

MS36-P19

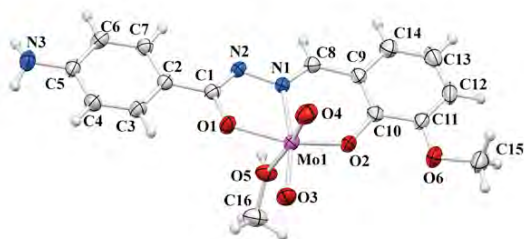
The mononuclear MoO₂²⁺ complexes with stereochemically rigid 4-aminobenzhydrazone based ligands

Gordana Pavlović¹, Danijela Cvijanović², Jana Pisk³, Marina Cindrić³, Višnja Vrdoljak³

1. University of Zagreb, Faculty of Textile Technology, Zagreb, Croatia
2. University of Zagreb, School of Medicine, Department of Chemistry and Biochemistry, Zagreb, Croatia
3. University of Zagreb, Faculty of Science, Department of Chemistry, Zagreb, Croatia

email: gpavlovic@tff.hr

A range of dioxidomolybdenum(VI) complexes has displayed very high catalytic activities and exquisite selectivity. The dioxidomolybdenum(VI) mononuclear complexes with 4-aminobenzoylhydrazone ligands (salicylaldehyde (H₂L¹), 3-methoxysalicylaldehyde (H₂L²), or 4-methoxysalicylaldehyde 4-aminobenzoylhydrazone (H₂L³) being of the type *cis*-[MoO₂L¹⁻³(D)]; D = MeOH, EtOH, H₂O, dmf] have been prepared and structurally characterized. The crystal structure analysis of mononuclear complexes (Fig.1.) reveals distorted octahedral Mo(VI) coordination by *ONO* donor atoms from dianionic tridentate 4-aminobenzoylhydrazone ligands, two oxido oxygen atoms from the MoO₂²⁺ moiety and the oxygen atom from coordinated alcohol molecules (D = MeOH, EtOH). The molybdenum oxido groups of the MoO₂²⁺ moiety show the expected mutual *cis* configuration and are located *trans* to the imine nitrogen atom and coordinated alcohol molecule. The bond distances range around Mo follows trend: Mo-Ot < Mo-O(phenolate) < Mo-O(hydrazone part) < Mo-N < Mo-O(ROH; R=Me, Et). The bicyclic system of two chelate rings is slightly folded along the axis of molybdenum-imino bond and by the offset of metal centre apart from chelate planes towards the terminal oxygen atom. The most deviation from chelate rings coplanarity is shown by the phenolate oxygen atom due to its participation in intermolecular interactions. The complexes were tested for catalytic epoxidation of cyclooctene under eco-friendly reaction conditions by using aqueous *tert*-butyl hydroperoxide (TBHP) as an oxidant. Due to *trans* effect of oxido oxygen atom, Mo-O(D) bond is the longest bond distance within molybdenum coordination sphere and it expected to be the point of maximum catalytic reactivity of the complexes. It is previously shown that pentacoordinated molybdenum systems activate oxidizing agent TBHP through adduct formation assisted by the O–H...O hydrogen bond. Another explanation of the substituent influence is *p*- π conjunctive effect with methoxy group due to increasing electron density of the phenyl ring.



Keywords: molybdenum complexes, 4-aminobenzoylhydrazone ligands

MS36-P20

Crystal structure and thermal and mechanical properties of a herringbone-type Cu^{II}-based solid coordination framework

Gotzone Barandika¹, Francisco Llano-Tomé², Begoña Bazán²⁻³, Miren Karmele Urriaga², María Isabel Arriortua²⁻³

1. Química Inorgánica, Universidad del País Vasco (UPV/EHU) and BCMaterials, Leioa, Spain
2. Mineralogía y Petrología, Universidad del País Vasco (UPV/EHU), Leioa, Spain
3. BCMaterials, Universidad del País Vasco (UPV/EHU), Leioa, Spain

email: gotzone.barandika@ehu.eus

Solid coordination frameworks (SCF) represent one of the most studied materials during the last decade thanks to the variety of structures that can be formed by using metal complexes as synthons.¹ In fact, combination of polycarboxylate anions and dipyriddy ligands is an effective strategy to produce SCF compounds, and we have previously reported on Cu^{II}-based SCFs exhibiting PDC (2,5-pyridinedicarboxylate) in combination with bpe (1,2-di(4-pyridyl)ethylene), bpa(1,2-di(4-pyridyl)ethane), and dpk (di-2-pyridyl ketone). The use of bpe and bpa as dipyriddy ligands produces 3-connected herringbone structures, and so far our main contribution to the study of this type of structures consists on the identification of two types of herringbone arrays (4-c and 3-c where c stands for “connected”) depending on the number of connections for each metal node. While M₁A₁B₁ stoichiometry corresponds to 4-c arrays, M₂A₂B stoichiometry corresponds to 3-c ones (M is the metal ion, and A and B are the organic ligands). Additionally, we also identified the structural parameters defining the 3-c herringbone arrays and observed a correlation between angles and distances in this type of structure.

In this context, this work is focused on the synthesis and characterisation of the compound [Cu₂(PDC)₂(4,4'-bipy)(H₂O)₂]·MeOH (where 4,4'-bipy is 4,4'-bipyridine and MeOH is methanol) with the aim of studying the influence of distinct dipyriddy ligands on the as-obtained characteristics materials. The compound crystallises in the monoclinic system (P 2₁/n, a=11.3583 Å, b=9.2348 Å, c=12.6150 Å, β=102.254°). Thermogravimetric analysis reveals that it is stable up to 280°C. Nanoindentation experiments on single crystals produced values of the E Young modulus between 1.325 GPa and 9.860 GPa, and values of the hardness between 0.030 GPa and 0.401 GPa depending on the crystal face.

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Keywords: CuII-based SCF; herringbone 2D-structure, nanoindentation

MS36-P21

New route to double perovskite oxides using the mixture of oxalate precursors

Marijana Jurić¹, Jasminka Popović¹, Lidija Androš Dubraja¹, Filip Torić², Damir Pajić²

1. Ruđer Bošković Institute, Zagreb, Croatia
2. Department of Physics, Faculty of Science, University of Zagreb, Zagreb, Croatia

email: Marijana.Juric@irb.hr

Properties of the mixed-metal oxides could be highly affected by the effect of crystallinity, particle size, phase composition and morphology. These can be tuned in part by changing the synthesis methods.

The possibility of using metal–organic coordination systems through the thermal decomposition process as molecular precursors in the synthesis of nanomaterials with high surface and specific morphology has been considered only recently. It has been observed that the use of a well-defined heterometallic precursor can produce crystalline oxide materials under conditions that are significantly milder than those applied in traditional solid-state synthesis. Also, the single-source precursors provide better control over the stoichiometry of the metal ions in the final products as well as the homogeneity of the materials due to the mixing of the metals at the molecular level. The existence of bridging or chelating ligands in the precursors prevents metal separation during oxide formation. For example, the $C_2O_4^{2-}$ anion easily decomposes to the vapour phases CO_2 and CO , by the low-temperature routes, and hence, heterometallic oxalate complexes are very convenient for the preparation of mixed metal oxides.^[1]

Most of the perovskite compounds that have potential technological interests are not simple systems, but rather ternary oxides such as $A(B'B'')O_3$. Heterometallic oxalate complexes do not always contain the appropriate stoichiometry for the formation of the desired single phase oxide. So, we have tested whether the multimetallic oxides containing two or more metals could be prepared by mixing two or more different oxalate precursor in various ratios prior to thermal decomposition.^[2]

A highly crystalline materials $Ba(M_{1/3-x}M'_x{}^{\text{IV}}Nb_{2/3}^{\text{V}})O_3$ ($M = Ni^{\text{II}}$, $M' = Co^{\text{II}}$; $x = 0–1/3$) were obtained after thermal decomposition of the mixture of the well-defined and structurally characterized heterometallic oxalate-based compounds $Ba_2(H_2O)_5[NbO(C_2O_4)_3]HC_2O_4 \cdot H_2O$,^[1] $[Ni(bpy)_3]_2[NbO(C_2O_4)_3]Cl \cdot 12H_2O$ ^[3] and $[Co(bpy)_3]_2[NbO(C_2O_4)_3]Cl \cdot 12H_2O$,^[3] grinded in an agate mortar in different ratios.

The phase formation and structural ordering of the tri- or tetrametallic perovskite oxides obtained by this modified molecular precursor route have been characterized by powder X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy. The magnetic properties of newly prepared materials which adopt the disordered cubic structure (with random distribution of B' and B'' ions) have been also investigated.

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Keywords: mixed-metal oxides, molecular oxalate precursors, thermal decomposition