

STRUCTURAL CHANGES IN INSOLUBLE METAL NITROPRUSSIDES ON AGEING

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Abstract—The processes which take place in freshly precipitated insoluble metal nitroprussides, $M[Fe(CN)_5NO] \cdot xH_2O$ ($M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$ and Cd^{2+}), their crystalline phases and their aged products have been studied by X-ray diffraction, Mossbauer, IR and thermogravimetric techniques. The processes entail a loss of zeolitic water. The stable phases are orthorhombic ($Pnma$) dihydrates ($Mn^{2+}, Fe^{2+}, Cu^{2+}, Cd^{2+}$ and Zn^{2+}) and face-centred cubic ($Fm\bar{3}m$) tetrahydrates for Co^{2+} and Ni^{2+} . Copyright © 1996 Elsevier Science Ltd

Insoluble metal nitroprussides are normally prepared by mixing solutions of soluble nitroprussides and the pertinent cations. These precipitated powder samples have been studied by X-ray diffraction (XRD) and characterized as face-centred cubic (f.c.c.) structures ($Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}$ and Zn^{2+}),¹⁻⁷ while Cd^{2+} has been reported as f.c.c. and orthorhombic³⁻⁷ and the Cu^{2+} salt as cubic and tetragonal.³⁻⁷ Single crystals grown by slow diffusion techniques have been studied by Mullica *et al.*⁸⁻¹² The results for the crystals and for powders are different; Mn^{2+}, Fe^{2+} and Cd^{2+} : monoclinic;^{8,9} Co^{2+} : f.c.c.;¹⁰ Cu^{2+} : orthorhombic;¹¹ and Zn^{2+} : hexagonal.¹² There are also widely divergent results on the degrees of hydration of these insoluble metal nitroprussides (see Table 1).

In a recent paper,¹³ we have reported a study of ferrous nitroprusside as precipitated samples and as slowly grown crystals with different degrees of hydration. Different XRD powder patterns and Mossbauer spectra were observed for this compound when it was studied as fresh precipitate (f.c.c., $Fm\bar{3}m$, dihydrate), slowly grown crystals (monoclinic, $P2_1/n$, trihydrate) and monodehydrated crystals. Recent measurements on aged precipitates show that the cubic (f.c.c., $Fm\bar{3}m$) ferrous nitroprusside undergoes a transformation

to a compound with XRD powder pattern and Mossbauer spectra characteristic of the monodehydrated crystals, which is the stable phase in this system. It is possible that similar transformations caused by loss of zeolitic water can take place in other insoluble metal nitroprussides, which could explain the divergent results in Table 1. To shed light on this problem, we have undertaken a study of $Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$ and Cd^{2+} nitroprussides in their freshly precipitated form, as crystals and as aged products in a dry atmosphere. In this paper we report on the transformations and phases that are produced.

EXPERIMENTAL

Precipitated nitroprusside samples were prepared by slowly mixing dilute aqueous solutions of sodium nitroprusside (NaNP) and the metal chloride, sulfate or nitrate. The precipitates obtained were washed several times with distilled water, filtered and dried under mild conditions in air and in a desiccator with silica gel. Crystals of these metal nitroprussides were grown from the same aqueous solutions using the 'slow diffusion tube' method.¹² These crystals were left for at least a week at room temperature previous to study. The precipitated samples were studied fresh and after 2 years of ageing in air at room temperature. The degree of hydration of all the studied samples was determined

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