Mössbauer Spectra of Octahedral *cis–trans*-Isomers

By ROGER R. BERRETT and BRIAN W. FITZSIMMONS
(*Department of Chemistry, Birkbeck College, London, W.C.*1)

THIS Communication concerns the relationship between local symmetry and parameters obtained by Mössbauer effect[1] measurements carried out on octahedral *cis–trans*-isomers of low-spin bivalent iron, *viz.*, *cis*- and *trans*-$Fe(CN)_2(CNCH_3)_4$. Although an instance of *cis–trans*-isomerism has been investigated using this technique before,[2] a study of an octahedral system is here reported for the first time.

In addition, a recent paper[3] mentions briefly the possibility of using Mössbauer effect measurements as a means of distinguishing between such isomers so we were prompted to describe our experiments at this stage. Of the various parameters obtainable by Mössbauer spectroscopy, the quadrupole splitting (ΔE) reflects the extent of any distortion of the electric field at the nucleus. The magnitude of ΔE depends upon the electric field gradient tensor (eV_{ZZ}) and the quadrupole moment of the 3/2 state of ^{57}Fe. For an axially symmetric field gradient ($V_{XX} = V_{YY}$) we have:

$$\Delta E = \tfrac{1}{2}eV_{ZZ}Q(1 - \gamma) \qquad (1)$$

where e is the electronic charge, Q the quadrupole moment, γ the antishielding factor and V the electric field gradient. A second parameter, the isomer shift (δ) is inversely proportional to the electronic charge density at the nucleus.

The crystal structures of *cis*- and *trans*-$Fe(CN)_2(CNCH_3)_4$ are known.[4] We have measured their Mössbauer spectra using a constant-velocity apparatus and conventional counting equipment. The results are:

Compound	ΔE(mm./sec.)	δ(mm./sec.)
cis-$Fe(CN)_2(CNCH_3)_4$	0·24 ± 0·04	0·00 ± 0·02
trans-$Fe(CN)_2(CNCH_3)_4$	0·44 ± 0·04	0·00 ± 0·02

(Isomer shifts expressed relative to stainless steel)

The ΔE-values are approximately in the ratio of 2 : 1. This may be understood by means of a calculation treating the cyanide ions as point charges (q):

FIGURE

trans-isomer

$V_{ZZ} = 2q(r-z)^{-3} + q(r + z)^{-3}$
at z

$V_{ZZ} = 4q/r^3$
at nucleus

cis-isomer

$V_{ZZ} = 3qz^2(r^2 + z^2)^{-5/2} - 2q(r^2 + z^2)^{-3/2}$
at z

$V_{ZZ} + -2q/r^3$
at nucleus

These gradients are axially symmetric so that Equation (1) may be used. Assuming that the antishielding factor is the same in each case, it follows that $\Delta E_{trans}/\Delta E_{cis} = 2$. It is to be noted that the calculation indicates that the sign of the field gradient changes on passing from a *trans*- to a *cis*-isomer. We hope to investigate this point further in the future.

In this class of compound, δ depends to a large extent upon the extent of delocalisation of $t_{2}g$ electrons into the vacant ligand orbitals.[5] Here, δ for the *cis*- is equal to that of the *trans*-isomer indicating that the amount of π-bonding in each case is much the same. This must be a result of the closeness in π-bonding strength of $CNCH_3$ and CN^-.

We wished to study other isomeric pairs in order to test these ideas further. In this connection we have also measured the spectra of compounds designated *cis*- and *trans*-Fe(phenanthroline)$_2$(CN)$_2$ on the basis of their infrared spectra.[6] Their Mössbauer spectra are identical within experimental error. This leads us to the conclusion that differences in the infrared spectra of these compounds arise from causes other than *cis–trans*-isomerism.

(*Received, January 6th,* 1966; *Com.* 011.)

---

[1] G. K. Wertheim "The Mössbauer Effect: Principles and Applications", Academic Press, New York and London, 1964.
[2] R. H. Herber and R. G. Hayter, *J. Amer. Chem. Soc.*, 1964, **86**, 301.
[3] L. M. Epstein and D. K. Straub, *Inorg. Chem.*, 1965, **4**, 1551.
[4] H. M. Powell and G. B. Stanger, *J. Chem. Soc.*, 1939, 1105; R. Hume and H. M. Powell, *J. Chem. Soc.*, 1957, 719.
[5] J. Danon, *J. Chem. Phys.*, 1964, **41**, 3378.
[6] A. A. Schilt, *Inorg. Chem.*, 1964, **3**, 1323.