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AN ANOMALISM OF THE ELECTRIC FIELD GRADIENT AROUND IRON NUCLEUS OBSERVED IN POLYCHLORINATED FERROCENES

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An anomalously large value of the quadrupole splitting has been observed in the ^{57}Fe Mössbauer resonance spectra of octa- and decachloroferrocenes and discussed in terms of electronic and steric influence of the substituent on the Mössbauer parameters.

An early ^{57}Fe Mössbauer spectroscopic study of ferrocene and related compounds showed that the bonding of the iron atom is not affected by ring substitution.$^{1)}$ We have, however, observed an anomalism in the quadrupole splitting (qs) value induced by ring substitution. In the present study, an accumulative effect of an electronegative substituent on the Mössbauer parameters has been studied systematically by using a series of polychlorinated ferrocenes, $C_{10}H_{10-n}Cl_nFe$ with n = 1, 2, 4, 6, 8, 10, which were prepared according to the method previously reported$^{2)}$ and purified by means of liquid chromatography on alumina. Since structures of these compounds have already been established,$^{2)}$ we identified them on the basis of their elemental analyses. The Mössbauer spectra were measured against a ^{57}Co(Pt) source moving in a constant acceleration mode at room temperature. The velocity scale (mm/sec) was normalized with respect to metallic iron. The quadrupole splitting and isomer shift (is) values in unit of mm/sec have an estimated error of not more than 0.02 mm/sec.

Successive ring substitution, as shown in Figure 1, does not significantly affect the value of the isomer shift. On the other hand, the qs value changes discontinuously from 2.51 mm/sec for hexachloroferrocene to 2.74 mm/sec for octachloroferrocene, as illustrated in Figure 2, the latter of which is one of the highest value observed in ferrocene derivatives, while the qs value changes only slightly with increasing number of the substituent in the remaining compounds. It is known that e_{2g} electrons make a predominant contribution to the electric field gradient (efg) around the iron nucleus of ferrocene and the sign of the efg tensor is positive.$^{3)}$ The anomalously large qs values observed in octa- and decachloroferrocene can not exclusively be ascribed to an accumulative electronic effect of the substituents, because the effect of each substituent is too small to explain the large change in the qs.

Replacement of ring-hydrogen by chlorine is expected to increase considerably the internal steric strain. Such steric strain could be released by rotation or tilt of cyclopentadienyl rings unless more than six ring-hydrogens are replaced by

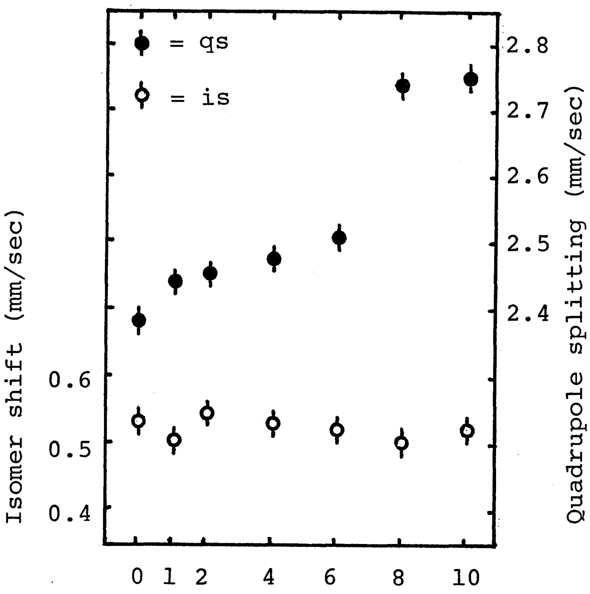

Figure 1. Variation of isomer shift and quadrupole splitting with the number of substituent (n) in the compound, $C_{10}H_{10-n}Cl_nFe$.

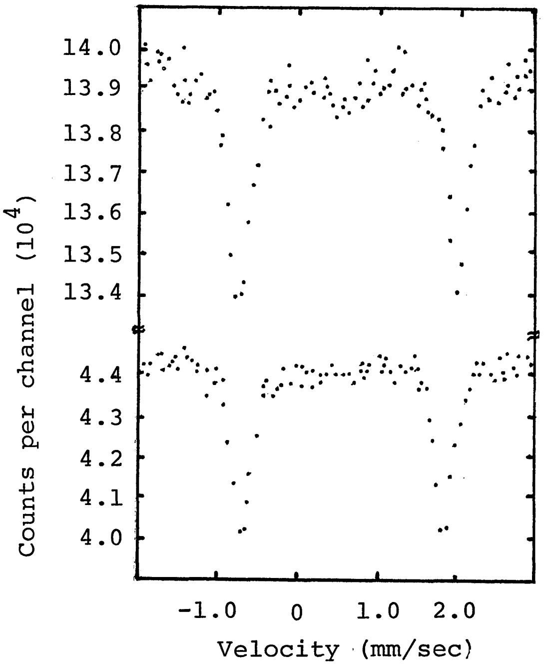

Figure 2. The Mössbauer spectra of octachloroferrocene (top) and hexachloroferrocene (bottom) at 78 K.

chlorines. Tetramehtylethyleneferrocene, in which cyclopentadienyl rings are tightly fixed and mutually inclined, has Mössbauer parameters similar to those of ferrocene itself. The fact clearly shows that the ring-tilt and the hindered rotation of the rings have no effect on the Mössbauer parameters. Careful inspection of the molecular model of decachloroferrocene reveals that there would be a significant steric interaction between adjacent chlorines rather than heteroannularly-staggered chlorines, and an interatomic distance Fe-Cl (3.42 Å) is much shorter than that (3.79 Å) expected from the van der Waals radii of iron and chlorine atoms.* Therefore, the anomalous change of the qs observed in this study may possibly be explained in terms of such proximity effect of the substituent on the e_{2g} orbitals of the iron.

References.
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2) F. L. Hedberg, H. Rosenberg, J. Amer. Chem. Soc., 95, 870 (1973).
3) R. L. Collins, J. Chem. Phys., 42, 1072 (1965).
4) M. R. Churchill, J. Wormald, Inorg. Chem., 8, 1970 (1969).

Footnotes:

* Half of the Fe-Fe distance (3.98 Å) observed in biferrocenylene,[4)] in which the iron atoms are somewhat displaced outside from the center of the ring probably by the Fe-Fe steric interaction, is used as the van der Waals radius of iron. A similar value for the Fe-Fe distance was reported on the structure of bis(as-indacenyliron).

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