

Only a few silver(I) monocarboxylates have been characterized, of which the acetate Ag(OAc) [1] and the trifluoroacetate Ag(OTfa) are important examples [2]. Outstanding structural features are carboxylate bridged silver(I) dimers which are further bridged to chains. We have obtained several new Ag(I) carboxylates of which silver(I) isobutyrate, Ag(i-OBu), is especially interesting because the [Ag(i-OBu)]₂ dimers are connected to layers.

For the synthesis of Ag(i-OBu) 0.5 mmol silver carbonate are dissolved in 25 ml isobutyric acid. After five weeks of isothermic evaporation cuboid shaped single crystals had formed. Ag(i-OBu) crystallizes in the monoclinic space group P2₁/c (no. 14) with $a = 1333.7(3)$, $b = 835.9(1)$, $c = 1005.5(2)$ pm, $\beta = 98.74(2)^\circ$, $Z = 4$.

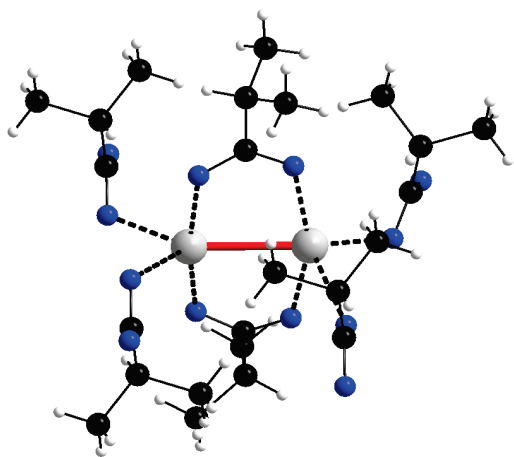


Fig 1. [Ag(i-OBu)]₂ dimers with two isobutyrate anions completing the coordination sphere of each Ag(I) ion as part of the crystal structure of silver(I) isobutyrate

Within the [Ag(i-OBu)]₂ dimers, the Ag—Ag distance is 281.4(4) pm, only slightly larger than in [AgOAc]₂ (279.4(4) pm) [1] and considerably shorter than in [Ag(OTfa)]₂ (296.7(3) pm) [2]. In Ag(i-OBu), the coordination sphere of Ag(I) is completed by two additional oxygen atoms of isobutyrate anions belonging to neighbouring dimers such that the isobutyrate ligands have two different bridging functions. Of course, the Ag—O distances are shorter within the dimers, as short as 219 pm, and much longer between the dimers, 243–259 pm. The shortest Ag—Ag distance between dimers is 331.3(5) pm, maybe not within the range of argentophilic attractions but still rather short. These short Ag—Ag distances and the 2+2 coordination by oxygen atoms lead to a two-dimensional arrangement, such that the present Ag(i-OBu) must be considered as the first Ag(I) mono carboxylate with a layered structure.

[1] Olson, L.P., Whitcomb, D.R., Rajeswaran, M., Blanton, T.N., Stwertka, B.J., Chem. Mater., 2006, 18, 1667–1674. [2] Griffin, R.G., Ellett, J.D., Mehring, M., Bullitt, G., Waugh, J.S., J. Chem. Phys., 1972, 57, 2147–2155.

Keywords: Silver dimers, Isobutyrate, Crystal structure

FA4-MS34-P10

Characterization and Antimicrobial Activities of Cobalt-Pyrazine-2,3-dicarboxylate Complexes.

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Novel cobalt-pyrazine-2,3-dicarboxylate complexes with 1,10-phenanthroline (phen), [Co(pzdc)(phen)₂]₂H₂O (1), N,N,N',N'-tetramethylethylenediamine (tmen), (H₂tmen)-[Co(pzdc)₂(tmen)]·9H₂O (2) and 2,2-dimethyl-propane-1,3-diamine (dmpen), [Co(CO₃)(dmpen)₂](pzdc)0.5·H₂O (3) have been synthesized and characterized by elemental and thermal analyses, spectroscopic (IR and UV-Vis.) and X-ray diffraction techniques. In 1 and 2, pyrazine-2,3-dicarboxylate ligand coordinated to the Co(II) ions through one nitrogen atoms of pyrazine ring and oxygen atoms of carboxylate group as a bidentate ligand and distorted octahedral geometries of 1 and 2 are completed by phen and tmen ligands, respectively. In 2, the tmen molecules exhibit chemically different functions; it coordinated to the Co(II) ion as a bidentate ligand and in the other form it protonated and acts as counter ion. In complex 3, Co(III) ion is coordinated by four nitrogen atoms of dmpen and two oxygen atoms of CO₃ ligand and the pzdc behaves as a counter ion. Furthermore, structures of 1 and 2 contain extensive hydrogen bonding between crystal water molecules to form infinite 2D water layers and 1D water chains, respectively. In vitro antimicrobial activities of new complexes were tested against selected wild type and clinical microorganisms by MIC. Complexes exhibited antimicrobial activity at high concentrations against the bacteria, fungi and clinical isolate tested.

Keywords: Pyrazine complexes, Cobalt complexes, Antimicrobial activities

FA4-MS34-P11

Crystallographic study of the system Ni(NO₃)₂ – cyclam - [Ni(CN)₄]²⁻. Juraj Černák^a, Monika Stolárová^a, Milagros Tomás^b, Larry R. Falvello^b, ^aInstitute of Chemistry, Department of Inorganic Chemistry, P. J. Šafárik University in Košice, Slovakia, ^bUniversity of Zaragoza-C.S.I.C., Department of Inorganic Chemistry and I.C.M.A., Zaragoza, Spain

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Within our broader study on Ni(II) ($S = 1$) complexes as low-dimensional magnetics [1] we have studied the system Ni(NO₃)₂ – cyclam - [Ni(CN)₄]²⁻ (cyclam = 1,4,8,11-tetraazacyclotetradecane). The ligand cyclam was chosen as it usually blocks four equatorial coordination sites around the central atom and thus promotes, in the presence of suitable bridging units (in our case the [Ni(CN)₄]²⁻ anion) the formation of one-dimensional structures. By direct reaction the complex Ni(cyclam)Ni(CN)₄ (1) was prepared in the form of microcrystalline powder. On the other hand, the use of diffusion techniques led to a mixture of single crystals: yellow [Ni(cyclam)(NO₃)₂] (2) which has already been described [2], and two novel complexes, pale violet Ni(cyclam)Ni(CN)₄·2H₂O (3) and yellow [Ni(cyclam)(CN)]NO₃·H₂O (4). Both 3 and 4 exhibit the expected one-dimensional structures. In the structure of 3 there are present two crystallographically independent chains [-Ni(cyclam)-NC-

$\text{Ni}(\text{CN})_2\text{-CN-}]_n$ 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.

This work was supported by the Slovak grant agency APVV under contracts Nos. APVV-VVCE-0058-07 and APVV-0006-07, and by grant agency VEGA (grant 1/0089/09). Support from the Ministry of Science and Innovation (Spain), under grant MAT2008-04350, is also acknowledged.

[1] Černák, J.; Pavlová, A.; Orendáčová, A.; Kajňáková M.; Kuchár J. *Polyhedron*, 2009, 28, 2893. [2] Thom, V.J.; Fox, C.C.; Boeyens, J.C.A.; Hancock, R.D. *J. Am. Chem. Soc.* 1984, 106, 5947.

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

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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]

[1] Kong Q., Lee J.H., Plech A., Wulff M., Ihee H., Koch, M.H.J. *Angew.Chem.Int.Ed.* 120, 5632 (2008). [2] Cervellino A., Giannini C., Guagliardi A. *J. Appl. Cryst.* 36, 1948 (2003). [3] Cervellino A., Ceriotti A., Guagliardi A., Masciocchi N., *in preparation* (2010).

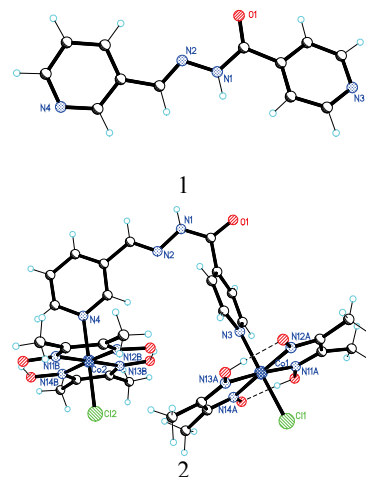
Keywords: powder diffraction, pair distribution function, crystallographic and NMR solution state structures

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
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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.

[1] Chakravorty A., *Coord. Chem. Rev.*, 1974, 13, 1. [2] Botoshanskii M.M., Dworkin A.A., Simonov Yu.A., Malinowski T.I., *Crystal structure of inorganic compounds* (Rus.), Shtiintsa, Kishinev, 1974, p. 26.