Novel Porous Supramolecular Networks: Synthesis, characterization and Sorption Properties

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3rd Generation compounds of the Kitagawa’s classification\textsuperscript{[1]} are capable to respond to their environment owing their dynamic framework. One of the most powerful strategies used to synthesize these compounds is the molecular building block approach for which; the units are connected via weak coordination bonds and/or intermolecular interactions in self-assembly processes. The peculiarity of our laboratory is to use complexes as building blocks to build materials of this 3rd generation. We focus in this communication to synthesis, structural studies and water sorption of three porous supramolecular networks: Co(amp)\textsubscript{3}Cr(ox)\textsubscript{3}.\textsubscript{6}H\textsubscript{2}O\textsuperscript{[2]} (I) and Cu\textsubscript{2}(amp)\textsubscript{4}ClM(ox)\textsubscript{3}.\textsubscript{6}H\textsubscript{2}O\textsuperscript{[3]} (see figure ), M= Cr\textsuperscript{3+} (II), Fe\textsuperscript{3+}(III), amp=2-picolylamine, ox= oxalate.

Compound I was obtained by mixing a solution of 2-picolylamine and CoCl\textsubscript{2}.6H\textsubscript{2}O with that of K\textsubscript{3}Cr(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}.3H\textsubscript{2}O while compound (II) and (III) were obtained by mixing a solution of 2-picolylamine and CuCl\textsubscript{2}.4H\textsubscript{2}O with that of K\textsubscript{3}M(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}.3H\textsubscript{2}O (M= Fe\textsuperscript{3+}, Cr\textsuperscript{3+}). The dehydrated phases of these compounds were obtained by heating them at the temperature higher than their temperature of dehydration for the powder samples or by using special dehydration device made in “Laboratoire de Cristallographie Resonnance Magnétique et Modélisations (CRM2)” for the single crystal samples. They were then characterized by Thermogravimetric Analysis (TGA) and X-Ray Diffraction (XRD) analysis.

The results showed that the both compounds are composed of layers formed with [Co(amp)\textsubscript{3}]\textsuperscript{3+} (D) and [Cr(ox)\textsubscript{3}]\textsuperscript{3–} (A) ions for (I) and [Cu\textsubscript{2}(amp)\textsubscript{4}Cl]\textsuperscript{3+} (D) with [M(ox)\textsubscript{3}]\textsuperscript{3–} (M= Cr, Fe) (A) ions for compound (II) in repeating DADADA... pattern. Compound (I) has a brown color, crystallizes in the P\textsubscript{2}\textsubscript{1}/n space group and hosts a new dodecameric water cluster between the layers. The dehydrated phase has a green color and remains crystallized in the same space group while during dehydration the volume of the unit cell reduces by about 20 %. This compound completely rehydrates in air in 90 min. The second compound crystallizes in the C\textsubscript{2}/c space group and their layers build architectures with pores directed along the c axis. During its dehydration, the compound remains crystallized but this time in the P\textsubscript{2}\textsubscript{1}/n space group for monohydrated phase and its volume reduces of about 10%. This compound however, does not rehydrate in air but this is done when drops of water are added to the sample. The comportment (hydration and dehydration) of these components is indicative of the fact they can serve as specific adsorbent.

Keywords: Porous Supramolecular Network, crystal to crystal transformation, water adsorption