

Structural characterization of dimercury(1⁺) pentacyanonitrosylferrate(2⁻), Hg₂[Fe(CN)₅NO]

V. Venegas^{a)}

Escuela Superior de Física y Matemáticas, Departamento de Ciencia de Materiales, Instituto Politécnico Nacional, UP-ALM, Edif. 9, Lindavista 07738, México D.F., México

G. Rueda-Morales

Escuela Superior de Física y Matemáticas, Departamento de Física, Instituto Politécnico Nacional, UP-ALM, Edif. 9, Lindavista 07738, México D.F., México

E. Reguera^{a)}

Escuela Superior de Física y Matemáticas, Departamento de Física, Instituto Politécnico Nacional, UP-ALM, Edif. 9, Lindavista 07738, México D.F., México

F. Caleyó^{a)}

Instituto Nacional de Investigaciones Nucleares, G. Ciencia de Materiales, AP 18-1027, Col. Escandón, México 11801, D.F., México

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The titled compound, Hg₂[Fe(CN)₅NO], was synthesized and studied by X-ray powder diffraction, infrared spectroscopy, Mössbauer spectroscopy, and atomic force microscopy. The results arising from this study indicate that this compound is anhydrous and crystallizes in the *P*222 orthorhombic symmetry. The unit cell parameters were quantified as $a = 16.5905(9)$ Å, $b = 12.3145(8)$ Å, and $c = 8.7576(5)$ Å. The measured and calculated density values are $D_m = 1.149$ g/cm³ and $D_c = 1.145$ g/cm³, respectively, with $Z = 2$. © 2000 International Centre for Diffraction Data. [S0885-7156(99)00603-X]

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I. INTRODUCTION

The most widely studied polycyanides are the prussides (hexacyanides). Within many of these transition metal hexacyanides, channels are formed by systematic [Fe(CN)₆]³⁻ vacancies in the structure and this characteristic can cause the material to take up water and other small molecules. In the case of transition metal nitroprussides (nitrosylpentacyanides), generally there are no vacancies, and channels in these compounds are considerably smaller offering greater selectivity in the separation of very small molecules (Mullica *et al.*, 1990; Mullica *et al.*, 1993).

Extensive structural studies of many nitroprussides have been performed due to the interest in their semipermeable membrane properties and their applications. For alkaline, alkaline-earth and divalent transition metals, extensive structural studies have been reported from single crystal complexes (Gentil *et al.*, 1976; Mullica *et al.*, 1989; Mullica *et al.*, 1990; Reguera *et al.*, 1996). For other metals (e.g., Ag⁺ and Hg⁺) these structural studies are impeded by the poor quality of the crystals obtained during the crystal growth processes. In such cases, the structural characterization must be carried out using powder samples (Venegas *et al.*, 1999). In this work, we present the synthesis of Hg₂[Fe(CN)₅NO] and its characterization by X-ray powder diffraction, infrared spectroscopy (IR), Mössbauer spectroscopy, energy dispersive spectroscopy (EDS), and differential thermal analysis (DTA). Morphological studies, using atomic force microscopy (AFM) have also been carried out.

To our knowledge, a similar study has not been previously reported for this compound.

II. EXPERIMENT

A. Sample preparation

The compound was prepared by a precipitation reaction from an aqueous solution of sodium nitroprusside, Na₂[Fe(CN)₅NO]·2H₂O, and mercurous nitrate, Hg₂(NO₃)₂·2H₂O, in a 1:2 molar ratio. The precipitated powder was washed several times with distilled water and finally dried with acetone. Density was measured at room temperature by the pycnometric method using bromoform.

B. EDS, IR, and Mössbauer spectra

The cation ratio Hg⁺ to Fe²⁺ was determined by EDS, using a Jeol JSM6300 scanning electron microscope. IR absorption spectra of Nujoll mulls of Hg₂[Fe(CN)₅NO] using CaF₂ plates, were recorded at room temperature on a Fourier transform infrared spectrometer from ATTI Matson. Mössbauer spectra were recorded at room temperature and at 20 K with a ⁵⁷Co/Rh source using a Mosstech spectrometer. The values of the Mössbauer parameters, isomer shift (δ), quadrupole splitting (Δ), and line width, were calculated by fitting the Mössbauer spectra with a least squares minimization algorithm and pseudo-Lorentzian line shape. The values of isomer shift are reported relative to sodium nitroprusside.

C. Atomic force microscopy and DTA

Grain size measurements were performed by AFM with a Park Scientific Instruments AFM Microprobe CP, in a

^{a)}Permanent address: Facultad de Física-IMRE, Universidad de La Habana, San Lázaro y L, Vedado 10400, La Habana, Cuba.