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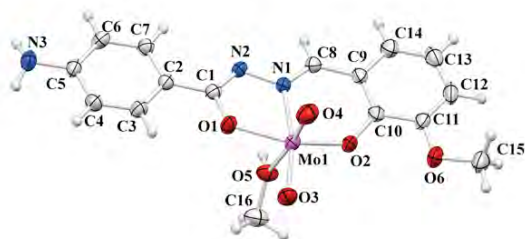
The mononuclear MoO₂²⁺ complexes with stereochemically rigid 4-aminobenzhydrazone based ligands

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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

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

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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.