

$\text{Ni}(\text{CN})_2\text{-CN-}]_n$ with trans-positioned bridging cyanide ligands in both cation and anion. The water molecules of crystallization are located between the chains and link them by hydrogen bonds. In the crystal structure of **4** the chains are built up of $[\text{Ni}(\text{cyclam})]^{2+}$ cations linked by cyanide anions solely; as a consequence the chains formed are positively charged and the positive charge is counterbalanced by uncoordinated NO_3^- anions. The water molecules of crystallization are involved in a hydrogen bonding system linking the chains, anions and water molecules.

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Keywords: cyanide complexes, cyclam complexes, nickel compounds

FA4-MS34-P12

Powder diffraction as a tool for studying clusters and molecules in solution Antonio Cervellino^a, Antonietta Guagliardi^{b,c}, Norberto Masciocchi^b, Alessandro Ceriotti^d, ^aSwiss Light Source, Paul Scherrer Institut, Switzerland, ^bDipartimento di Scienze Chimiche ed Ambientali, Università dell'Insubria, Como, Italy ^cIstituto di Cristallografia, Consiglio Nazionale delle Ricerche, Bari, Italy, ^dDipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Milano, Italy

E-mail: antonio.cervellino@psi.ch

The brilliance of third-generation synchrotron sources allows nowadays the detection of a meaningful scattering signal from extremely small atomic arrangements (including nanostructures and even relatively small molecules in suspension or solution), provided a certain level of contrast with the solvent. [1] This makes the method especially suited for high nuclearity metal carbonyl clusters. Although the resulting relatively smooth diffraction patterns are not yet amenable for direct structure solution, it is nowadays easy – using total scattering techniques, like PDF or the Debye Function Analysis [2] method – to compare the experimental pattern with calculated ones, derived from structure models of the solvated molecule (ideally, in its gaseous form). These models can be inferred in other ways, most commonly from structure solution of the same substance in crystallized form. The door is then open for using Reverse Monte Carlo-based algorithms for modifying and relaxing the initial structure model, aiming at improving the knowledge of the molecular conformation (in the solvated form) through a better match with the recorded pattern. The theoretical and experimental requirements of the method are discussed, with reference to some metal-organic small- and medium-sized clusters. [3]

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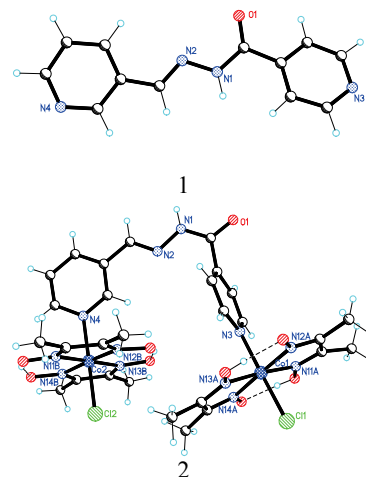
Keywords: powder diffraction, pair distribution function, crystallographic and NMR solution state structures

FA4-MS34-P13

A new Schiff Base as a bridge in binuclear Cobalt(III) Dioximate. Olga Ciobanica^a, Paulina Bourosh^b, Vasile Lozan^a, Ion Bulhac^a, Yurii Simonov^b
^aInstitute of Chemistry Academy of Sciences of Moldova, Chisinau, R. Moldova, ^bInstitute of Applied Physics Academy of Sciences of Moldova, Chisinau, R. Moldova

E-mail: olgaciobanica@yahoo.com

By condensation of isonicotinic acid hydrazide with 3-pyridine aldehyde the new Schiff Base HL (**1**) was obtained. The interaction of $[\text{CoCl}(\text{DmgH})_2\text{H}_2\text{O}]$, (where $\text{DmgH}_2 = \text{dimethylglyoxime}$) with HL the binuclear complexes with composition $[(\text{CoCl}(\text{DmgH})_2)_2\text{HL}]$ (**2**) was synthesized. Both compounds were characterized by using the IR-, UV/Vis- and NMR-spectroscopy. Single crystals were grown by slow evaporation of neat methanol solution of the ligand and complexes. The X-ray analysis of single crystal HL shows that free molecule adopts *E*-conformation around central bond N1-C . Torsion angle N2N1CO1 is 6° . The HL has a lot of active center, which can be used for coordination to the metal atom, N1 , N2 , N3 , N4 and O1 . Crystal structure of **2** shows that the HL is coordinated to two $[\text{CoCl}(\text{DmgH})_2]$ neutral residues through the nitrogen atoms of N-heterocyclic, HL acting as a bridging bidentate neutral ligand. At the same time the HL for coordination through the two terminal nitrogen atoms in the coordination process changes its conformation to *Z*, making some turns around the ordinary bond, particularly around the bond N1-C . The torsion angle of N2N1CO1 in HL coordinated to **2** is 174° . In the binuclear unit, each Co(III)



cation is hexacoordinated by five nitrogen atoms and one Cl in a square-bipyramidal environment. Its basal plane is made up by a bidentate DmgH^- , an anion Cl^- and a bidentate HL ligand occupy the apical sites. Two DmgH^- residues are bound via $\text{O-H}\cdots\text{O}$ hydrogen bonds, typical for all *bis*-ligand com-

plexes of α -dioximes [1,2]. The $\text{O}\cdots\text{O}$ distances range from 2.45 to 2.50 Å and correlate with the hydrogen bonding in the octahedral complexes of Co(III) , containing the $[\text{Co}(\text{DmgH})_2]$ core. The N_4 equatorial atoms are almost planar (± 0.023 Å for Co1 and ± 0.014 Å for Co2) and the deviation of the cobalt atoms from this plane are -0.053 Å and -0.030 Å, respectively. The axial Co-N distances 1.945 and 1.964 Å are significantly longer than the equatorial Co-N distances (the average distances Co-N 1.893 and 1.882 Å), Co-Cl 2.228 and 2.230 Å. Co-Co distance in the complex is equal to 7.211 Å. The crystal packing is discussed.

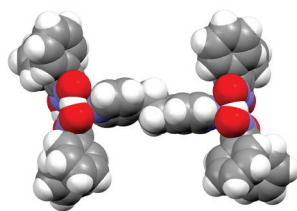
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Keywords: Ligand design, Coordination complexes, Crystal characterization

FA4-MS34-P14

Two Wheel-and-Axle Binuclear Copper(II) Dioximates Mediated by Bpetha Ligand. Eduard B. Coropceanu,^a Lilia Croitor,^b Mark M. Botoshansky^c and Marina S. Fonari^b. ^a*Institute of Chemistry, Academy of Sciences of R. Moldova, Academy str., 3, MD2028, Chisinau, Moldova,* ^b*Institute of Applied Physics, Academy of Sciences of R. Moldova, Academy str., 5, MD2028, Chisinau, Moldova;* ^c*Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Technion City, 32000 Haifa, Israel*
E-mail: ecoropceanu@yahoo.com

Porous transition metal-based structures primarily relied on coordinative interactions are of current interest owing to the need to development new materials for technologies and economies. Molecules with a shape not suitable for close packing tend to form crystals with other available molecules. Therefore, the creation of potentially porous frameworks is possible through the design of host molecular geometries that prevent close packing. Our continuous efforts [1,2] have been applied for using the strategy of 'metal oximate' building blocks in conjunction with neutral bridging ligands for design and synthesis of binuclear wheel-and-axle complexes in a controlled fashion. The d⁹ coordination of the Cu(II) cation favors the robust square-pyramidal (5-coordinate) geometry. 1,2-Bis(4-pyridyl)ethane (bpetha) acquires variable flexibility and functionality which can direct specific framework properties (dimensionality, void space, and topology). The interaction of copper(II) acetate with classic dioximes in the presence of bpetha resulted in two novel binuclear complexes of the compositions [Cu₂(dmgH)₄bpetha] (**1**), and [Cu₂(dphH)₄bpetha] (**2**) (Figure), where dmgH₂= dimethylglyoxime, dphH₂= diphenylglyoxime. The main structural feature of both compounds is an availability of a



binuclear unit [Cu₂(diox)₄(bpetha)] (diox = dmgH or dphH residue) where each Cu(II) atom has an identical N₅-environment formulated by four oximic nitrogen atoms of two monodeprotonated ligands in a slightly

distorted square planar mode and the nitrogen atom of the bridging bpetha molecule in the apical position. The Cu...Cu separation equals to 13.68 Å in **1** and 13.42 Å in **2**, respectively. The bulky phenyl substituents preclude the effective crystal packing in **2**, the volume of the solvent-accessible voids revealed value of 10.3%. For comparison, in [Cu₂(dphH)₄bpy] (where bpy=4,4'-bipyridine) [2] the solvent area occupied by the disordered DMF molecules revealed value of 23.1%. The key finding of this study is a definite availability of a robust copper dioximate building block for the rational crystal design.

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Keywords: copper compounds, coordination compounds, crystal structure analysis

FA4-MS34-P15

One Dimensional Coordination Polymer of Nickel(II)-Squarate with N,N,N',N'-tetramethylethylenediamine, {[Ni(μ-sq)(H₂O)₂(tmen)]·H₂O}_n. Necmi Dege^a, Hakan Erer^b, Okan Zafer Yeşilel^b, Yelda Bingöl Alpaslan^a, ^a*Faculty of Arts and Sciences, Department of Physics, Ondokuz Mayıs University, Samsun, Turkey,* ^b*Faculty of Arts and Sciences, Department of Chemistry, Osmangazi University Eskişehir, Turkey*
E-mail: necmid@omu.edu.tr

A novel 1D coordination polymer {[Ni(μ-sq)(H₂O)₂(tmen)]·H₂O}_n (H₂sq = squaric acid and tmen = N,N,N',N'-tetramethylethylenediamine) has been synthesized and structurally characterized by X-ray crystallography. The spectral (IR and UV-vis.) and magnetic susceptibility are reported. The structure of the complex consists of the bidentate tmen ligand bound to Ni(II) center and a bridging squarate in the 1,3-bonding mode. The distorted octahedral geometry of Ni(II) is completed by two aqua ligands. The structure contains chains of squarato-O¹,O³-bridged polynuclear nickel(II) units held together by intermolecular hydrogen bonds interactions between water molecules and oxygen atoms of squarate ligand forming a novel R6 motif. The crystal structure of the complex is presented in Fig. 1. The complex crystallizes in the monoclinic system and space group P2₁/c. The nickel atom has a distorted octahedral geometry with one tmen nitrogen [Ni1-N2 = 2.140(2) Å], one aqua ligand [Ni1-O5 = 2.085(2) Å] and two squarate oxygen [Ni1-O1 = 2.068(1) and Ni1-O2 = 2.080(1) Å] atoms in the equatorial positions and one tmen nitrogen [Ni1-N1 = 2.136(2) Å] and one aqua ligand [Ni1-O6 = 2.095(2) Å] in the apical position. The Ni-Ntmen bond lengths are comparable with those similar nickel complex, [1].

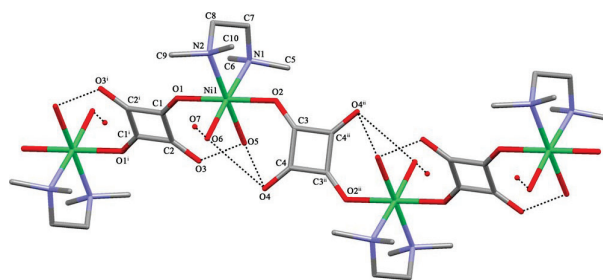


Fig. 1 The molecular structure of **1** showing the atom numbering scheme

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Keywords: squarate complex, N,N,N',N'-tetramethylethylenediamine complex, coordination polymer