Mössbauer Quadrupole Splittings in Low-spin Iron(II) Complexes

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IT has recently been shown that for low-spin iron(II) complexes of the type $Fe(CN)_2L_4$ (L = isocyanide), the magnitude of the quadrupole splitting (Q.S.) in the Mössbauer spectra of the *cis*- and *trans*-isomers is approximately in the ratio 1:2 as predicted from a simple point-charge model.[1] We report that this model, although undoubtedly an oversimplification, is applicable to a wide range of low-spin iron(II) complexes containing a variety of neutral and anionic ligands. Mössbauer spectroscopy is therefore a useful tool in elucidating the stereochemistry of such compounds. We present some results in the Table and list a number of conclusions which can be drawn from these data.

(1) The 1 : 2 ratio holds for ligands such as Cl^- (I and II) and $SnCl_3^-$ (III and IV), as well as for or CN^- (VII and VIII).

(2) For the compounds containing two different anionic ligands *viz.* Cl^- and $SnCl_3^-$, and the same neutral ligand, the Q.S. is additive as predicted

TABLE

	Compound	Quadrupole splitting[a] at 80° K (mm./sec.)
(I)	*cis*-$FeCl_2(ArNC)_4$[b,f]	0·83
(II)	*trans*-$FeCl_2(ArNC)_4$[b]	1·59
(III)	*cis*-$Fe(SnCl_3)_2(ArNC)_4$[b,c]	0·54
(IV)	*trans*-$Fe(SnCl_3)_2(ArNC)_4$[b,c]	1·06
(V)	*cis*-$FeCl(SnCl_3)(ArNC)_4$[b,c]	0·67
(VI)	$[FeCl(ArNC)_5]^+ClO_4^-$[b,c]	0·70
(VII)	*cis*-$Fe(CN)_2(CNEt)_4$[d]	0·29
(VIII)	*trans*-$Fe(CN)_2(CNEt)_4$[d]	0·59
(IX)	$Fe(CN)_2(phen)_2$[d,e]	0·60
(X)	$Fe(CN)_2(dipy)_2$[e]	0·61
(XI)	*trans*-$FeBr_2(depe)_2$[b,g]	1·45
(XII)	*trans*-$FeCl_2(depe)_2$[b]	1·42
(XIII)	*trans*-$FeCl(SnCl_3)(depe)_2$[b,c]	1·34
(XIV)	*trans*-$FeHCl(depe)_2$[b]	<0·13

[a] Error = ± 0·01 mm./sec.
[b] This work (depe = $Et_2PH_2C{\cdot}CH_2PEt_2$).
[c] New complexes which have been characterised by analysis and solution i.r. spectra.
[d] Ref. 1. [e] Ref. 2. [f] Ar = *p*-methoxyphenyl.

by the model (I, III, and V). Thus in *cis*-$FeCl_2(ArNC)_4$ (Ar = *p*-methoxyphenyl), each Cl^- contributes 0·42 mm./sec.; in *cis*-$Fe(SnCl_3)_2(ArNC)_4$, each $SnCl_3^-$ contributes 0·27 mm./sec. We would, therefore, predict the Q.S. in *cis*-$FeCl(SnCl_3)(ArNC)_4$ to be 0·42 + 0·27 = 0·69 mm./sec., in excellent agreement with the experimental value of 0·67 mm./sec.

(3) The model predicts that the Q.S. for $[FeCl(ArNC)_5]^+$ should equal that for *cis*-$FeCl_2(ArNC)_4$. Again the experimental results are in reasonable agreement.

(4) The quadrupole splitting is relatively insensitive to the nature of the neutral ligand. Thus the ratio of the quadrupole splittings in *trans*-$FeCl(SnCl_3)(depe)_2$ (depe = $Et_2PCH_2{\cdot}CH_2PEt_2$) and *cis*-$FeCl(SnCl_3)(ArNC)_4$ is 2 : 1 as predicted from the model, despite the widely differing donor–acceptor properties of the neutral ligand. For *trans*-$FeCl_2(ArNC)_4$ (Q.S., 1·59 mm./sec.) and *trans*-$FeCl_2(depe)_2$ (Q.S., 1·42 mm./sec.) the agreement is not as good. However, since (VIII) is definitely *trans* and (IX) and (X) have closely similar Q.S.,[1,2] it seems likely that (IX) and (X) are also *trans* rather than *cis* as previously proposed on the basis of solid-state i.r. spectra.[3]

(5) In the dichloride complexes, the absolute magnitude of the Q.S. can be predicted by use of the point-charge formalism and on the assumption that the neutral ligands do not contribute. Thus

$$\Delta E_Q = \tfrac{1}{2}e^2(1 - \gamma_\infty)q_{\text{lat}}Q$$

where we take $(1 - \gamma_\infty)$ as 10·1 and Q as 0·3 barns.[4] With a value of 2·3 Å for r(Fe–Cl),† ΔE_Q = 1·5 mm./sec. for *trans*-$FeCl_2(ArNC)_4$, which is in surprisingly good agreement with the observed values in view of the uncertainties in the calculation. On this basis, however, a dibromide should have a smaller Q.S. (*ca.* 0·2 mm./sec. less) than the corresponding dichloride, whereas, in fact, the Q.S. is slightly larger for $FeBr_2(depe)_2$ than for $FeCl_2(depe)_2$.

Finally we have found that the Q.S. in complexes containing Fe–H bonds apparently cannot be treated by use of this simple model [*e.g.* (XIV)].

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† No values are available for r(Fe–Cl) in low-spin octahedral complexes. r(Fe–Cl) is 2·38 Å in $FeCl_2,4H_2O$ (B. R. Penfold and J. A. Grigor, *Acta Cryst.*, 1959, **12**, 850) and although this is a high-spin complex, change of spin type is not usually associated with large changes in bond length (M. T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Comm.*, 1966, 307).

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