Structural and magnetic characterization of three novel copper(II) complexes with methyl(2-pyridyl)ketone oxime and pseudohalides

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The family of 2-pyridyl oximes, of general formula (py)RC=NOH with py = pyridine and R = H, alkyl or aryl group, are very popular ligands in the field of molecular magnetism. This is due to their ability to form polynuclear complexes, acting as versatile and flexible bridging ligands that efficiently mediate magnetic exchange between paramagnetic ions. [1] Within this family, our research group have studied the synthesis of polynuclear compounds with methyl(2-pyridyl)ketone oxime (mpkOH) as ligand, which has been less explored than paOH, ppkOH or dpkOH (R = H, Ph and py, respectively). Whereas several manganese or nickel compounds have been characterised, there are only a handful of copper complexes with mpkOH whose X-ray structures have been reported. [2-4]

In this work, we present the synthesis, structural and magnetic characterization of three new copper complexes with mpkOH and azide or thiocyanate as co-ligands. Reaction of a methanolic solution of copper perchlorate or nitrate with mpkOH and sodium azide leads to the formation of the mononuclear complex [Cu(N_3)(mpkO)(mpkOH)] (**1**).

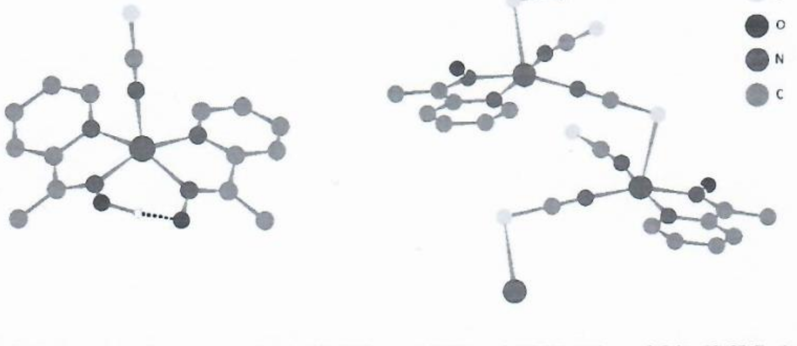

Figure 1: Perspective drawing of [Cu(SCN)(mpkO)(mpkOH)] (**2**) and [Cu$(SCN)_2$(mpkOH)]$_n$ (**3**).

When potassium thiocyanate is employed instead of sodium azide, two different products are isolated depending both on the starting copper salt and the $Cu^{II}:SCN^-$ molar ratio. Mononuclear complex [Cu(SCN)(mpkO)(mpkOH)] (**2**) is obtained only if copper perchlorate is used. However, copper nitrate in 1:2 $Cu^{II}:SCN^-$ molar ratio, leads to the formation of the chain $[Cu(SCN)_2(mpkOH)]_n$ (**3**).

In all cases, copper ions are pentacoordinated in a square-pyramidal geometry. In **1** and **2**, four N atoms from one neutral mpkOH molecule and one $mpkO^-$ anion are at the base of the pyramid, the apical position being occupied by the pseudohalide. The distortion from the ideal geometry is larger in complex **1** ($\tau = 0.37$) than in **2** ($\tau = 025$).

Complex $[Cu(SCN)_2(mpkOH)]_n$ (**3**) can be described as a zig-zag chain of Cu^{II} ions. The base of the pyramid is also defined by four N atoms, two of them from a bidentate mpkOH, and the remaining ones from two thiocyanate anions. The coordination sphere is completed at the apical site by the S atom from one SCN^- which is N-bonded to the base of the neighbour Cu^{II} ions. This way, half of the thiocyanate anions act as end-to-end bridges between metal centers, establishing a $\cdots Cu–SCN^-–Cu\cdots$ regular 1D motif, as depicted in figure 1.

Characterization of all complexes was carried out through vibrational and electronic spectroscopy and their magnetic behaviour was studied through variable temperature susceptibility measurements and electron paramagnetic resonance. Weak antiferromagnetic intramolecular interactions between copper ions have been found in **3**.

Acknowledgments: This work was supported by CSIC (Programa de Apoyo a Grupos), ANII and PEDECIBA-Química (Uruguay).

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