Powder X-ray diffraction study of disilver(1^+) pentacyanonitrosylferrate(2^-)

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The crystal structure of disilver(1^+) pentacyanonitrosylferrate(2^-) was studied by X-ray powder diffraction. IR and Mössbauer spectroscopies, thermogravimetric analysis and density measurements were also carried out. This compound is monoclinic, and its lattice parameters are: $a=10.986(3)$ Å, $b=6.4080(10)$ Å, $c=7.4545(19)$ Å, $\alpha=\delta=90°$, $\beta=102.54°(2)$. © *1999 International Centre for Diffraction Data.* [S0885-7156(98)00404-7]

I. INTRODUCTION

Metal pentacyanonitrosylferrates, commonly known as nitroprussides, constitute a well-studied family of coordination complexes. Alkali metal nitroprussides crystallize in noncubic space groups (monoclinic and orthorhombic crystal systems) (Bottomley and White, 1979; Amalvy *et al.*, 1986; Soria *et al.*, 1996). Divalent transition metal nitroprussides have also been well characterized from the structural point of view (Gentil *et al.*, 1976; Mullica *et al.*, 1989; Mullica *et al.*, 1990; Reguera *et al.*, 1996). Silver nitroprusside, which is usually used as an intermediate during the preparation of other members of this family of compounds, has not been previously studied. In this communication, we report the synthesis and characterization by X-ray diffraction and other techniques of disilver(1^+) pentacyanonitrosylferrate(2^-), whose formula is $Ag_2[Fe(CN)_5NO]$. A space group for this compound is also suggested.

II. EXPERIMENT

Sample preparation: A silver nitroprusside sample was prepared by slowly mixing dilute aqueous solutions of sodium nitroprusside and silver nitrate (Reguera *et al.*, 1996). The precipitate was washed several times with distilled water and dried with acetone. Density was determined by the pycnometric method using bromoform as fluid at room temperature (27 °C). IR spectra were taken using a Fourier transform infrared spectrometer (ATTI Matson, Genesis Series) in Nujoll mulls using CaF_2 plates.

Thermogravimetric analysis was performed with Mettler TA4000 System at heating rate of 5 °C/min in air. The Mössbauer spectra were recorded at room temperature and at 20 K with a ^{57}Co/Rh source using a constant acceleration spectrometer (MS1101, from Mosstech) in the transmission mode. The Ag to Fe ratio in the studied sample was established through X-ray fluorescence spectrometry using a JEOL microprobe system.

III. RESULT AND DISCUSSION

A. Sample characterization

The studied compounds is obtained as a very fine pale pink powder. Its nature as a pentacyanonitrosylferrate complex was established by IR spectroscopy where the characteristic bands of the nitroprusside anion, CN stretching at 2100 cm^{-1} and NO stretching at 1900 cm^{-1}, are observed (see Figure 1). Chemical analysis indicated a 2:1 silver to iron ratio. IR and TGA measurements show that this compound is anhydrous. In consequence, its chemical formula is $Ag_2[Fe(CN)_5NO]$. The ^{57}Fe Mössbauer spectrum of the studied compound is a single quadrupole doublet, indicating the existence of only one structural site for iron. The Mössbauer parameters at room temperature, $\delta=0.008(2)$ mm/s (relative to sodium nitroprusside) and $\Delta=1.779(4)$ mm/s are characteristic of low spin iron(II). These values of isomer shift (δ) and quadrupole splitting (Δ) are very similar to those observed for other metal nitroprussides (Reguera *et al.*, 1992), showing that the strongly bonded CN and NO ligands effectively shield iron(II) from changes in the outer environment. No magnetic ordering was observed through the Mössbauer spectrum, at least up to 12 K.

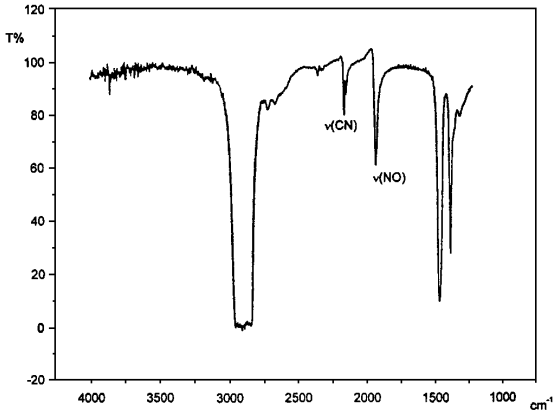

Figure 1. Room temperature IR spectrum of disilver(1^+) pentacyanonitrosylferrate(2^-).

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