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Three-dimensional Electron Diffraction unveil Single-Crystal-to-Single-Crystal Transformation in Bis-Oxamate Coordination Compounds

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Most physical properties of molecular solids, such as electrical conductivity and magnetism, depend on the organization of molecular entities in the solid state. Therefore, knowledge of the structure is mandatory to establish a structure-property correlation. The most common technique to determine crystal structure is single-crystal X-ray diffraction (SCXRD). SCXRD has been extensively employed to investigate single-crystal-to-single-crystal (SCSC) transformations, wherein structural changes are triggered by external stimuli such as heat or irradiation while maintaining crystal integrity. However, in many cases, growing crystals of sufficient size for SCXRD experiments is not achievable, mainly because of fast reactions and difficult crystallization systems. Therefore, following SCSC transformations becomes a challenge when only sub-micrometric crystals are available. Structure determination by three-dimensional electron diffraction (3D ED) techniques is becoming essential in these cases as it allows collecting single-crystal diffraction data at the nanoscale. 3D ED already proved its efficiency for characterizing diverse materials, including beam sensitive and hydrated materials [1-2]. In this work we report the characterization of three newly synthesized compounds undergoing SCSC transformations with molecular formula $[M_2(L)_2(H_2O)_4].4H_2O$, where (L) is 4,4-sulfonylbis[(phenylamine)bis(oxamate)], M = Zn^{2+} **(1)**, Co^{2+} **(2)**, and $[Zn_{1.96}Co_{0.04}(L)_2(H_2O)_4].4H_2O$ **(3).** Thermogravimetric analysis shows two mass losses, one around 60ºC and one second at about 120ºC attributed to loss of lattice and coordinated water molecules. Because of the small crystal size, the structure was mainly solved using 3D ED data at low temperature, and SCXRD at Sirius Manacá. Interestingly, SCSC transformations can be induced at low and constant temperature in the TEM using the high vacuum environment together with the cryo-plunging method, as we present for compounds **1** and **2.** It leads to a partially desolvated compound **2** (**2-des**), without lattice water molecules, and a fully desolvated compound **1** (**1-des**) where water molecules from the coordination sphere are also removed. Moreover, the crystal structures are highly affected by the SCSC transformation going from a dimer type of structure to a chain-like arrangement. This desolvation can also be achieved by increasing temperature as shown in the PXRD data. In terms of properties, magnetic investigation of **2** and **2-des** showed a typical behavior of anisotropic high spin cobalt(II) complex while solid state dilution of cobalt(II) in a zinc(II) matrix in the complex **3** presents slow relaxation of magnetization under applied magnetic field, characteristic of single molecule magnet behavior.

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