

of metal–ligand interactions. Within our systematic study of the coordination chemistry of the substituted R-malonate ligands, we have observed that the flexibility and versatility of such ligands can produce a great variety of topologies. In this work, we present three copper(II)-methylmalonate coordination complexes synthesized with the same co-ligand. However, $[\text{Cu}(4,4'\text{-bpy})_2(\text{Memal})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ (1) is one-dimensional, whereas $[\text{Cu}_2(4,4'\text{-bpy})(\text{Memal})_2(\text{H}_2\text{O})_2]_n$ (2) and $\{[\text{Cu}(4,4'\text{-bpy})][\text{Cu}(4,4'\text{-bpy})_2(\text{Memal})(\text{NO}_3)(\text{H}_2\text{O})]_n \cdot n\text{NO}_3 \cdot 4n\text{H}_2\text{O}$ (3) are three-dimensional (Memal = methylmalonate dianion and 4,4'-bpy = 4,4'-bipyridine). The role played by the methylmalonate ligand being different in the three complexes: in 1, it is a simple two-fold connector, in 2 it forms a (4,4) with the copper(II) ions and in the case of 3, it pillars a $[\text{Cu}(4,4'\text{-bpy})]_n$ (4,4) network. The flexibility of the Memal ligand is responsible for this versatility. The crystal structure of 3 was solved after realising that it crystallizes in the form of merohedral twins, with a tetragonal cell and $P4_2/n$ space group. However, two areas can be identified within the crystal, they can be carefully separated to yield two crystals of orthorhombic cell and $Pc2_1/n$ space group, with inverted structure. Funding for this work was provided by the Spanish Ministerio de Ciencia e Innovación through projects MAT2007-60660, and “Factoría de Cristalización” (Consolider-Ingenio2010, CSD2006-00015). J.P. thanks the CSD2006-00015 for a postdoctoral contract.

Keywords: metal-organic frameworks; copper; twin resolution

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Crystal Engineering of Metal Barbiturates as Potential NLO Materials. Marlena Gryl^a, Katarzyna M. Stadnicka^a. ^a*Faculty of Chemistry, Jagiellonian University, Krakow, Poland.*
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Polar organic-inorganic crystal phases are known to be highly efficient non-linear optical materials [1]. Combination of inorganic and organic components provides mechanical and optical resistance, guarantees structural flexibility and high nonlinear efficiency. Barbituric acid and barbiturate molecules, possessing suitable hydrogen bond donors and acceptors, seem to be valuable components in crystal engineering of materials with specific, programmed properties. Moreover there are already known barbituric acid derivatives which exhibit NLO properties [2, 3] as well as there is a possibility to design polar cocrystals comprised of barbituric acid and urea molecules [4]. Recently we have discovered the usage of barbituric acid and selected inorganic metal salts to form polar cocrystals. Among several crystal structures of metal barbiturates obtained, the cadmium barbiturate dihydrate (Iba2) and copper barbiturate trihydrate (Fdd2) - previously reported in the literature [5], are polar whereas the rubidium barbiturate monohydrate is centrosymmetric ($P2_1/c$). The obtained phases have been structurally characterised and compared. The recognised coordination polyhedrons form layers linked by barbiturate ions, with additional interactions *via* hydrogen bonds. The polar crystal structures can be considered as potential NLO

materials.

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Keywords: crystal engineering; cocrystals; nonlinear optics

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Synthesis and Crystal Structures of Four Heptanuclear Mixed-valence $[\text{Fe}(\text{CN})_6\{\text{FeL}\}_6]\text{Cl}_2$ Complexes. Jan Moncol^a, Ivan Šalitroš^a, Roman Boča^a. ^a*Department of Inorganic Chemistry, Slovak Technical University, SK-81237 Bratislava, Slovakia.*

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Prussian blue analogues with Schiff bases ligand types are known to form a wide range of coordination compounds with transition metals [1,2], but only one structure of the heptanuclear mixed-valence iron complex formed of the $\{\text{Fe}(\text{CN})_6\}$ core and six N-coordinated mononuclear precursors has been reported [3]. The crystal structures of four heptanuclear mixed-valence $[\text{Fe}(\text{CN})_6\{\text{FeL}\}_6]$ complexes were studied. Various triamines Schiff-condensed with o-salicylaldehyde yielded pentadentate ligands L that form Fe(III) complexes $[\text{Fe}^{\text{III}}(\text{L})\text{Cl}]$. These precursors were used in assembling mixed-valence heptanuclear $[\{\text{Fe}^{\text{II}}(\text{CN})_6\}\{\text{Fe}^{\text{III}}(\text{L})\}_6]\text{Cl}_2 \cdot x\text{H}_2\text{O}$ complexes bridged through the CN group.

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Keywords: crystal structure; mixed-valence; iron complex

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Novel Co(II) and Ni(II)-Nitrito Complexes with NNN Type Ligand. Cigdem Hopa^a, Mahir Alkan^a, Raif Kurtaran^a, Hulya Kara^b, Robert Hughes^c, Mairi F. Haddow^c. ^a*Department of Chemistry, Balıkesir University, Balıkesir, Turkey.* ^b*Department of Physics, Balıkesir University, Balıkesir, Turkey.* ^c*Department of Chemistry, Bristol University, Bristol, UK.*
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Two novel monomeric $[\text{Co}(\text{bdmpp})(\text{ONO})_2]$ (1), $[\text{Ni}(\text{bdmpp})(\text{ONO})_2]$ (2), (bdmpp=2,6-bis(3,5-dimethylpyrazol)pyridine) complexes have been synthesized and characterized by single crystal X-ray diffraction analysis, elemental analysis, IR spectroscopy, UV-Vis spectroscopy and thermal analysis. Compound 1

crystallizes in monoclinic space group $P2_1/n$, $a=10.1737(2)$ $b=12.6997(3)$ $c=13.6447(3)$ Å, $\beta=101.1920(10)^\circ$ and compound **2** crystallizes in monoclinic space group $P2_1/n$, $a=8.2966(3)$ $b=19.9133(6)$ $c=10.5516(3)$ Å, $\beta=102.653(2)^\circ$. In compound **1**, the cobalt center is hepta-coordinated by the three N atoms of the bdmpp ligand, two O atoms from one nitrito group and two O atoms from the other nitrito group. In compound **2**, nickel center is hexa-coordinated by the three N atoms of the bdmpp ligand, two O atoms from one nitrito group and the other nitrito group is bonded with an O(3) atom.

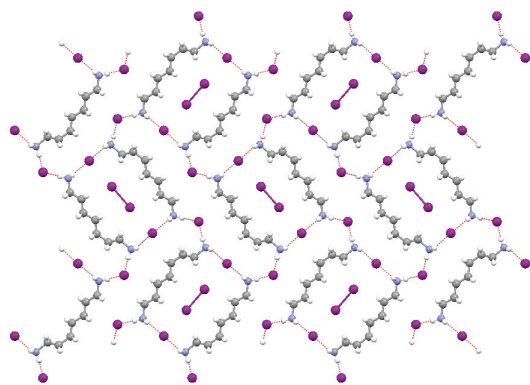
Keywords: transition-metal complexes; single-crystal analysis; thermal analysis

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Iodine Inclusion in Heptane-1,7-Diammonium Diiodide Salts. Charmaine van Blerk^a, Gert J. Kruger^a. ^aDepartment of Chemistry, University of Johannesburg, P O Box 524, Auckland Park, Johannesburg, 2006, South Africa. E-mail: cvanblerk@uj.ac.za

Investigations into structure-property relationships and applications of *n*-alkyl-diammonium salts are of continued interest and form the basis of our continuing investigations of these materials since they have important applications. [1 – 4] We have previously investigated the dihalide salts of a variety of *n*-alkyl-diamines [5 – 7] and this current work focuses on the crystal chemistry of two diiodide salts of heptane-1,7-diamine.

Compound **(I)** is heptane-1,7-diammonium diiodide and compound **(II)** is heptane-1,7-diammonium iodine diiodide. Both compounds crystallize in an orthorhombic crystal system with compound **(I)** occupying the space group $Pbca$ and compound **(II)** occupying the space group $Pbcn$. Significant differences exist in their crystal structures and we present and discuss their crystal chemistry in this work. The figure below shows the packing diagram of compound **(II)** viewed down the *c* axis. Both compounds produce an interesting array of three-dimensional hydrogen-bonding patterns consisting of multiple ring and chain motifs. Large ring motifs (a small inner ring with graph set $R^2_4(25)$ and a large outer ring with graph set $R^6_8(41)$) can be calculated for compound **(II)** and the ring motifs are evident in the figure below.



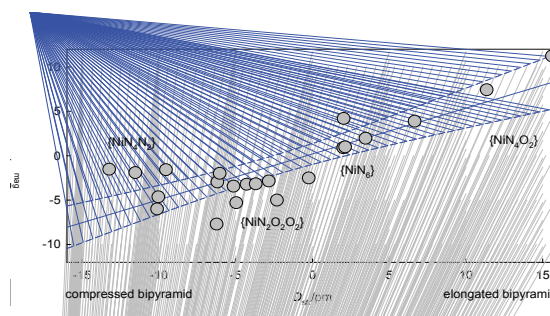
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Keywords: *n*-alkyl-diammonium halide salts; single crystal X-ray diffractometry; iodine inclusion

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Amagnetostructural D-correlation in Mononuclear Ni(II) Complexes. Roman Boča. Institute of Inorganic Chemistry (FCHPT), Slovak University of Technology 812 37 Bratislava, Slovakia. E-mail: roman.boca@stuba.sk

A series of about 20 mononuclear Ni(II) complexes with a different donor set has been synthesized and structurally characterized. The metal-ligand distances (corrected to the heterogeneous donor set) have been used in obtaining a tetragonality parameter, D_{str} . In parallel, the SQUID magnetic data have been analyzed in terms of the spin Hamiltonian formalism, from which the axial zero-field splitting parameter D_{mag} (that characterizes the magnetic anisotropy) has been retrieved by a data fitting procedure. The values of D_{mag} correlate with D_{str} along a straight line and a rationalization of this novel magneto-structural D-correlation brings the crystal-field theory. Thus a rational tuning of the magnetic anisotropy becomes a realistic task.



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Keywords: magnetic properties of molecules; structural correlation; nickel compounds

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New Generation of Metal String Complexes: Strengthening Metal-metal Interaction via Naphthyridyl Group Modulated Oligo- α -pyridylamido Ligands. Shie-Ming Peng^{a,b}. ^aDepartment of Chemistry, National Taiwan University, Taipei, 106, Taiwan (ROC). ^bInstitute of