

Making, Using, Transforming Crystals: A Hydrogen Bonded Material that Reacts with Vapours and Crystals.

Dario Braga Fabrizia Grepioni Lucia Maini Marco Polito Stefano Giaffreda Katia Rubini, Chemistry G. Ciamician, Univ. of Bologna, Via F. Selmi 2, Bologna, BO 40126 ITALY.

The organometallic zwitterion $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]$ reacts as a crystalline solids with both vapours and solids in solvent-free processes. When exposed to hydrated vapours of volatile acids (HCl , CF_3COOH , HBF_4 , HCOOH) or bases (NH_3 , NMe_3 , NH_2Me) the corresponding salts are produced quantitatively. All these reactions are reversible, with the acid or base molecules being easily removed by thermal treatment under vacuum regenerating the starting material. The same compound reacts as a solid with crystalline alkali salts MX ($\text{M} = \text{K}^+$, Rb^+ , Cs^+ , NH_4^+ ; $\text{X} = \text{Cl}^-$, Br^- , I^- , PF_6^- , though not in all permutations of cations and anions). Manual co-grinding of the powdered materials generates supramolecular complex of formula $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]_2 \cdot \text{M}^+\text{X}^-$. In some cases the mechanochemical complexation requires *kneading* of the two solids with a catalytic amount of water. All reactions, whether solid-gas or solid-solid, imply breaking and forming of supramolecular interactions, e.g. rearrangements of the hydrogen bond networks. The method of characterization is based on a combination of powder and single-crystal X-ray diffraction and on the possibility of controlling the crystallization process via *seeding* (see scheme).

