A Nuclear Gamma-ray Resonance Study of Several $[FeX_6]$-type Ferrous Complexes

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The study of the nuclear γ-ray resonance (the Mössbauer effect) has recently been extended to metal compounds, especially those of iron and tin.[1] A number of iron compounds have so far been investigated. However, there have been few studies of the effect of the nature of the ligand on the spectrum of various $[FeX_6]$-type ferrous complexes. The purpose of the present work is to clarify the features of the chemical bond between the central iron atom and the ligand in the complexes.

The potassium calcium hexanitroferrate(II)[2] and potassium hexathiocyanatoferrate(II)[3] used as absorbers were synthesized by conventional methods. Commercial analytical-grade potassium hexacyanoferrate(II) and hexaquoferrous ammonium sulfate (Mohr's salt) were also used as absorbers without further purification. The resonance absorption spectra of 14.4 keV. γ-rays in these compounds were measured at room temperature with a source of ^{57}Co diffused into copper foil. The sample was moved at a constant velocity by means of a mechanical drive.

Figures 1 and 2 illustrate the nuclear γ-ray resonance spectra of potassium hexacyanoferrate(II) and Mohr's salt, and of potassium calcium hexanitroferrate(II) and potassium hexathiocyanatoferrate(II), respectively. The latter two compounds show the same spectra as those reported by previous investigators.[4] The results suggest that the isomer shifts of the hexa-coordinated ferrous complexes increas in positive value when the π bonding character between the ligands and the iron atoms decreases in the sequence of:

$$CNCH_3{}^* > CN^- > NO_2{}^- > SCN^- > OH_2$$

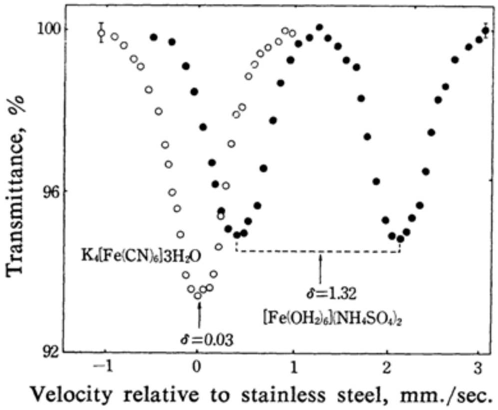

Fig. 1. Nuclear γ-ray resonance absorption spectra of $K_4[Fe(CN)_6]3H_2O$ and $[Fe(OH_2)_6](NH_4SO_4)_2$.

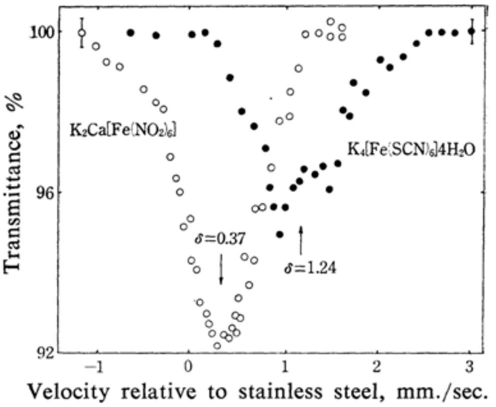

Fig. 2. Nuclear γ-ray resonance absorption spectra of $K_2Ca[Fe(NO_2)_6]$ and $K_4[Fe(SCN)_6]\cdot 4H_2O$.

The little larger value of the isomer shift in hexanitroferrate(II) than that in hexacyanoferrate(II) suggests that the bond between the nitro ligands and the iron atoms still has a considerable π bonding character, whereas the much larger isomer shift in hexathiocyanatoferrate(II) shows a poor π bonding character, probably because of lesser availability of d orbitals in sulfur atoms.

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* The Mössbauer spectrum of $[Fe^{II}(CNCH_3)_6](HSO_4)_2$ was reported previously.[5] The value of the isomer shift was −0.08 mm./sec. relative to stainless steel at room temperature.

[5] H. Sano, This Bulletin, **38**, 684 (1965).