

**A8 - Structure Solution from Powder Diffraction - Applications II****A8 - O1****COMPLEX INTERMETALLIC COMPOUNDS IN THE MG-IR SYSTEM SOLVED BY POWDER DIFFRACTION****Radovan Černý<sup>1</sup>, Guillaume Renaudin<sup>1</sup>, Yaroslav Tokaychuk<sup>1</sup> and Vincent Favre-Nicolin<sup>1</sup>**<sup>1</sup>University of Geneva, 24 quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland<sup>2</sup>CEA/Grenoble, 17, rue des Martyrs, F-38054 Grenoble Cedex 9, France

In the Mg–Ir phase diagram only the composition interval 0–25 at. % Ir was investigated [1]. Nothing is known about compounds with higher iridium content. Recently, new compound with the composition of  $\text{Mg}_5\text{Ir}_2$  (28.6 at. % Ir) was reported [2], and found to crystallize with the hexagonal  $\text{Al}_5\text{Co}_2$  type structure. Here we report on two new topologically closed-packed intermetallic compounds rich in iridium with new structure types. Their crystal structures were fully characterized by high resolution synchrotron powder diffraction (SNBL,  $\sim 0.5$  Å, sample in a 0.2 mm glass capillary), global optimization of a structural model in direct space using the simulated annealing (in parallel tempering mode) using the program FOX [3] and refined by FullProf.2k.

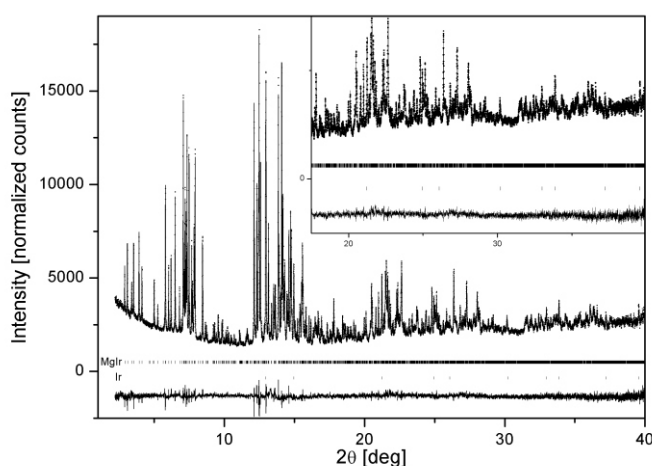
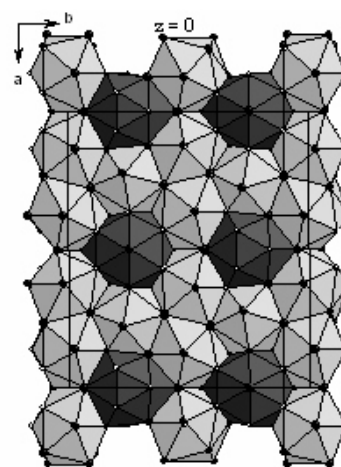
**MgIr:**

S.g. *Cmca*, 25 independent atoms,  $a = 18.46948(6)$ ,  $b = 16.17450(5)$ ,  $c = 16.82131(5)$  Å, 76 parameters,  $R_{\text{wp}} = 0.094$ ,  $\chi^2 = 3.02$ ,  $R_B = 0.056$ , measured composition (EDAX)  $\text{Mg}_{52(2)}\text{Ir}_{48(2)}$ . The structural model was independently confirmed by the single crystal X-ray diffraction [4]. The Ir–Ir interatomic distances in MgIr are in the range of 2.424(4) – 2.667(2), and are the shortest ever observed in an Ir-containing compound.

**Mg<sub>2</sub>Ir<sub>3</sub>:**

S.g. *C2/m*, 11 independent atoms,  $a = 18.5700(2)$ ,  $b = 5.18716(3)$ ,  $c = 8.49240(6)$  Å,  $\beta = 97.2211(5)^\circ$ , 27 parameters,  $R_{\text{wp}} = 0.141$ ,  $\chi^2 = 1.44$ ,  $R_B = 0.053$ . The structure is derived from that of the hexagonal Laves phase  $\text{MgIr}_2$ , which was also observed by us, by stacking of deformed  $\text{MgIr}_2$  blocks that are two  $\text{IrMg}_{12}$  icosahedra thick.

- [1] Binary Alloy Phase Diagrams. (1996). Second Edition, version 1.0, ASM International.
- [2] Černý, R., Joubert, J.-M., Kohlmann, H. & Yvon, K. (2002). *J. Alloys Comp.* **340**, 180-188.
- [3] Favre-Nicolin, V. and Černý, R., *J. Appl. Cryst.* **35** (2002) 734-743 see also: <http://objcryst.sourceforge.net>
- [4] Černý, R., Renaudin, G., Favre-Nicolin, V., Hlukhyy, V. and Pöttgen, R. *Acta Cryst. B*, in press.

**Figure 1:** Rietveld plot of MgIr.**Figure 2:** Structural slab of MgIr. Ligand atoms: Ir as small white and Mg as large black spheres.



A8 - O2

## SOLVING A PUZZLE: CHEMICAL AND STRUCTURAL CHARACTERIZATION OF BISMUTH AMMONIUM OXALATE HYDRATE

Vanhoyland G.<sup>1</sup>, Le Bail A.<sup>2</sup>, Mullens J.<sup>1</sup> and Van Poucke L.C.<sup>1</sup>

<sup>1</sup>Laboratory for Inorganic and Physical Chemistry, IMO, Limburgs Universitair Centrum, Wetenschapspark 1, 3590 Diepenbeek (Belgium)

<sup>2</sup>Laboratoire des Fluorures, Université du Maine, 72085 Le Mans (France)

As part of a systematic study of the Bi-Sr-Ca-Cu system, single and multi metal oxalate compounds were synthesized. For the monometallic bismuth oxalate, the well known  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$  and  $\text{Bi}_2(\text{C}_2\text{O}_4)_3$  were obtained, except for very low Bi concentration. Under these particular conditions a crystalline compound was obtained with a tetragonal unit cell. Before any attempt could be made to solve the crystal structure of this unknown compound, a thorough chemical characterization was necessary. However, from conventional TGA measurements alone no sound conclusion could be made with regard to the stoichiometry. By combining information obtained from

several hyphenated thermal analysis techniques, infrared and a quantitative chemical analysis,  $\text{Bi}(\text{NH}_4)(\text{C}_2\text{O}_4)_2 \cdot 3.71\text{H}_2\text{O}$  was then deduced to be the correct chemical formula. From the structural analysis, the reversible water exchange, as observed with HT-XRD and TGA, could be explained by the trapping of water molecules in the open bismuth-oxalate network. In contrast to the ammonium ions, these water molecules are not connected to the network by means of hydrogen bridges, which explains their high mobility.

A8 - O3

## Zr DERIVATIVES OF DI- AND TETRA- PHOSPHONIC ACIDS: STRUCTURAL VARIABILITY STUDIED BY X-RAY POWDER DIFFRACTION DATA

Ferdinando Costantino, Riccardo Vivani

Dipartimento di Chimica, Via Elce di Sotto 8, 06123 Perugia, Italy

The recent methodologies developed for structural determination from X-ray powder diffraction, allowed us to solve the structures of many Zr phosphonates prepared in our laboratory.

Metal phosphonate based materials are today widely investigated from a fundamental point of view and also for their potential application in molecular and ionic recognition, catalysis, and solid state proton conductivity.

Reaction of zirconium (IV) fluorocomplexes with R-amino-N,N-bis methylphosphonic and diamino-N, N, N', N' - tetraphosphonic acids led to the formation of insoluble microcrystalline solids with a great structural variability; solids with different connectivity and dimensionality were obtained by varying the nature of R groups, using different building blocks.

Common structural features in all these solids were found, such as non-covalent interactions that played a crucial role in the connectivity, acting as "structure orienting factors".

A class of structures of new Zr phosphonates solved "ab-initio" using conventional powder diffractometer will be presented, and the application of different methods for structure solution will be also discussed.

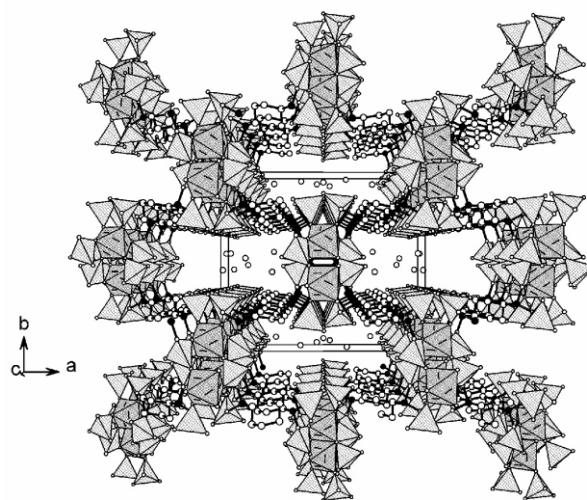


Fig. 1 Structure of Zr 1,4-diaminocyclohexyl tetraphosphonate.

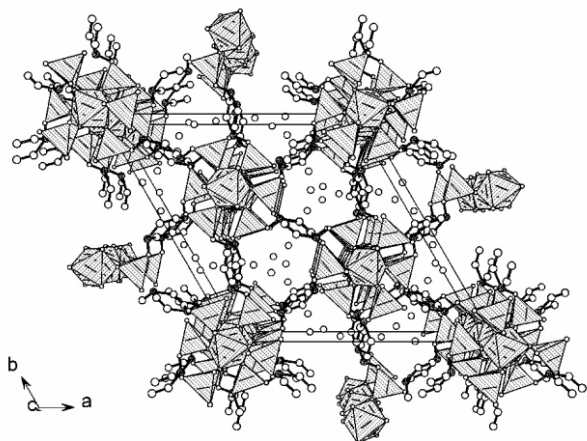


Fig. 2. Structure of Zr 1,4-piperazine diphosphate.

1. G. Alberti, M. Casciola, U. Costantino, R. Vivani, *Adv. Mater.*, 1996,8,291
2. G. Alberti, in *Comprehensive Supramolecular Chemistry*, ed G. Alberti and T. Bein, Pergamon Press, Oxford, 1996, vol 7, Chap.5.
3. U. Costantino, M. Nocchetti, R. Vivani, *J. Am. Chem. Soc.*, 2002,124,8428.

A8 - O4

## THE GEOMETRICAL ISOTOPE EFFECT IN CrOOH/CrOOD

Torbjörn Gustafsson,<sup>1</sup> Mizuhiko Ichikawa<sup>2</sup> and Takeshi Tsuchida<sup>3</sup>

<sup>1</sup>Department of Materials Chemistry, Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden

<sup>2</sup>Division of Physics, Graduate School of Science, Hokkaido University, 060-0810 Sapporo, Japan

<sup>3</sup>Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, 060-8628 Sapporo, Japan

The CrOOH system is well known for its reported unusually large geometrical isotope effect on deuteration. The material has a layered structure with chromium ions occupying octahedral holes in pairs of close packed layers of oxide ions. The chromium oxygen sandwiches are perpendicular to the hexagonal *c*-axis and connected by hydrogen bonds. All hydrogen bonds in the structure are thus parallel and oriented along the *c*-direction. It is known from previous diffraction studies that the hydrogen and deuterium compounds are isostructural so the geometrical isotope effect is directly visible in the elongation of the crystallographic *c*-axis. The hydrogen bond in this compound is about 2.5 Å. The hydrogen atom is usually centred for shorter bonds and off centred for bonds longer than ~2.5 Å. It is thus possible that the deuteration induces a change from a centred hydrogen bond to a non-centred for this

compound. This is supported by the large changes observed in the IR-spectrum on deuteration.

Recent neutron powder diffraction data indicate a super-lattice formation comprising a doubling of the hexagonal *a*-axis for the deuterated compound. There is not any indication of a super-lattice formation in the neutron diffraction data from the hydrogen containing compound. On the other hand, X-ray diffraction does not show super-lattice formation for any of the two compounds.

These observations are compatible with an **isotope induced super-lattice formation**. Since the super-lattice is not visible in the X-ray data it is probable that an ordering of the deuterium atoms causes it. A satisfactory model for the deuterated compound is still to be found.



A8 - O5

## STRUCTURE DETERMINATION OF POWDER $\gamma$ - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ BY JOINT REFINEMENTS OF ITS Cu AND Co SOURCE X-RAY AND NEUTRON DIFFRACTOGRAMS

H. Fansuri<sup>1</sup>, D.K. Zhang<sup>1</sup>, M. Elcombe<sup>2</sup>, A. Studer<sup>2</sup>, D. French<sup>3</sup>

<sup>1</sup>Centre for Fuels and Energy, Curtin University of Technology, Australia  
<sup>2</sup>Bragg Institute, Australia; <sup>3</sup>CSIRO Division of Energy Technology, Australia  
 \*hfansuri@vesta.curtin.edu.au

The [lattice?] structure of  $\gamma$ - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ , an active catalyst for partial oxidation of propylene to acrolein, has been refined using a combination of Cu and Co source of x-ray and high resolution neutron diffraction. 98 parameters were refined simultaneously using a RIETICA refinement software from three diffractograms, each of which has 5750, 2125, and 2900 contributed reflections. The structure has the same symmetry as two International Crystal Structure Database (ICSD) models for  $\gamma$ - $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  (nos. 2650 and 63640).

The unit cell parameters obtained from the refinement are  $a = 7.7120$  (1),  $b = 11.5264$  (2),  $c = 11.9746$  (2) Å,  $\beta =$

$115.2816$  (14),  $V = ?$ , and  $D_x = ?$ . The unit cell parameters, atomic coordinate and thermal factors are easily refined and the results are within the parameters in the two ICSD models with better or the same accuracy for all atoms, which is very difficult to achieve if the refinement is done only from either the x-ray or the neutron diffractogram. The information obtained from this study is very important as it serves as the starting point in the investigation into the real time structure dynamics of the catalyst in order to better understand the mechanisms of partial oxidation of propylene to acrolein on the catalyst.

A8 - O6

## STRUCTURAL INVESTIGATION OF A NEW "FAMILY" OF CHIRAL 3D NICKEL GLUTARATES WITH INTERSECTING 20-MEMBERED RING CHANNELS

N. Guillou, C. Livage, J. Chaigneau and G. Férey

Institut Lavoisier, UMR CNRS C8637, Université de Versailles Saint-Quentin-en-Yvelines, 45 Avenue des Etats-Unis, F-78035 Versailles, France

Nickel hybrids constitute an important new focus of research in material chemistry, offering potential applications in adsorption, catalysis, nonlinear optical devices and magnetic materials. The plasticity of nickel oxide condensation, which generates a wide range of structural edifices, has been demonstrated once again, by recent results on large pore zeolitic compounds (1, 2). Due to the difficulty to grow single crystals of nickel hybrids, powder diffraction is most of the time essential (3). We report here one of the most significant results on this topic, with the description of a series of nickel glutarates. Three compounds,

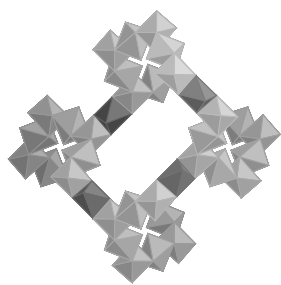
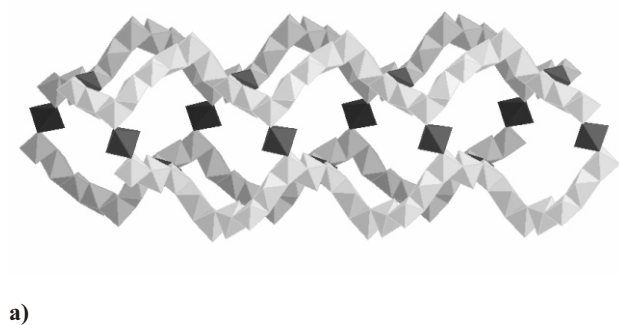
$\text{Ni}_{20}(\text{glutarate})_{20}(\text{H}_2\text{O})_8 \cdot 40\text{H}_2\text{O}$  (1),  
 $\text{Ni}_{20}(\text{3-methylglutarate})_{20}(\text{H}_2\text{O})_8 \cdot 24\text{H}_2\text{O}$  (2) and  
 $\text{Ni}_{20}(\text{2-methylglutarate})_{20}(\text{H}_2\text{O})_8 \cdot 18\text{H}_2\text{O}$  (3),  
 were prepared as green powders from hydrothermal reactions. Their structures were solved *ab initio* from conventional X-ray sources or synchrotron powder data. All powder patterns were indexed in the cubic symmetry by using DICVOL91, with a similar unit cell parameter [ $a = 16.5812(7)$  Å,  $a = 16.75633(7)$  Å and  $a = 16.5419(3)$  Å for (1), (2) and (3), respectively]. Systematic extinctions were consistent with the two chiral space groups  $P 4_1 3 2$  and  $P 4_3 3 2$ . All structures present the same amazing chiral three dimensional inorganic network of edge sharing nickel

octahedra, generated by two independent nickel atoms located on the threefold and twofold axes. This complicated oxide network can be simply described from helices running along the  $a$  axis (Fig. 1). Each helix is connected to four out-of-phase parallel neighbouring ones through a nickel octahedron, generating corrugated twenty membered rings. That also induces the formation of perpendicular helices.

The oxide framework is decorated by two independent deprotonated organic anions (Fig. 2). The first one (dark grey) has two multidendate carboxylate groups which are each coordinated to three nickel atoms. The second one (light grey) presents two carboxylates with a  $\mu_2$  oxygen and a non bonded one and has a statistic occupancy of 2/3. Bridging water molecules complete octahedral nickels environments. The main difference between the three structures seems to concern this disordered organic anion. The twenty membered rings intersect each other to generate very large crossing tunnels in the [111] direction, which contain disordered water molecules.

Thermal behaviour of nickel glutarate (1) has been studied by temperature dependent X-ray diffraction and thermogravimetric analysis. Disordered occluded water

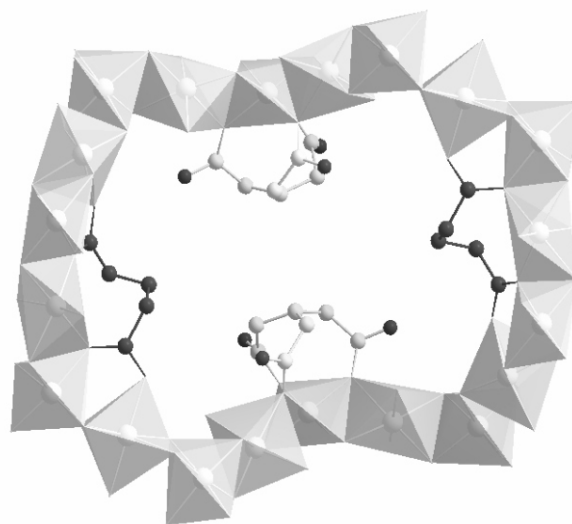




b)  
**Fig. 1.** (a) View of four helices (light grey) connected by nickel octahedra (dark grey); (b) view of these four helices in the perpendicular direction.

molecules leave the structure without significant structural change, to render the material porous after activation at 200°C under vacuum [ $346(10) \text{ m}^2 \text{ g}^{-1}$ ]. The loss of the eight coordinated water molecules is combined to crystallographic changes observed at 240°C. Symmetry and space group are conserved with a contraction of the unit cell [ $a = 15.653(1) \text{ \AA}$ ]. Curiously, a drastic decrease of the porosity is observed, which corresponds to structural rearrangements, mainly of the organic moieties. Its total rehydration allows recovering the original structure and shows the flexibility of this topology, with a reversible breathing of the 3D nickel oxide network.

1. P. M. Forster and A. K. Cheetham *Angew. Chem. Int. Ed.*, 2002, **41**, 457.
2. N. Guillou, C. Livage, M. Drillon and G. Férey *Angew. Chem. Int. Ed.*, 2003, **42**, 5314.
3. N. Guillou, C. Livage, W. van Beek, M. Nogučs and G. Férey *Angew. Chem. Int. Ed.*, 2003, **42**, 457.



**Fig. 2.** Polyhedral view of a corrugated twenty membered ring in structure of (1) with the two independent glutarate ions. The light grey one is disordered with statistic occupancy of 2/3.