The ^{57}Fe Mössbauer Spectrum of Phthalocyaninedipyridineiron(II)

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WE report the Mössbauer spectrum of phthalocyaninedipyridineiron(II).[1] The spectrum at 295° K consists of a doublet with a quadrupole splitting of 2·04 mm./sec. and an isomer shift of +0·06 mm./sec. with respect to a ^{57}Co in Pd source. The quadrupole splitting decreased to

1·89 mm./sec. on cooling to 77° K, and the isomer shift increased to +0·14 mm./sec. The compound has been reported to be diamagnetic,[2] and we have confirmed this observation. The observed splitting is thus the largest yet recorded for a spin-paired sixfold co-ordinated Fe^{II} ion.

The quadrupole splitting expected for low-spin Fe^{II} in octahedral or tetragonal crystal fields is zero in the absence of bonding effects. We therefore explain the high value observed for the quadrupole splitting in this compound in terms of a large difference in the covalent bonding of the iron to the pyridine and to the phthalocyanine ligands, the former being only weakly bound.

Investigation of related compounds has shown that the quadrupole splitting is sensitive to the nature of the co-ordinating ligand. The splittings observed at room temperature for the imidazole and γ-picoline adducts of ferrous phthalocyanine are 1·79 and 1·95 mm./sec., respectively. These values are significantly smaller than those observed for the pyridine compound, whereas the isomer shifts are identical within experimental error.

Our results indicate that asymmetric bonding can have a considerable influence on the electric field gradient in transition-metal complexes. Mössbauer spectroscopy is a sensitive method for investigating such effects.

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[1] P. A. Barrett, D. A. Frye, and R. P. Linstead, *J. Chem. Soc.*, 1938, 1157.

[2] H. Senff and W. Klemm, *J. prakt. Chem.*, 1940, **154**, 73.