# The Fe-57 Mössbauer Effect in Ferrocyanide Derivatives

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The measurement of the nuclear gamma-ray resonance absorption, the so-called Mössbauer effect, has been applied to the study of the electronic environment in various compounds, because the position and structure of resonance lines depend on the state of the chemical bonding of the atom. It has been reported in potassium ferrocyanide that the cyano groups are combined with the central iron atom by $\sigma$ and $\pi$ bonding.[1] The purpose of the present work is to study the effect of outer sphere ions or groups on the Mössbauer spectrum in the ferrocyanide derivatives, and to explain the lower value of the isomer shift of the ferrocyanide ion in Prussian blue and Turnbull's blue than that in potassium ferrocyanide.

Four ferrocyanide derivatives, $H_4[Fe(CN)_6]$,[2] $H_4[Fe(CN)_6](C_2H_5)_2O$,[2] $[Fe(CN)_2(CNCH_3)_4]$[3] and $[Fe(CNCH_3)_6](HSO_4)_2 3H_2O$[4], were prepared by conventional methods. The resonance absorption spectra of 14.4 keV. gamma rays in these compounds and potassium ferrocyanide, Prussian blue and Turnbull's blue were measured at room temperature with a source of cobalt-57 diffused into copper foil. The sample was moved at a constant velocity by means of a mechanical drive. Both the isomer shift and the quadrupole splitting were determined from the gamma ray resonance spectrum. The infrared absorption spectra in the KBr disk of these compounds were also measured.

Table I shows that the isomer shifts of $[Fe(CNCH_3)_6](HSO_4)_2 3H_2O$, $[Fe(CN)_2(CNCH_3)_4]$,

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[1] L. M. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962); L. R. Walker, G. K. Wertheim and V. Jaccarino, *Phys. Rev. Letters*, **6**, 233 (1961); E. Fluck, W. Kerller and W. Neuwirth, *Angew. Chem.*, **75**, 461 (1963).

[2] J. Liebig, *Ann.*, **87**, 127 (1853); K. C. Browning, *J. Chem. Soc.*, **77**, 1233 (1900).

[3] J. Meyer, H. Domann, W. Müller, *Z. anorg. u. allgem. Chem.*, **230**, 336 (1937).

[4] E. G. I. Hartly, *J. Chem. Soc.*, **97**, 1066, 1725 (1910).

TABLE I. RESULTS FROM THE MÖSSBAUER SPECTRA AND INFRARED SPECTRA

| Compound | Isomer shift relative to stainless steel mm./sec. | Quadrupole splitting mm./sec. | Wave number cm$^{-1}$ |
|---|---|---|---|
| $K_4[Fe(CN)_6]3H_2O$ | $+0.03\pm0.01$ | $0.00\pm0.01$ | 2050 |
| $H_4[Fe(CN)_6]$ | $-0.01\pm0.01$ | $0.00\pm0.01$ | 2090<br>2110 |
| $H_4[Fe(CN)_6](C_2H_5)_2O$ | $-0.01\pm0.01$ | $0.00\pm0.01$ | 2090<br>2110 |
| $[Fe(CN)_2(CNCH_3)_4]$ | $-0.08\pm0.01$ | $0.00\pm0.01$ | 2090<br>2200 |
| $[Fe(CNCH_3)_6[(HSO_4)_2 3H_2O$ | $-0.08\pm0.01$ | $0.00\pm0.01$ | 2230 |
| Prussian blue and Turnbull's blue | $-0.05\pm0.03$<br>$+0.55\pm0.03$ | $0.00\pm0.02$<br>$0.50\pm0.03$ | 2075 |

$H_4[Fe(CN_6]$ and $H_4[Fe(CN)_6](C_2H_5)_2O$ are lower than that of $K_4[Fe(CN)_6]3H_2O$, and that the wave numbers of the C-N stretching vibration increase in accordance with the decrease in the isomer shift. The results suggest that the $d\varepsilon$ electrons of the iron atom are attracted through the cyano group by the methyl groups, and that then the total $s$ electron density on the iron nucleus increases. The fact that the isomer shifts of the spin-paired iron atom in Prussian blue and Turnbull's blue are lower than that in potassium ferrocyanide may be explained by assuming some co-ordination bonding between nitrogen atoms and spin-free iron(III) ions.

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