METAL OXIMATES: AN OLD PLATFORM FOR MODERN CRYSTAL DESIGN

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Complexes containing two or more metal ions are of increasing interest because of their relevance to biological systems and to molecular magnetism as they are ideal candidates for the synthesis of single-molecule magnets (SMMs) [1]. Despite the interest in the properties of such systems, synthetic methods have yet to reach the level of efficiency attained with mononuclear complexes. Of particular concern in this context is the development of such directed routes in which the metals are connected by ‘robust’ ligands so that fragmentation of the complexes in their subsequent reactions is inhibited. The advantage of such ‘metalloligands’ is the possibility to use either the free coordination sites of the ligand or to manipulate by the axial ligand in order to bind a second metal of the same or different kind. We have favored the strategy of ‘metal oximate’ building blocks [2] to design and synthesise multinuclear complexes in a controlled fashion. Herein, we report a series of homometal binuclear Zn, Cd and Cu complexes of a wheel-and-axle shape.

Structure and space-filling model for [Cd2(Hniox)2(CH3COO)4.2H2O(γ,γ’-dipy)] (2) and [Cu2(Hdmg)4(γ,γ’-dipy)] (3).

The neutral complexes [M2(Hniox)2(CH3COO)4.2H2O(γ,γ’-dipy)] (1, 2), (where M = Zn, Cd, Hniox = 1,2-cyclohexanedionedioxime, γ,γ’-dipy=4,4’-dipyridine) were obtained in a quantitative yield, while [Cu2(Hdmg)4(γ,γ’-dipy)] (3) was registered as a major component in two compounds, [Cu2(Hdmg)4(γ,γ’-dipy)].2H2dmg and [Cu2(Hdmg)4(γ,γ’-dipy)].[Cu(Hdmg)2(γ,γ’-dipy)].(γ,γ’-dipy)2H2dmg (H2dmg = dimethylglyoxime) [3]. In 1 and 2 the metal atom is chelated by H-bonded two acetate anions and one Hniox neutral ligand affording an asymmetric platform, while in 3 two Hdmg- residues formulate the symmetric
platform. The six-coordinate geometry in 1 and 2 is completed by \( \gamma,\gamma' \)-dipy and water molecules, the latter precludes the polymeric chain development in 1 and 2 and is responsible for the association of the binuclear units in the H-bonded layers. In 3 the five-coordinate geometry is completed by \( \gamma,\gamma' \)-dipy, and the binuclear host demonstrates a perfect inclusion either for the initial \( \text{H}_2\text{dmg} \) and \( \gamma,\gamma' \)-dipy molecules or for Cu(II) monomer, \([\text{Cu(Hdmg)}]_2(\gamma,\gamma'\text{-dipy})\). The detailed study of these systems is still in progress.

References