

On the Microporous Nature of Transition Metal Nitroprussides

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Received: December 10, 2002; In Final Form: July 14, 2003

Nitroprussides of divalent transition metals form a family of microporous molecular materials. Their properties in this sense depend on the transition metal cation involved and also on the preparative method, which determine their crystal structures. The stable phases of this family of materials belong to one of the following crystal structures: orthorhombic (*Pnma*) (Mn^{2+} , Fe^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+}), cubic (*Fm3m*) (Co^{2+} and Ni^{2+}), and orthorhombic (*Amm2*) (Cu^{2+}). These materials are stable up to above 160 °C, while their dehydration takes place around 100 °C. On dehydration, *Amm2* copper complex changes into a tetragonal (*I4mm*) phase. The microporous nature of these materials is discussed according to their crystal structure and correlating structural and adsorption data. The accessibility to the pore system was evaluated through adsorption of H_2O , CO_2 , and N_2 . Pores of both orthorhombic and cubic structures are accessible to H_2O and CO_2 in experiments carried out at 23 and 0 °C, respectively; however, they are inaccessible to N_2 at -196 °C. This behavior is discussed as related to the large polarizing power of the nitrosyl (NO) ligand which distorts the local environment of the iron atom and reduces the effective window cross section. The small pores of tetragonal copper nitroprusside were inaccessible to the adsorbates used.

1. Introduction

The studied materials are salts of the pentacyanonitrosylferrate(II) anion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, and of appropriate cations. Since only the N atoms of the CN ligands are able to link to the involved cation, in a tridimensional structure the NO ligand always remains unlinked at the O end. This leads to materials with a system of channels appropriate for small molecule separation.¹ The octahedral coordination sphere of the cation is commonly completed with coordinated water molecules. The microporous framework is usually filled with zeolitic waters which are hydrogen-bonded to the coordinated ones.^{2–9} If both coordinated and zeolitic waters are removed, the available volume of these pores is significantly increased. The formation of an additional system of bigger and interconnected pores depends on the crystal structure adopted by the complex salt, and it is related to the occurrence of structural vacancies of both the complex anion and the cation (discussed below).

Nitroprussides are emerging as novel materials with promising applications in molecular communication and for storage information devices.^{10–12} Their microporous nature opens the possibility of controlling the electronic structure and their physical properties through exchangeable species, e.g., filling their pores with appropriate molecular species, as has been observed in hexacyanides using ionic exchange.¹³

While hexacyanometalates have received certain attention as a prototype of microporous molecular materials,^{1,14–18} the information available on pentacyanonitrosylferrates in this sense is very limited.¹ The crystal structure of nitroprussides has been resolved in the past decade.^{2–9,19,20} This allows an evaluation of their behavior as microporous materials correlating structural

and adsorption data. In this contribution, the microporous nature of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} nitroprussides is discussed from their crystal structure and H_2O , N_2 , and CO_2 adsorption isotherms. That information is complemented with thermal and spectroscopic data.

2. Experimental Section

The studied materials were obtained mixing 0.01 M aqueous solutions of sodium nitroprusside and of a soluble salt of the above-mentioned cations (Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+}). The formed precipitates were then isolated by filtration, followed by successive washing to obtain a filtrate free of the starting anions and cations. The reagents used were analytical grade from Sigma and Merck. The resulting solids were air-dried and then stored in a desiccator over silica for aging. The nature and chemical composition of the obtained samples were established from infrared (IR) spectra, energy-dispersed X-ray spectroscopy (EDS), X-ray diffraction (XRD), thermogravimetry (TG), and Mössbauer data. The materials obtained in this manner were studied as fresh samples (air-dried at room temperature for a week) and after aging for five years.

IR spectra were collected using an FT-IR spectrophotometer (model Equinox 55 from Bruker) and samples diluted in KBr pressed disks. Parallel spectra were obtained from Nujol mulls in order to discard a possible mechano-chemical reaction of the analyte with the KBr matrix.²¹ To obtain IR spectra of dehydrated samples a homemade glass cell with CaF_2 windows was used. EDS spectra were recorded with a Norand analytical unit coupled to a scanning electron microscope (JEOL model 35M). XRD patterns were run with $\text{Cu K}\alpha$ radiation using a HZG4 diffractometer (from Jena). Some XRD patterns were also recorded using synchrotron radiation with $\lambda = 1.7477$ Å (at LNLS, Sao Paulo, Brazil). TG data were obtained using a TA instrument (model 1052) operated in the high-resolution mode and under a dried nitrogen flow. Mössbauer spectra were

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