

$V=1437.7(3)\text{\AA}^3$ ;  $Z=2$  for (2). The copper(II) ions present a square base pyramidal geometry in these reported complexes with a Cu-Cu distance of 5.013 and 5.017 Å for (1) and (2) respectively. Both compounds present antiferromagnetic behaviour with  $T_m$  of 15.5 and 32 K for (1) and (2). The magnetic behaviour will be compared with other reported Cu-VPO systems.<sup>1</sup>

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[1] Moreno Y., Vega A., Ushak S., Baggio R., Peña O., Le Fur E., Pivan J.Y., Spodine E., *J. Mater. Chem.*, 2003, **13**, 2381.

**Keywords:** magnetic materials, copper, VPO system

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#### Partial Phase Diagram of Pd-Mn System Studied by Electron Diffraction and Microscopy

Rokuro Miida, Tokyo University of Science, Suwa, Chino Nagano, Japan. E-mail: miida@rs.suwa.tus.ac.jp

Among ordered phases reported in the present alloy system, four of Pd<sub>3</sub>Mn (or Pd<sub>3</sub>Mn II), Pd<sub>2</sub>Mn, Pd<sub>5</sub>Mn<sub>3</sub> and PdMn were confirmed to be stable, but no indications of Pd<sub>3</sub>Mn I and Pd<sub>21</sub>Mn<sub>11</sub> were obtained.

In the solid solution range from 25 to 50at%Mn, the crystal structure continuously transforms from D0<sub>23</sub> type to L1<sub>0</sub> type with increasing Mn content. The magnitude of  $c_0/a_0$  of the basal lattice is 1.0 for 25.0-26.5at%Mn, and then decreases down to 0.91 at 36.1at%Mn. The Pd<sub>3</sub>Mn phase is defined in the range from 25.0 to 26.5at%Mn, because  $c_0/a_0=1.0$  in this range is the characteristic of D0<sub>23</sub> type structure. The electron micrograph shows the arrangement of minority atoms (Mn) in D0<sub>23</sub> type. For Mn content more than 37at%, the PdMn phase with L1<sub>0</sub> type is stable above 600°C. In the compositions between Pd<sub>3</sub>Mn and PdMn phases, the occupation probability of Mn at each atom-site was expressed in terms of alloy composition.

The Pd<sub>2</sub>Mn phase is stable below 700°C. The electron micrograph shows the arrangement of Mn atoms, which supports the structural model reported already [1]. The Pd<sub>5</sub>Mn<sub>3</sub> phase was confirmed by electron diffraction patterns with different incidences. This phase is ranked as the second ordered structure of the PdMn phase. On the basis of ordered structures confirmed there, a partial phase diagram was proposed for Pd-rich Pd-Mn alloys.

[1] Kádár G., Krén E., Márton M., *J. Phys. Chem. Solids*, 1972, **33**, 212.

**Keywords:** electron diffraction, ordered structures, phase diagrams

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#### Crystal Structure of $\beta$ -KU<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> – a Member of the Group with NZP Structure Type

Elena Gobecheva<sup>a</sup>, Yuri Kabalov<sup>a</sup>, Sergei Tomilin<sup>b</sup>, Anatolii Lukinikh<sup>b</sup>, Andrei Lizin<sup>b</sup>, <sup>a</sup>Faculty of Geology, Moscow State University, Russia. <sup>b</sup>Federal State Unitary Enterprise «State Scientific Center Of Russian Federation –Research Institute Of Atomic Reactors», Dimitrovgrad, Russia. E-mail: elglob@mail.ru

The study of synthetic double Potassium-Uranium orthophosphate KU<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> is part of a program on the crystal chemistry of double orthophosphates with general formula (M1)<sub>0→1</sub>(M2)<sub>0→3</sub>{[L<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>]<sup>P</sup>}<sub>3z</sub>, where (M1)<sub>0→1</sub> and (M2)<sub>0→3</sub> are types of extraframework cation positions in holes with the indications of position numbers and L is the framework position, that includes determination of phases obtained by sol-gel technique. The NaZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NZP) structural type [1] is widely distributed among them. The distinguishing characteristic feature of the NZP structure is that the same crystallographic positions in this structure can accommodate elements, both small and large, in oxidation states from +1 to +5 with retention of the principal framework. In this work the compound  $\beta$ -KU<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was recently studied by x-ray powder diffraction and Rietved method in space group R-3c. The synthesis of new framework phosphates belonging to

the NZP structural type, as well as detailed analysis of the geometric and topological features of the structures of new and known NZP-type phosphates aimed at revealing correlations between the crystal structures of these compounds and the practically valuable physicochemical properties, have attracted considerable attention in recent years [2].

[1] Hong H.Y.-P., *Mat. Res. Bull.*, 1976, **11**(2), 173-182. [2] Alamo J., *Solid State Ionics.*, 1993, **63-65**, 547.

**Keywords:** phosphates, X-ray diffraction, Rietveld method

#### P.08.14.8

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#### Transition Metal Hydroxy-Terephthalates: Structure-Magnetism Relationship

Anne Carton<sup>a</sup>, Michel François<sup>a</sup>, Pierre Rabu<sup>b</sup>, <sup>a</sup>LCSM, University H.Poincaré, Nancy, France. <sup>b</sup>IPCMS UMR7504 CNRS-ULP, Strasbourg, France. E-mail: anne.carton@lcsm.uhp-nancy.fr

The title compounds belong to the family of hybrid lamellar materials where transition metal ions form layers spaced by organic anions. Metal hydroxy-terephthalates M<sub>x</sub>(OH)<sub>2x-2</sub>(tp) (tp =C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>, M = Zn, Mn, Fe, Co, Ni, Cu) have been synthesized by hydrothermal route and their crystallographic structures were determined. Zn<sub>3</sub>(OH)<sub>4</sub>(tp) has been characterized from X-ray single crystal diffraction data: C2/c,  $a=28.100\text{\AA}$ ,  $b=6.310\text{\AA}$ ,  $c=14.836\text{\AA}$ ,  $\beta=121.56^\circ$ . The zinc atoms exhibit tetrahedral, octahedral and bi pyramidal coordinations, forming step-like layers bridged by terephthalate moieties. As for the paramagnetic ions, the layered structures of the model compounds Co<sub>2</sub>(OH)<sub>2</sub>(tp) (C2/m,  $a=19.943\text{\AA}$ ,  $b=3.289\text{\AA}$ ,  $c=6.289\text{\AA}$ ,  $\beta=95.75^\circ$ ) [1] and Cu<sub>2</sub>(OH)<sub>2</sub>(tp) (P-1,  $a=10.143\text{\AA}$ ,  $b=6.339\text{\AA}$ ,  $c=3.484\text{\AA}$ ,  $\alpha=99.17^\circ$ ,  $\beta=95.75^\circ$ ,  $\gamma=98.76^\circ$ )[2] were determined *ab-initio* from XRPD data. The metallic cations lie in oxygen octahedra. Despite similar structures, different magnetic behaviors are observed depending on the metal ion and on symmetry differences. Low-temperature ferromagnetic-like ordering will be discussed on the basis of the structural features.

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**Keywords:** lamellar hybrid compound, transition metal, structure-properties relationship

#### P.08.14.9

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#### Structures of New Molecular Conductors Based on Functionalized Organic Donors

Leokadia Zorina<sup>a</sup>, Rimma Shibaeva<sup>a</sup>, Salavat Khasanov<sup>a</sup>, Sergey Simonov<sup>a</sup>, Lyudmila Kushch<sup>b</sup>, Eduard Yagubskii<sup>b</sup>, Cecile Meziere<sup>c</sup>, Stephane Baudron<sup>c</sup>, Patrick Batail<sup>c</sup>, Enric Canadell<sup>d</sup>, <sup>a</sup>Institute of Solid State Physics, RAS, Chernogolovka, Russia. <sup>b</sup>Institute of Problems of Chemical Physics, RAS, Chernogolovka, Russia. <sup>c</sup>Chimie Inorganique, Matériaux et Interfaces, CNRS-Université d'Angers, France. <sup>d</sup>Institut de Ciencia de Materials de Barcelona (CSIC), Bellaterra, Spain. E-mail: zorina@issp.ac.ru

Functionalized organic donors are remarkable for the ability to form hydrogen bonds of cation...cation and cation...anion types, which can effectively control the crystal architecture of molecular conductors [1]. Hydrogen bond network is well developed in the crystals of four new radical cation salts based on amide functionalized EDT-TTF donors EDT-TTF-CONH<sub>2</sub> (D1) and EDT-TTF-(CONH<sub>2</sub>)<sub>2</sub> (D2) [2].

Semiconducting  $\alpha'$ -(D1)<sub>4</sub>[FeNO(CN)<sub>5</sub>] (1),  $\alpha'$ -(D1)<sub>4</sub>[Co(CN)<sub>6</sub>] (2),  $\beta$ -(D1)<sub>6</sub>[Fe(CN)<sub>6</sub>] (3) and (D2)<sub>4</sub>[FeNO(CN)<sub>5</sub>]NB (4) salts have been prepared and characterized by X-ray single crystal diffraction experiments and band structure calculations. (D1)<sub>2</sub>-dimers or (D2)<sub>n</sub>-extended zigzag chains of donors connected through functional groups are found to be stable structural motifs in 1-4. The 1 and 2 salts are isostructural but contain anions of different charge, -2 and -3, respectively. The degree of charge transfer affects on electronic structures of the crystals that results in changing their transport properties:  $\sigma_{RT}(2)/\sigma_{RT}(1)=50$ . In the crystals 4 a superstructure with

incommensurate vector  $\pm(0.5, 0.3, 0.2)$  has been observed and studied.

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**Keywords:** X-ray analysis, organic conductors, layered structures

#### P.08.14.10

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#### Family of Organic Layered Salts Based on BEDT-TTF with the $[\text{OsNOCl}_5]^{2-}$ Anion

Sergey Simonov<sup>a</sup>, Irina Shevyakova<sup>b</sup>, Leokadia Zorina<sup>a</sup>, Salavat Khasanov<sup>a</sup>, Lev Buravov<sup>b</sup>, Vyacheslav Emel'yanov<sup>c</sup>, Enric Canadell<sup>d</sup>, Rimma Shibaeva<sup>a</sup>, Eduard Yagubskii<sup>b</sup>, <sup>a</sup>*Institute of Solid State Physics, Chernogolovka, Russia.* <sup>b</sup>*Institute of Problems of Chemical Physics, Chernogolovka, Russia.* <sup>c</sup>*Institute of Inorganic Chemistry, Novosibirsk, Russia.* <sup>d</sup>*Institut de Ciència de Materials de Barcelona (CSIC), Bellaterra, Spain.* E-mail: simonovsv@rambler.ru

Four new BEDT-TTF radical cation salts with the  $[\text{OsNOCl}_5]^{2-}$  anion have been synthesized:  $\alpha'$ -(BEDT-TTF)<sub>4</sub> $[\text{OsNOCl}_5]^{2-}$ NB (**1**),  $\delta$ -(BEDT-TTF)<sub>4</sub> $[\text{OsNOCl}_5]^{2-}$ <sub>1.33</sub>NB<sub>0.67</sub> (**2**),  $\kappa$ -(BEDT-TTF)<sub>4</sub> $[\text{OsNOCl}_5]^{2-}$ BN (**3**) and  $\beta$ -(BEDT-TTF)<sub>2</sub> $[\text{OsNOCl}_5]^{2-}$  (**4**) [1]. The salts were characterized by single crystal X-ray diffraction, electrical resistance measurements, and electronic band structure calculations. Evidence for commensurate structural modulations was found for **2** and **3**. The crystals of **1**, **3** and **4** are semiconductors while those of **2** exhibit a M-I transition around 160 K. Analysis of the correlation between the crystal structure, transport properties and electronic structure of this and related salts suggests the possibility of smoothly changing the conductivity of  $\kappa$ -phases with two donors and two dimers from semiconducting to metallic as well as the need to reconsider the origin of the metal-to-insulator transitions of  $\delta$ -type salts.

[1] Simonov S.V., Shevyakova I.Yu., Zorina L.V., Khasanov S.S., Buravov L.I., Emel'yanov V.A., Canadell E., Shibaeva R.P., Yagubskii E.B., *J. Mater. Chem.*, in press.

**Keywords:** crystallographic analysis, low-dimensional conductors, organic molecular crystal structures

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#### Factors Determining Polymorphism of Leflunomide

Daniel Fernández<sup>1</sup>, Daniel Vega<sup>1,2</sup>, Javier A. Ellena<sup>3</sup>, <sup>1</sup>*Escuela de Ciencia y Tecnología, Universidad Nacional de General San Martín, Buenos Aires, Argentina.* <sup>2</sup>*Unidad de Actividad Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina.* <sup>3</sup>*Departamento de Física e Informática, Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, Brazil.* E-mail: fernande@tandar.cnea.gov.ar

Leflunomide is a medicament for the treatment of rheumatoid arthritis. The aim of this work was to explore its properties in the crystalline state. Single crystals of the two polymorphic modifications of leflunomide were grown by slow evaporation techniques from different solvents. The X-ray diffraction analysis revealed that forms I and II of leflunomide belong to space group P2<sub>1</sub>/c with two and one independent molecules per asymmetric unit, respectively. Two out of the three molecules are very similar in conformation whereas the third one differs in the orientation of the amide group. The molecules arrange in a chain which in the form I is organized by N-H...O and N-H...N hydrogen bonds, while that in the form II shows just the N-H...N interaction. This way, the choice of the solvent of crystallization appeared to be decisive to obtain the desired polymorphic modifications of the compound.

**Keywords:** leflunomide, polymorphism, crystal structure

#### P.08.14.12

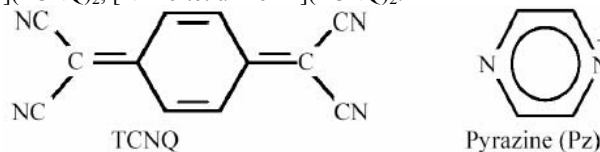
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#### New Electroconducting Radical Anion Salts Based on TCNQ with Organic Cations

Olga Kazheva<sup>a</sup>, Vladimir Starodub<sup>b</sup>, Gennady Shilov<sup>a</sup>, Oleg Dyachenko<sup>a</sup>, <sup>a</sup>*Department of Substance Structure, Institute of*

*Problems of Chemical Physics, Chernogolovka, Russia.* <sup>b</sup>*Kharkov National University, Kharkov, Ukraine.* E-mail: koh@icp.ac.ru

X-ray study of the first molecular semiconductors based on TCNQ  $\pi$ -acceptor with pyrazine derivatives has been carried out: (N-Et-Pz)(TCNQ)<sub>3</sub> [1], [N-Et-2,5-di-Me-Pz](TCNQ)<sub>2</sub>, [N-Me-2,5-di-Me-Pz](TCNQ)<sub>2</sub>, [N-Me-tetra-Me-Pz](TCNQ)<sub>2</sub>.



It has been established that the salts have a layered structure where conducting TCNQ layers alternate with non-conducting cationic layers. Lately organic and metal-containing TCNQ complexes have been gaining increased scientific interest since they can be used as organic sensors, high-speed optical memory devices, photo-switches, organic light emitting diodes, bio-sensors etc. [2]. Among them the so called hybrid materials were revealed that combine magnetism and electroconductivity and even superconductivity [3,4].

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**Keywords:** structure-properties relationships, TCNQ compounds, X-ray crystal structure analysis

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#### Haem-binding Properties and Crystallisation of the Bacterial Protein HemS

Sabine Schneider, Max Paoli, *School of Pharmacy, University of Nottingham, Nottingham, UK.* E-mail: paxss2@nottingham.ac.uk

Iron is one of the most important nutrients for the majority of living organisms due to its essential role in many biological processes like respiration and oxygen transport. Despite being one of the most abundant chemical elements, iron is scarcely available under physiological conditions, because of its insolubility and toxicity.

Pathogenic bacteria rely on their host as source of iron and have evolved several strategies to circumvent their iron dependency. One mechanism relies on "stealing" iron in the form of haem from host's haem proteins through a set of inter-linked haem transporters [1]. These unique systems have intriguing molecular biology mechanisms.

The haem uptake system of the gastrointestinal pathogen *Yersinia enterocolitica* consists of 5 proteins. Located on the outer membrane, the receptor HemR sequesters haem from host haem proteins or directly binds free haem. When internalised, the ligand is taken up by the periplasmic carrier HemT and passed onto the hetero-dimer HemUV, an integral inner membrane permease. In the cytosol, haem is held by the soluble protein HemS [1,2,3].

HemS purifies red from *E. coli*, has a solet peak at 412 nm and binds haem in vitro in a pH- and buffer-dependent manner. Homologues of HemS can only be found in the phylum of the Proteobacteria, with a sequence identity greater than 30%. Sequence alignments show three conserved histidine and one conserved methionine residues which might be involved in haem-iron coordination. Since tertiary structure predictions showed no significant similarity to any known structure, HemS could adopt a novel fold.

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**Keywords:** haem proteins, ligand transport, crystallography