sub>5</sub>Hal][AuCl<sub>4</sub>]NO<sub>3</sub> are orthorhombic, sp. gr. Pnma. [M(NH<sub>3</sub>)<sub>5</sub>Hal][AuBr<sub>4</sub>]<sub>2</sub>·nH<sub>2</sub>O crystallizes in the triclinic crystal system, sp. gr. P-1.

It was shown that DCS's containing [AuCl<sub>4</sub>]<sup>-</sup> anions can be obtained with high yield (60-80%) with stoichiometry of M:Au (1:1) and DCS's containing [AuBr<sub>4</sub>]<sup>-</sup> with stoichiometry M:Au (1:2). Compounds with [AuBr<sub>4</sub>]<sup>-</sup> have structures with stacks of complex anions along a axis (figure shows packing



for [Rh(NH<sub>3</sub>)<sub>5</sub>Br][AuBr<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O) with Au...Au distances 3.966(1) – 5.816(1) Å.

The thermal decomposition of the DCS's in different atmospheres has been examined by thermal analysis. The mechanism of the process has been suggested on the basis of the data of thermal analysis, powder X-ray diffraction and IR spectroscopy. It has been demonstrated that ultrafine powders of solid solutions Ir-Au and Rh-Au can be prepared on thermal decomposition of the synthesized compounds. Phase composition and particle sizes of the bimetallic products have been found to be essentially determined by the process conditions: atmosphere, temperature, heating rate.

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**Keywords:** crystal structure analysis, gold compounds, thermal decomposition.

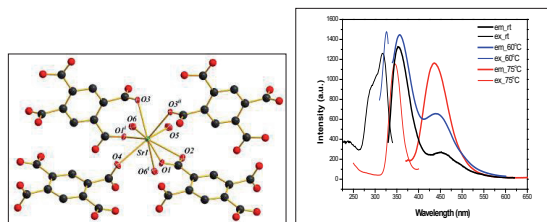
### MS81.P37

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#### Assembly a new water-insoluble strontium metal-organic framework and its luminescent studies

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The research in the field of metal-organic frameworks (MOFs) has grown exponentially in the last decade due to potential applications of MOFs such as gas storage, catalysis, magnetism, luminescence, and gas separation. Recently, we have reported a new magnesium complex with BTEC which can be easily prepared by direct-mixing method starting from the acid, metal hydroxide, and water.<sup>1</sup> It is desired to apply such a kind of environmentally friendly and efficient chemical processes to the syntheses of diverse chemical compounds, such as metal-organic frameworks or metal coordination polymers. The compound [Sr<sub>2</sub>(BTEC)(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O (**1**) (H<sub>4</sub>BTEC = benzene-1,2,4,5-tetracarboxylic acid) is a new strontium metal-organic framework which is insoluble in water and emits strong luminescence at around 437 nm after dehydration. Single-crystal X-ray diffraction shows that the structure of compound **1** possesses an extended 3D framework. Each SrO<sub>9</sub> polyhedron shares its three edges with other three SrO<sub>9</sub> polyhedra forming thus an inorganic layer lying in the bc plane. The layers are pillared by the BTEC ligands and form a 3D metal-organic framework.



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**Keywords:** strontium complex, metal-organic framework, luminescent