

STRUCTURE INVESTIGATION ON THE HEXACYANOFERRATE-(II) AND -(III) COMPLEXES

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It has been well established by single crystal diffraction investigations that the $\{\text{Fe}(\text{CN})_6\}^{n-}$ complexes ($n=3, 4$) form regular octahedra with the iron in the centre and linear Fe-C-N chains extending to the corners. The iron K-edge fine-structures of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ shown in fig.1 indicate that the chemical states of the Fe in the two complexes are similar and cannot be viewed as Fe^{3+} and Fe^{2+} ions, respectively, surrounded by six CN^- groups.

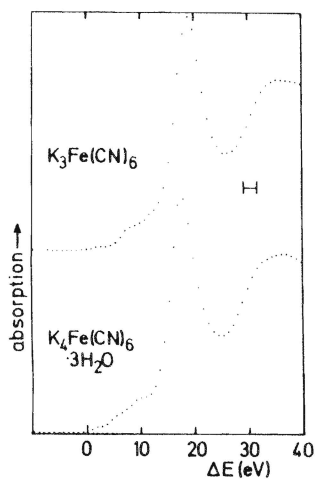


Fig.1 Fe K-edge fine structure. The zero point of the energy scales is at 7111 ± 1.5 eV. The bar represents the energy resolution (fwhm).

Our near edge data agree very well with those of Obashi¹. The K-edge structures can be interpreted with molecular orbital calculations¹, which yield one more binding electron for the Fe(II) complex. This is

in agreement with the higher chemical stability of the Fe(II) complex. The results of single crystal diffraction data^{2,4,5} of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ however yield a longer Fe-C-bond length for the Fe(II) complex (see table 1 and fig. 1).

distance R_D		compound	ref. no.
Fe - C	Fe - N		
1.980	3.009	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	2
1.89	3.04	$\text{H}_4\text{Fe}(\text{CN})_6$	3
1.903	3.037	$\text{K}_3\text{Fe}(\text{CN})_6$	4
1.922	3.090	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{D}_2\text{O}$	5
1.926		$\text{Cs}_2\text{LiFe}(\text{CN})_6$	6
1.90		$\text{Cs}_2\text{MgFe}(\text{CN})_6$	7
1.93	3.08	$\text{Cs}_2\text{KFe}(\text{CN})_6$	8
1.88		$\text{Cs}_2\text{BaFe}(\text{CN})_6$	9
1.90	3.05	$(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 1.5 \text{H}_2\text{O}$	10
1.90	3.05	$\text{LaFe}(\text{CN})_6 \cdot 4 \text{H}_2\text{O}$	11
2.045	—	Ferrocene	12

Table 1 Distance values in Å for $\text{Fe}(\text{CN})_6$ -groups in different compounds in the literature.

If, on the other hand, one takes into consideration diffraction data for other samples^{3, 6-11} containing hexacyanoferrate groups, ignoring the possible influence of different cations on the Fe-C bond length, one finds a trend to the expected shorter Fe-C distance in the Fe(II)-complexes (see fig. 2 and table 1).

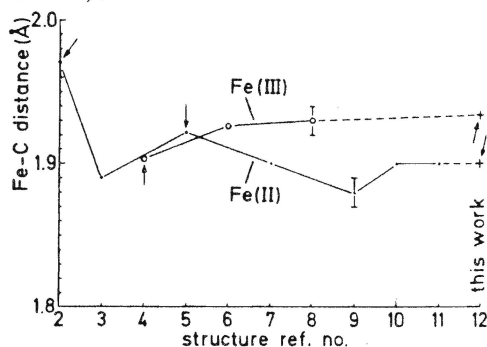


Fig.2 Fe-C distances for $\text{K}_3\text{Fe}(\text{CN})_6$ (↑), $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (×) and other compounds out of the literature (chronological, see table 1) and from EXAFS (crosses are R_E^1 -values from table 2).

The EXAFS measurements of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ were done on powder samples at room temperature at the Deutsches Elektronen-Synchrotron DESY. As a reference material for the Fe-C-phase shift we used ferrocene, which has ten equal Fe-C bonds (see table 1).

Fourier filtering¹³ of $\chi(k) = \frac{1}{k} \sum A_j(k) \sin \arg_j(k)$ yields amplitude $A_j(k)$ and $\arg_j(k) = 2kR_j + \Phi_j(k)$ for the first two shells ($j = 1, 2$). R_j is the interatomic distance and $\Phi_j(k)$ the phase shift. $\chi(k)$ is the normalised EXAFS and k is the photoelectron wavenumber. The absolute values of the Fourier transforms $F(r)$ of $\chi(k) \cdot k^3 \cdot w(k)$ are shown in fig. 3. Due to the choice of the window function $w(k)$ and the k-scale zero energy ($E_0 = 7106$ eV, i.e. 5 eV below the K-edge of metallic Fe) the C and N peaks are well separated. The window function is a Gaussian in k with 10% amplitude at $k_{\min} = 2.7 \text{ \AA}^{-1}$ and $k_{\max} = 14.3 \text{ \AA}^{-1}$ and zero outside this k-range. The peak regions of $|F(r)|$ were retransformed separately with square window functions, yielding $A_j(k)$ and $\arg_j(k)$. One can now calculate the Fe-C bond length differences ΔR between different samples for each k-value, i.e. as a function of k , by assuming

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nearly equal Fe-C phase shifts $\Phi_j(k)$ allowing only for small differences (± 3 eV) in the E_0 values:

$$R(k) = (\arg_1 - \arg_2) / 2k$$

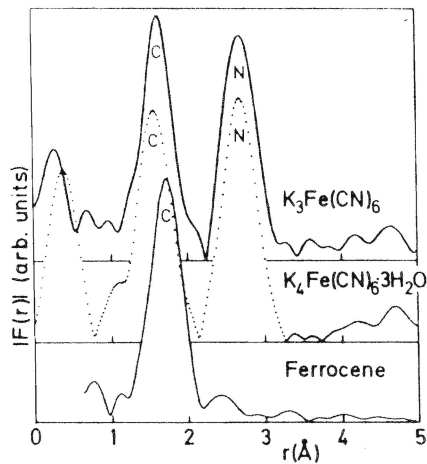


Fig. 3 Absolute values of the Fourier transforms.

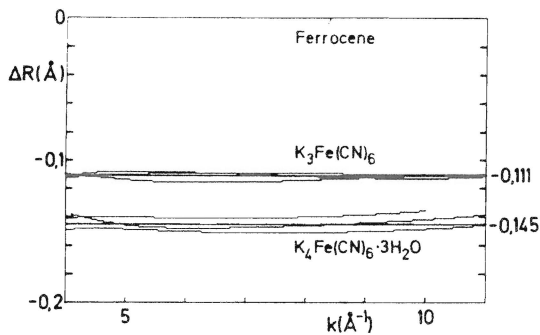


Fig. 4 Relative determination of Fe-C bond lengths

The results for a number of measurements are shown in fig. 4. They clearly show the longer Fe-C bond ($\Delta R = 0.034 \text{ \AA}$) in the Fe(III)-complex. The resulting average ΔR values seem to be accurate to $\pm 0.005 \text{ \AA}$. By assuming $R = 2.045 \text{ \AA}$ for Fe-C in ferrocene¹², one gets the values R_E^I in table 2 for the hexacyanoferrates.

	$K_3Fe(CN)_6$		$K_4Fe(CN)_6 \cdot 3H_2O$	
	Fe-C	Fe-N	Fe-C	Fe-N
R_E^I (\AA)	1.934		1.900	
R_E^E (\AA)	1.947		1.908	
σ^2 (\AA^2)	0.0013	0.0025	0.0025	0.0014
c	0.583	1.415	0.775	1.296

Table 2 EXAFS results, R_E^I with ferrocene phase shift, R_E^E with phase shift of Teo and Lee¹⁴; σ^2 and c with amplitudes of Teo and Lee.

If the phase shift calculated by Teo and Lee is used unphysical k-scale zero energies of 25 to 30 eV above the K-edge of metallic Fe have to be used and

still the $R(k)$ vary strongly with k (see fig. 5). These data yield the R_E values in table 2. Here one has to take into account errors of $\pm 0.02 \text{ \AA}$.

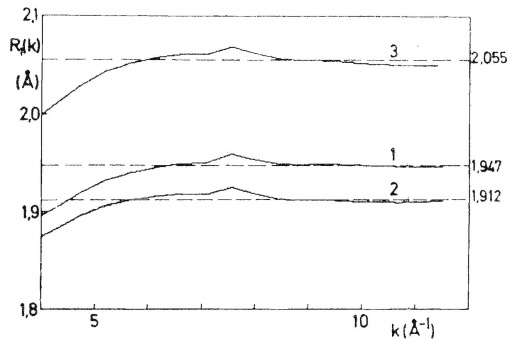


Fig. 5 Fe-C distances with calculated phase shifts¹⁴. The dashed lines are the R_E values in table 2

For the N-neighbours, which are shadowed by the C-atoms, we find a deviation of the experimental phase shifts from the usual values in both complexes. This can be shown in the following way. In the single scattering case one would find:

$$\Delta\Phi(k) = \arg_N(k) - \arg_C(k) - 2k(R_N - R_C) = \alpha_N(k) - \alpha_C(k)$$

where α_C and α_N are the backscattering phase shifts of C and N. Their difference is small and nearly constant as C and N have neighbouring atomic number (dots in fig. 6, after ref.14).

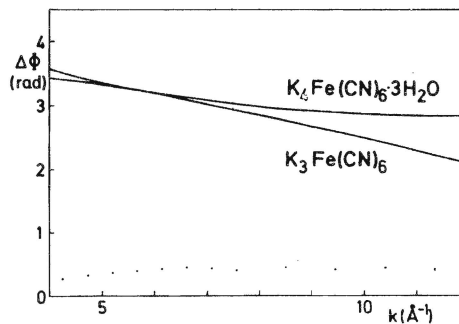


Fig. 6 See text.

Fig. 6 shows the experimental phase difference $\Delta\Phi(k)$ for $R_N - R_C = 1.15 \text{ \AA}$ (assumed here for both complexes). The deviation from $\alpha_N - \alpha_C$ is approximately π rad and decreases slowly with k .

Comparison of the $\arg_N(k)$ of the two hexacyanoferrates yields a distance difference $R_N(\text{Fe(III)}) - R_N(\text{Fe(II)}) = 0.023 \pm 0.008 \text{ \AA}$. This value is only valid under the additional assumption of transferability of also the multiple scattering phase shift components.

The amplitude functions $A(k)$ of the two hexacyanoferrates can be described in the following form:

$$A(k) = cNR^{-2} \cdot |f_T(k)| \cdot \exp(-2k^2\sigma^2)$$

where $|f_T(k)|$ is the calculated¹⁴ backscattering amplitude, c is a constant amplitude reduction factor, N is the coordination number (six in this case), and σ^2 is the mean square relative displacement of the atoms. This is demonstrated by the plot of the function

$$L(k) = \ln\{A(k) / (|f_T(k)| \cdot 6/R^2)\}$$

against k^2 shown in fig. 7.

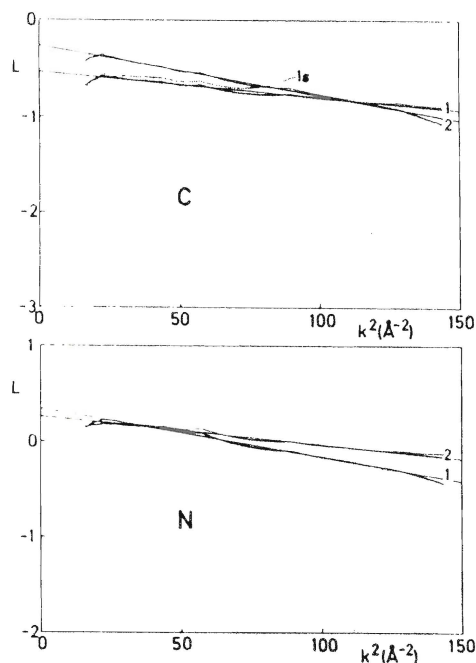


Fig. 7 Reduced amplitudes $L(k)$ for $K_3Fe(CN)_6$ (1) and $K_4Fe(CN)_6 \cdot 3H_2O$ (2). The ^{13}C -amplitude of an aqueous solution of (1) is included (1s), to show that the homogeneity of the powder samples is sufficient.

The straight lines in the figure have slopes $2\sigma^2$ and $L(0) = \ln(c)$. For the C-shells both σ^2 and c are in the usual range (see table 2). The N-shells show reasonable σ^2 values whereas the values for c are higher than usual by a factor of about 2 due to the "shadowing" by the C atoms.

These two effects, the approximately constant amplitude enhancement by a factor of ca. 2 and the additional phase shift of ca. π rad, seem to be typical for multiple scattering in a linear chain, as they are also observed, although less clearly, in the fourth shell of fcc-metals.

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