

Mössbauer Study of the Valency Effects in Copper Ferrocyanides

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Abstract Mössbauer spectra of ferrocyanides $\text{Cu}_2^{2+}|\text{Fe}^{\text{II}}(\text{CN})_6|^{4-}$ and $\text{Cu}_4^+|\text{Fe}^{\text{II}}(\text{CN})_6|^{4-}$ have been studied. No quadrupole interaction was observed to exist and the isomer shift for $\text{Cu}_2^{2+}|\text{Fe}^{\text{II}}(\text{CN})_6|^{4-}$ was found to be more negative suggesting for this compound an increase in the back-donation from the metal d_{π} -orbitals to the empty p_{π} ligand orbitals, decreasing the d -electron density on the iron ion. These results are supported by infrared spectroscopy.

1. INTRODUCTION

The ferrocyanides are diamagnetic complexes having six cyanide ligands, $(\text{CN})^-$, forming an octahedron around the iron ion. Due to the presence of strong ligand fields at the iron site ($10Dq \approx 35000 \text{ cm}^{-1}$), all the ferrocyanides ions are covalent complexes. In these complexes the cyano ligands remain linked to the iron by σ bonds but partial $\pi(d_{\pi}-p_{\pi})$ bonding has been suggested due to back-donation of electrons from the filled metal d_{π} -orbitals to the empty ligand p_{π} -orbitals¹.

Under influence of a crystal field with octahedral symmetry (O_h) the five d orbitals of iron split into a doubly degenerate e_g level and a threefold degenerate t_{2g} level of lower energy. In a low spin case such as ferrocyanides, the six d -electrons are in the t_{2g} orbitals with their spins paired. Since t_{2g}^6 possesses cubic symmetry there is no contribution from the valence electrons to the electric field gradient at the Fe nuclei. The cubic symmetry of the octahedral disposition of the six ligands around the iron atom also does not give any contribution to the electric field gradient. This explains the reason why only a single Mössbauer absorption peak appears in spin-paired complexes like ferrocyanides.

The Mössbauer effect results are analysed by studying the

changes in the behaviour of the isomer shift δ , which is a measure of the total s -electron density at the iron nuclei. Assuming a uniform charge distribution over the nuclear volume, the isomer shift is given by²

$$\delta = A |\psi_s(0)|^2 + B$$

where A is a constant depending on nuclear parameters, B a constant depending on the source properties and $|\psi_s(0)|^2$ is the s -electron charge density at the iron nuclei.

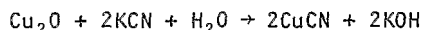
$|\psi_s(0)|^2$ contains contributions from all the occupied orbitals which participate in the chemical bonding. Other electrons with p , d and f -character do not have a direct interaction within the nucleus but, nevertheless, they have a significant indirect effect on δ by the shielding of the s -electrons. In the case of the iron ion the shielding is due to the presence of d -electrons. As the $3d$ -electron density increases, the s -electrons density at the nucleus decreases and vice-versa. Therefore, the s -electron density is influenced by the presence of the ligand (CN) because of its ability to act as a σ -donor as well as a n -acceptor.

2. EXPERIMENTS

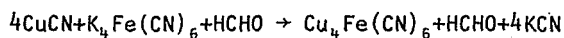
a) Preparation of Samples

I) Cupric ferrocyanides, $\text{Cu}_2^{2+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. The method of preparation of this compound is similar to that described in the literature³. Twenty grams of CuSO_4 are mixed with five grams of $\text{K}_4\text{Fe}(\text{CN})_6$ obtaining a precipitate, $\text{Cu}_2\text{Fe}(\text{CN})_6$, which is washed with distilled water several times in order to eliminate excess of the reagents and after that the precipitate is filtered and dried.

II) Cuprous ferrocyanides, $\text{Cu}_4^+[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. This compound is prepared from CuCN obtained by the following reaction



The solution of copper cyanide after filtration is mixed with a solution of potassium ferrocyanide and formaldehyde precipitating the cuprous ferrocyanide according to the reaction



The white precipitate is then filtered and dried in vacuum to avoid decomposition.

The compound remains stable (white) while there is an excess of CuCN. If washed with water it first becomes very light red, then it changes to light brown and finally to dark brown; these three phases characteristic of the decomposition of the compound⁴. The composition of this compound was checked by X-ray fluorescence in the Van der Graaf accelerator.

b) Measurements

Mössbauer spectra were obtained with a conventional spectrometer operated in the constant acceleration triangular wave mode with a source of ⁵⁷Co in Rh. The spectra were analysed by a least-square method; the effective thickness was always less than 5 mg Fe/cm².

Infrared spectra were obtained with a Perkin-Elmer Model 467 spectrophotometer.

X-ray diffraction data were obtained with a Siemens, model Kristalloflex 2, diffractometer. The X-ray tube was a CrK_α source with a vanadium filter, of wavelength 2.290920 Å.

3. RESULTS

The crystal structure of the compound $\text{Cu}_2^{2+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ has been reported in the literature³. It has a face centered cubic structure, belonging to the spatial group $O_h^5 - F_{m\bar{3}m}$ with Fe ions at the corners and centers of the faces of the unitary cell whereas the Cu ions occupy the centers of the edges, the center of the unit cell and the centers of internal octants. The Fe ions are bonded to the Cu ions at the edges of the unit cell through cyanide bridges forming a polymer chain of the Prussian blue type. In this kind of compounds the bonds of the Cu ions in the centers of edges are predominantly of covalent character⁵.

However, it seems there are no X-rays data in the literature referring to the compound $\text{Cu}_4^+[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. Due to its instability we

have obtained X-ray spectra of it for each stage of its decomposition. The results indicate that its crystalline structure remains the same when it passes from white to rose to brown, showing changes only in the intensities of the lines, suggesting that the Fe, Cu and CN keep the same relative positions within the crystalline lattice, maintaining the same volume. Our diffraction spectra indicate that the structure is a cubic primitive reticular with lattice parameter $a = (12.21 \pm 0.01) \text{ \AA}$.

Our Mössbauer effect results, fig. 1a, b, c and table 1 support the above X-ray information confirming that the substance remains basically the same and also discard the possibility of ferricyanide formation since all ferricyanides present Mossbauer spectra with quadrupole interaction⁶. One possible explanation is a change in the state of oxidation of the Cu^+ in interstitial sites.

Table 1 - Mössbauer parameters of cuprous and cupric ferrocyanides.

Compound	Isomer Shift (mm/s)	Line widths (mm/s)
$\text{Cu}_4^+ \text{Fe}^{\text{II}}(\text{CN})_6 ^{4-}$ (white)	$-(0.167 \pm 0.002)$	(0.280 ± 0.006)
$\text{Cu}_4^+ \text{Fe}^{\text{II}}(\text{CN})_6 ^{4-}$ (light red)	$-(0.169 \pm 0.001)$	(0.267 ± 0.004)
$\text{Cu}_4^+ \text{Fe}^{\text{II}}(\text{CN})_6 ^{4-}$ (brown)	$-(0.166 \pm 0.001)$	(0.247 ± 0.002)
$\text{Cu}_2^{2+} \text{Fe}^{\text{II}}(\text{CN})_6 ^{4-} \cdot 10\text{H}_2\text{O}$	$-(0.207 \pm 0.002)$	(0.317 ± 0.006)

These experimental results also indicate that the isomer shift for the $\text{Cu}_2^{2+} | \text{Fe}^{\text{II}}(\text{CN})_6 |^{4-}$ is more negative than for the $\text{Cu}_4^+ | \text{Fe}^{\text{II}}(\text{CN})_6 |^{4-}$.

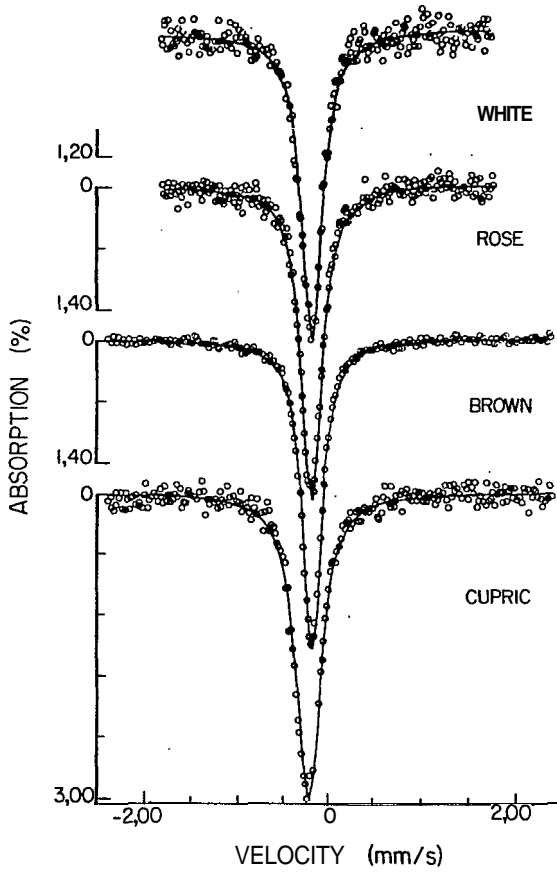


Fig. 1 - The room temperature Mössbauer spectra of $\text{Cu}_4^+ \text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ at several stages of the oxidizing process as compared with the one of the $\text{Cu}_2^{2+} \text{Fe}^{\text{II}}(\text{CN})_6^{2-}$. a) The compound freshly prepared (white colour) measured under vacuum. b) The same compound after some exposition to the atmosphere (rose colored) and measured under vacuum. c) The same compound after the completion of the oxidizing process (brown colored). d) The $\text{Cu}_2^{2+} \text{Fe}^{\text{II}}(\text{CN})_6^{2-}$ spectrum.

As the Cu^+ ion is less electronegative than the Cu^{2+} ion and the electronegativity of $(\text{CN})^-$ is high, it can be expected that the covalent character of the $(\text{CN})^- - \text{Cu}^{2+}$ binding should be bigger than the one of $(\text{CN})^- - \text{Cu}^+$. Due to the fact that the $(\text{CN})^-$ radicals are the only donors of negative charges to neutralize the positive charges on the metal ions, there will be a greater transfer of charges of the σ -type from $(\text{CN})^-$ to Cu^{2+} than to Cu^+ . As a consequence the $(\text{CN})^-$ ions in $[\text{Cu}_2^{2+} \text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ become more electropositive and, therefore, more receptive to back-donation from metal d_{π} (d_{xy} , d_{xz} , d_{yz}) orbitals than it does in $[\text{Cu}_4^+ \text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. This increased back-donation from the metal d -orbitals to the empty p_{π} ligand causes a decrease of the d -electron density on the metal, producing a decrease in the electronic repulsion of the s -electrons of iron, consequently increasing the s -electron density inside the iron nucleus and making the isomer shift more negative than in $[\text{Cu}_4^+ \text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$.

Orgel and Griffith⁷ have shown that carbon-metal bonding will tend to increase the C-N force constant, $K_{\text{C-N}}$, by drawing negative charge from the carbon atom and, as a consequence, the CN stretching frequency will increase and the M-C (M \equiv metal) stretching frequency will decrease. The back-donation from metal d_{π} -electrons to empty ligand p_{π} orbitals will tend to decrease $K_{\text{C-N}}$ and therefore, an opposite effect will occur.

Comparing the results obtained with these compounds using infrared spectroscopy, fig. 2 and table 2, we observe an appreciable decrease in the M-C stretching frequency going from $[\text{Cu}_2^{2+} \text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ to $[\text{Cu}_4^+ \text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. This leads us to conclude that there exists, for the Cu^{2+} case, a back-donation increase in the Fe-CN region confirming the result obtained by Mössbauer spectroscopy.

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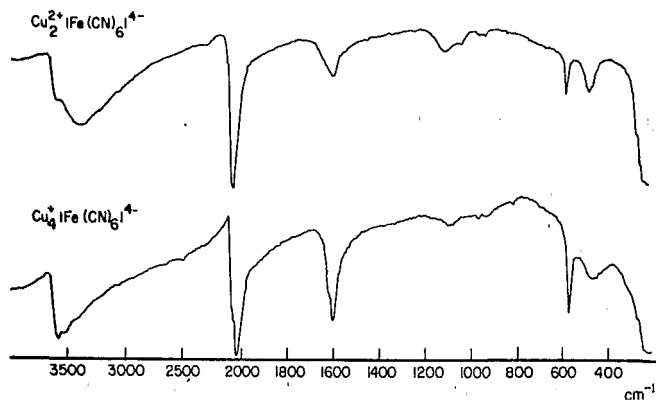


Fig.2 - The infrared spectra of $\text{Cu}^{2+}|\text{Fe}^{\text{II}}(\text{CN})_6|^{4-}$ and $\text{Cu}^+|\text{Fe}^{\text{II}}(\text{CN})_6|^{4-}$.

Table 2 - Infrared parameters of cupric and cuprous ferrocyanides.

Compound	C-N frequency	Fe-CN frequency
$\text{Cu}_2^{2+} \text{Fe}^{\text{II}}(\text{CN})_6 ^{4-}$	2085 cm^{-1}	585 cm^{-1}
$\text{Cu}_4^+ \text{Fe}^{\text{II}}(\text{CN})_6 ^{4-}$	2040 cm^{-1} 2070 cm^{-1} 2085 cm^{-1}	575 cm^{-1}

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Resumo

Foram estudados os espectros Mössbauer dos ferrosianetos $\text{Cu}_2^{2+}|\text{Fe}^{\text{II}}(\text{CN})_6|^{4-}$ e $\text{Cu}^+|\text{Fe}^{\text{II}}(\text{CN})_6|^{4-}$. Não obtivemos interação quadripolar e o deslocamento isomérico é mais negativo no $\text{Cu}_2^{2+}|\text{Fe}^{\text{II}}(\text{CN})_6|^{4-}$ sugerindo um aumento na *back donation* dos orbitais *d*, do metal para os orbitais vazios p_π dos ligantes diminuindo a densidade de elétrons *d* no íon ferro. A espectroscopia infravermelho confirma estes resultados.