

Bonding and Structure in Fe(II) Low-spin Compounds using the Mössbauer Effect

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Mössbauer centre shifts (C.S.) and quadrupole splittings (Q.S.) are presented for a wide range of six-coordinate low-spin compounds, many of which have not been prepared previously. The centre shift is an additive property of the number and type of ligands in a particular compound, and partial centre shifts (P.C.S.) values have been derived for twenty-two ligands. The P.C.S. values can be related to the bonding properties of the various ligands, and the bonding properties of the novel ligand N_2 have been examined and compared with those of CO. There is an inverse relationship between the P.C.S. values and the spectrochemical ranking of ligands. The trans : cis 2 : 1 quadrupole splitting ratio holds for ligands such as Cl^- , $SnCl_3^-$ as well as for CN^- , and the variation of Q.S. with change in neutral ligand L for trans- FeL_4Cl_2 is discussed in terms of the bonding properties of the neutral ligands.

The Mössbauer centre shift (C.S.) and quadrupole splitting (Q.S.) are potentially useful for elucidating bonding and structural changes in solids. In several Fe(II) low-spin compounds, the changes in C.S. have been attributed to π -bonding effects,¹ and a correlation has been noted between C.S. and the spectrochemical Δ for a small range of ligands.¹ Quadrupole splittings in the trans and cis isomers of octahedral Fe(II) compounds have been rationalized using the point-charge model outlined by Berrett and Fitzsimmons,² while Dale *et al.*³ have used molecular orbital theory to account for their results.

We report Mössbauer spectra⁴ of a large number of Fe(II) six-coordinate low-spin compounds, many of which have not been prepared previously. A partial centre shift (P.C.S.) value can be assigned to each ligand and in the majority of cases this value is essentially independent of the other ligands bonded to the iron atom. There is a good correlation between the P.C.S. values and the spectrochemical Δ values over the whole range of the spectrochemical series, and this correlation is rationalized in terms of the σ donor and π acceptor properties of the ligands. The P.C.S. values have been used to examine the bonding properties of novel ligands such as molecular nitrogen, and these values should also be helpful in preparing new Fe(II) compounds showing intermediate spin properties or high spin \rightleftharpoons low spin equilibria.

The geometry of several of the complexes is assigned using the quadrupole splitting values and the quadrupole splittings are rationalized in terms of a lattice contribution from the "ionic" ligands such as Cl, Br, I, and a valence contribution from the neutral ligands such as RNC and phosphines.

EXPERIMENTAL AND RESULTS

The preparation, analyses, infra-red spectra and conductivities of the new compounds will be presented in a later publication.⁵ The Mössbauer techniques and

spectrometer have been published previously.⁶ A ^{57}Co in Pd source was used for all spectra. All absorbers contained about 5 mg/cm^2 of natural iron, and all C.S. values are quoted relative to stainless steel (add 0.16 mm/sec to convert to sodium nitroprusside).

The Mössbauer centre shifts and quadrupole splittings from a selection of our compounds and others reported in the literature are listed in tables 1 and 2. Typical Mössbauer spectra of $\text{trans-FeCl}_2(\text{ArNC})_4$ and $\text{cis-FeH}_2(\text{CO})_4$ are shown in fig. 1. Many of the spectra in this study were distinctly asymmetric (fig. 1*a*). A discussion of the potential value of this asymmetry in determining the sign of the field gradient will be published.⁵

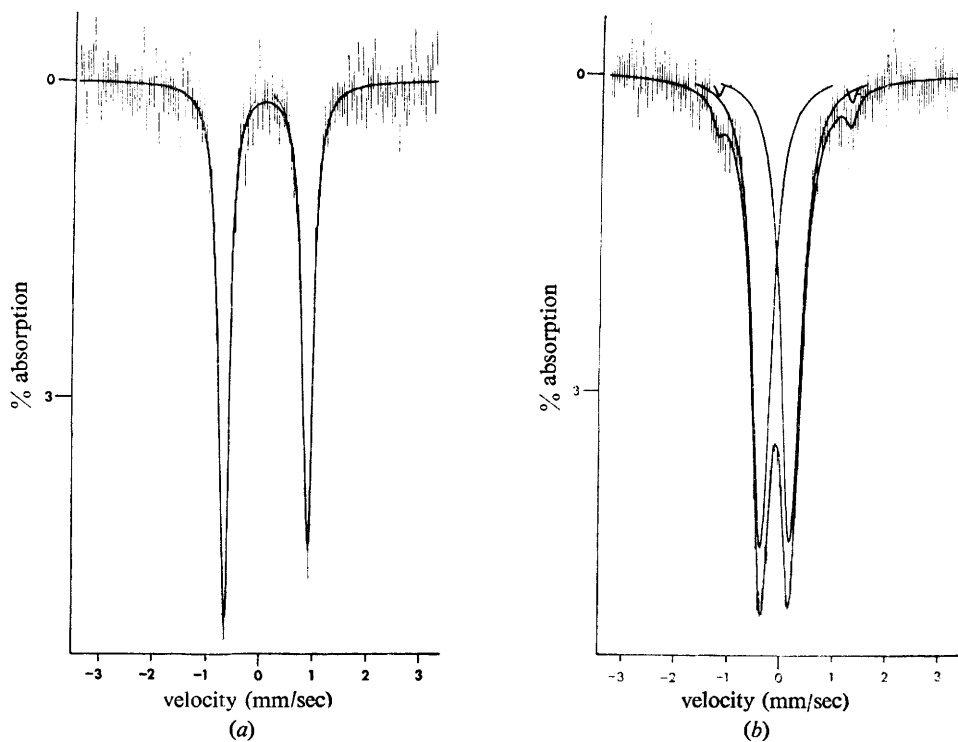


FIG. 1.—Mössbauer spectra of (a), $\text{trans-FeCl}_2(\text{ArNC})_4$ at 295°K ; (b) $\text{cis-FeH}_2(\text{CO})_4$ at 80°K .

The small peaks in (b) are due to $\text{Fe}(\text{CO})_5$.

Looking at table 1, a number of general observations can be made. The isocyanide compounds give much lower C.S. values than the compounds containing phosphine ligands. The SnCl_3^- ligand gives rise to lower centre shifts than the halides, while hydride and silyl ligands in $\text{cis-FeH}_2(\text{CO})_4$ and $\text{cis-Fe}(\text{SiH}_3)_2(\text{CO})_4$ give rise to centre shifts which are nearly as negative as that in $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$. The compounds $\text{trans-}[\text{FeH}(\text{N}_2)(\text{depe})_2]^+[\text{B}(\text{C}_6\text{H}_5)_4]^-$ and $\text{trans-}[\text{FeH}(\text{CO})(\text{depe})_2]^+[\text{B}(\text{C}_6\text{H}_5)_4]^-$ have very different centre shifts. In the depe compounds, the bromide and iodide have significantly higher C.S. values than chloride (compounds 18, 19, 20).

From table 2, it is evident that the 2:1 trans-cis quadrupole splitting ratio holds for ligands such as Cl^- , SnCl_3^- , CN^- and RNC . Also the Q.S. is additive for compounds containing two different ionic ligands. Thus the value for $\text{cis-FeCl}(\text{SnCl}_3)(\text{ArNC})_4$ is intermediate between those of $\text{cis-FeCl}_2(\text{ArNC})_4$ and

cis-Fe(SnCl₃)₂(ArNC)₄. In the chlorides, the Q.S. value varies from 1.54 mm/sec for trans-FeCl₂(ArNC)₄ to 1.29 mm/sec for trans-FeCl₂(depe)₂ to 1.13 mm/sec for trans-FeCl₂(depb)₂.

TABLE 1.—ROOM TEMPERATURE CENTRE SHIFTS *

1	trans-FeCl ₂ (ArNC) ₄ †	0.20	13	Na ₂ Fe(CN) ₅ NO . 2H ₂ O	-0.16
2	cis-FeCl ₂ (ArNC) ₄	0.12	14	K ₃ Fe(CN) ₅ CO	-0.01
3	trans-Fe(SnCl ₃) ₂ (ArNC) ₄	0.08	15	Na ₅ [Fe(CN) ₅ SO ₃]	0.06
4	cis-Fe(SnCl ₃) ₂ (ArNC) ₄	0.11	16	Na ₄ [Fe(CN) ₅ NO ₂]	0.10
		±0.03			
5	cis-FeCl(SnCl ₃)(ArNC) ₄	0.09	17	Na ₃ [Fe(CN) ₅ NH ₃] . H ₂ O	0.10
6	[FeCl(ArNC) ₅]ClO ₄	0.06	18	trans-FeCl ₂ (depe) ₂ †	0.43
		±0.02			
7	[Fe(SnCl ₃)(ArNC) ₅]ClO ₄	0.02	19	trans-FeBr ₂ (depe) ₂	0.50
8	cis-FeH ₂ (CO) ₄	-0.15	20	trans-FeI ₂ (depe) ₂	0.49
9	cis-Fe(SiH ₃) ₂ (CO) ₄	-0.10	21	trans-FeCl ₂ (depb) ₂ †	0.43
10	Fe(MeNC) ₆ (HSO ₄) ₂	-0.02	22	trans-[FeH(N ₂)(depe) ₂] ⁺	
11	Fe(EtNC) ₆ (ClO ₄) ₂	0.00		[B(C ₆ H ₅) ₄] ⁻	0.16
12	K ₄ Fe(CN) ₆	0.05	23	trans-[FeH(CO)(depe) ₂] ⁺	
				[B(C ₆ H ₅) ₄] ⁻	-0.04

* error in results = ±0.01 mm/sec, except where quoted (see ref. (4)).

† ArNC = p-methoxyphenyl isocyanide; depe = bis(diethylphosphino)ethane; depb = o-phenylene-bis(diethylphosphine).

TABLE 2.—ROOM TEMPERATURE Q.S.*

1	trans-FeCl ₂ (ArNC) ₄	1.54
2	cis-FeCl ₂ (ArNC) ₄	0.78
3	trans-Fe(SnCl ₃) ₂ (ArNC) ₄	1.05
4	cis-Fe(SnCl ₃) ₂ (ArNC) ₄	0.52
5	[FeCl(ArNC) ₅]ClO ₄	0.73
6	cis-FeClSnCl ₃ (ArNC) ₄	0.61
7	[Fe(SnCl ₃)(ArNC) ₅]ClO ₄	0.32
8	trans-FeCl ₂ (depe) ₂	1.29
9	trans-FeBr ₂ (depe) ₂	1.37
10	trans-FeI ₂ (depe) ₂	1.33
11	trans-FeCl ₂ (depb) ₂	1.13
12	trans-Fe(EtNC) ₄ (CN) ₂ †	0.60
13	cis-Fe(EtNC) ₄ (CN) ₂ †	0.29

* error = ±0.01 mm/sec; the sign of the Q.S. is taken to be negative for all trans compounds.⁵

† ref. (2).

DISCUSSION

CENTRE SHIFTS

We postulate that the C.S. is a simple algebraic sum of partial centre shift (P.C.S.) values for each ligand

$$\text{C.S.} = \sum_{i=1}^6 (\text{P.C.S.})_i \quad (1)$$

We calculate our C.S. values relative to stainless steel, and assume that the P.C.S. value for our isocyanide ligand, p-methoxyphenyl isocyanide, is 0.00 mm/sec, as

has been found for other isocyanide ligands which have been studied (table 1). We also assume that any change in C.S. is due solely changes in isomer shift (I.S.).*

For the above postulate to be valid for a large range of Fe(II) compounds, the C.S. must be insensitive to any small changes in bond angles and Fe-ligand bond distances which occur from compound to compound.

Also the P.C.S. values for a particular ligand must be comparatively insensitive to the bonding properties of the other ligands in the complexes. Thus, ideally, the change in P.C.S. value from one ligand to another should be large in comparison with the variation in the P.C.S. value of one ligand in different complexes.

We have calculated P.C.S. values (table 3) at 295°K mainly because more data are available at this temperature. These values have been calculated from 32 compounds and have been used to predict C.S. values for a further 32.^{4, 5} Only six out of the 32 predicted values do not give results in good agreement (~ 0.05 mm/sec) with the observed values. These discrepancies are undoubtedly due to a change in P.C.S. value of ligands, such as CO and RNC, from compound to compound. Despite these discrepancies, the derived values are widely applicable and the generally good agreement lends support to our initial assumptions.

TABLE 3.—PARTIAL CENTRE SHIFTS* AND PARTIAL Δ VALUES†

	P.C.S.	δ (cm ⁻¹)		P.C.S.	δ (cm ⁻¹)
NO ⁺	-0.20	15,400	NO ₂ ⁻	0.05	6,700
H ⁻	-0.08	7,700	NH ₃	0.05	5,400
SiH ₃ ⁻	-0.05		Pc/4†	0.05	
ArNC	0.00		depb/2	0.05	6,100
MeNC	0.00		depe/2	0.06	6,100
EtNC	0.00		dipy/2†	0.06	5,700
CO	0.00	8,200	phen/2†	0.07	5,700
CN ⁻	0.01	7,900	py	0.07	4,600
SO ₃ ²⁻	0.01	5,600	Cl ⁻	0.10	2,700
SnCl ₃ ⁻	0.04		Br ⁻	0.13	2,400
niox/2†	0.04		I ⁻	0.13	1,700

* error usually ± 0.01 mm/sec; † error estimated at ± 250 cm⁻¹.

† niox = cyclohexane-1,2-dione dioxime; py = pyridine; pc- = phthalocyanine; dipy = 2,2'-dipyridyl; phen = o-phenanthroline.

The range of P.C.S. values can be attributed to differences in σ donor and π acceptor properties of the ligands studied. In these compounds, the most important bonding interactions are σ bonding from the ligand to a hybrid d^2sp^3 iron orbital, and π back-bonding from the filled iron d_{xy} , d_{yz} , d_{zx} orbitals to empty π^* orbitals of the neutral ligands. Both interactions lead to an increase in s electron density at the nucleus, and a decrease in C.S. For σ bonding (L→M), donation of electrons into the $4s$ orbital will influence the s electron density at the nucleus more strongly than donation into $3d$ or $4p$, (which shield the $3s$ and $4s$ electrons), and thus the s electron density at the nucleus will increase as the σ donor power of the ligand increases. With increased π backbonding into empty π^* orbitals of the ligands, the d_{xy} , d_{yz} , d_{zx} orbitals become more delocalized and shield the $3s+4s$ electrons less, increasing the s electron density at the nucleus.

* C.S. = I.S.+S.O.D. where S.O.D. = second order Döppler shift and includes Z.P.M. = zero-point motion shift.^{4, 7}

Thus, as we would expect from the above considerations, the ligands giving the most positive P.C.S. values (I^- , Br^- , Cl^-) are the most ionic in character with comparatively little covalent bonding, whereas hydride (strong σ donor) and NO^+ (strong π acceptor) have the most negative P.C.S. values. The C.S. values for $trans-[FeH(N_2)(depe)_2]^+[B(C_6H_5)_4]^-$ and $trans-[FeH(CO)(depe)]^+[B(C_6H_5)_4]^-$ (table 1) suggest that CO is an appreciably better σ donor and/or π acceptor than N_2 .

The P.C.S. values for CO (calculated from $cis-FeH_2(CO)_4$), CN^- (calculated from $K_4Fe(CN)_6$), and RNC (calculated from $Fe(EtNC)_6(ClO_4)_2$) are similar and reflect the similar ($\sigma + \pi$) bonding characteristics of each ligand in the above compounds. However, there are several pieces of evidence which suggest that the P.C.S. values of RNC and CO and thus their bonding properties vary from compound to compound. For example, $cis-FeCl_2(ArNC)_4$ has an appreciably lower C.S. than $trans-FeCl_2(ArNC)_4$, while cis - and $trans-Fe(SnCl_3)_2(ArNC)_4$ have similar shifts. The difference in the values for the chlorides suggests that the P.C.S. value of ArNC decreases, (becomes more negative) by 0.02 mm/sec on going from the $trans$ to the cis complex. In the cis compound, two of the ArNC groups should become more effective π -acceptors because they will no longer be competing for d electron density with $trans$ ArNC groups. The σ donor power of the isocyanide ligands may also increase in the cis compound, and this may make an additional contribution to the observed change in C.S. values. If we tentatively attribute differences in the C.S. values of cis - $trans$ pairs to differences in π bonding, then we can separate σ and π interactions using the P.C.S. values as an estimate of $\sigma + \pi$, and $C.S._{trans} - C.S._{cis}$ as an estimate of the difference in π bonding for the two ligands. For example, on the above basis, we would suggest that the $SnCl_3^-$ and ArNC groups have similar π accepting properties, but that ArNC is an appreciably better σ donor. This prediction is consistent with the conclusion reached by Parshall⁸ from n.m.r. data for the $SnCl_3^-$ ligand.

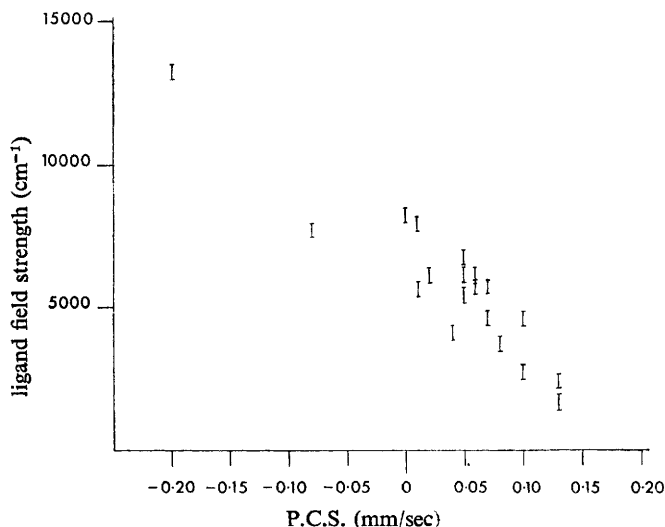


FIG. 2.—Plots of P.C.S. values against partial $\Delta(\delta)$ values (see table 3).

The order of P.C.S. values is made more meaningful by the correlation with the spectrochemical ranking of ligands (fig. 2). Unfortunately, most partial $\Delta(\delta)$ values for Fe(II) compounds are inaccurate because the $d-d$ bands are often masked by

charge transfer bands. The values in this figure have been calculated using a method suggested by McClure⁹ and results mainly given by Stephens.¹⁰ The values have often been estimated from the spectra of Co(III) complexes containing the appropriate ligand. However, despite the uncertainties in the partial Δ values, a good general correlation is evident.

This correlation is not surprising because just as the C.S. should decrease with an increase in σ and π bonding, so partial Δ values should increase. Thus, Jorgenson¹¹ has expressed Δ as

$$\Delta = \Delta\langle\text{Voct}\rangle + \sigma(\text{L} \rightarrow \text{M}) + \pi(\text{L} \leftarrow \text{M}) \quad (2)$$

neglecting π bonding from the ligand to the metal. $\Delta\langle\text{Voct}\rangle$, the crystal field term, is usually considered to be small, and Δ should then increase with increasing σ donation and π back-donation. Thus NO^+ , the strongest field ligand gives rise to the lowest (most negative) P.C.S., while bromide and iodide, the weakest field ligands, give rise to the most positive P.C.S.

Since there is an inverse relationship between P.C.S. and partial Δ , we would expect to find a limiting value of the C.S., beyond which there will be a transition from a low spin to a high spin or intermediate spin complex. From our data, and from a study of Fe(II) hydrotris (1 pyrazolyl) borate compounds,¹² we suggest that this upper limit should be about 0.5 mm/sec. This relationship should be useful in preparing compounds which exhibit intermediate spin or high spin-low spin equilibria.

QUADRUPOLE SPLITTINGS

The Q.S. values are valuable in elucidating the geometry of these complexes, and are often useful in examining the σ donor and π acceptor properties of the ligands—especially when used in conjunction with P.C.S. values.

The 2 : 1 trans : cis ratio is widely applicable.^{2, 4} This ratio can be predicted using a simple point charge model,² a general ligand-field model,¹³ or the McClure approach.⁵ The latter two approaches suggest that, although the 2 : 1 ratio will hold for a given combination of ligands, if one of the neutral ligands is changed, a significant change in Q.S. will result. However, the 2 : 1 ratio is still extremely useful in assigning the structures of these compounds. Thus, the trans and cis structures can be assigned to all the isocyanide complexes. The depe dihalides give Q.S. values closer to those of trans- $\text{FeCl}_2(\text{ArNC})_4$ than cis- $\text{FeCl}_2(\text{ArNC})_4$ suggesting that they are trans. $\text{FeCl}_2(\text{depb})_2$, however, gives a Q.S. intermediate between cis- $\text{FeCl}_2(\text{ArNC})_4$ and trans- $\text{FeCl}_2(\text{ArNC})_4$, and on the Mössbauer evidence alone, it would be difficult to assign this structure. N.m.r. and dipole moment data suggest that these phosphine complexes are trans.¹⁴ In order to assign the geometry of any Fe(II) octahedral structure containing the ligands in our larger study,⁵ partial quadrupole splittings (P.Q.S.) values are calculated. The approach used for calculating these values, and for evaluating bonding properties of the neutral ligands will now be outlined.

The quadrupole splitting ΔE_Q for a nucleus of quadrupole moment Q in an electric field gradient q is generally expressed as

$$\Delta E_Q = \frac{1}{2} e^2 q Q \left(1 + \frac{\eta^2}{3} \right)^{\frac{1}{2}}. \quad (3)$$

In both cis and trans isomers, $\eta = 0$ and

$$V_{zz}/e = q = (1-R)q_{\text{valence}} + (1-\gamma_{\infty})q_{\text{lattice}},$$

where q = field gradient due to the valence electrons (q_{valence}) or due to external charges (q_{lattice}); $Q = \sim 0.3$ barns.¹⁵ R and γ_{∞} = Sternheimer antishielding factors,

$$(1 - \gamma_{\infty}) = 10.1;$$

$$q_{\text{lattice}} = \frac{\sum_i Z_i (3 \cos^2 \theta_i - 1)}{r_i^3},$$

where θ_i = angle from the Z axis, r_i = Fe-ligand bond distance, Z_i = charge on ligand;

$$q_{\text{valence}} = - \sum_{d \text{ electrons}} \langle 3 \cos^2 \theta_i - 1 \rangle \langle r^{-3} \rangle_i,$$

where $\langle r^{-3} \rangle_i$ is the mean value of r^{-3} averaged over a particular d orbital, and $\langle 3 \cos^2 \theta_i - 1 \rangle$ for the various d orbitals are $+4/7$ for d_{z^2} , $-4/7$ for $d_{x^2-y^2}$ and d_{xy} and $+2/7$ for d_{xz} and d_{yz} . The total q_{valence} is considered to be the sum of the contributions made by individual electrons. Thus, for the Fe(II) free-ion (t_{2g}),⁶ $q_{\text{valence}} = 0$. Depending on the electron donating or withdrawing power of the ligands, the value of $\langle r^{-3} \rangle$ will vary for different orbitals, thus changing the "effective" population of these orbitals, and give rise to a q_{valence} .

In the following treatment, we assume that (i) the Fe—L bond distances (for a given ligand L) are constant from compound to compound, and all complexes have the highest possible symmetry. (ii) The contribution to the Q.S. from parts of the lattice other than the nearest neighbours is neglected. Generally this will not be a good assumption, but there are two pieces of evidence which strongly support it for the compounds in this study: (a) the frozen solution spectrum of trans-FeCl₂(depe)₂ is identical to that of the solid; (b) the trans : cis 2 : 1 ratio is based on the assumption that the contribution from other than nearest neighbours is neglected,* and the 2 : 1 ratio holds well.

To obtain a "reference value" on which to base our P.Q.S. values, we calculate a hypothetical Q.S. for the trans Cl—Fe—Cl group assuming that $r_{\text{Fe-Cl}} = 2.3 \text{ \AA}$,⁴ and that the bonds are ionic. $\Delta E_{Q_{\text{lattice}}}$ from this calculation equals -1.5 mm/sec . The negative value of the Q.S. is consistent with the area ratio data.⁵ Taking into account covalency and polarization which will tend to decrease the value of $\Delta E_{Q_{\text{lattice}}}$, we assume the Q.S. contribution from the FeCl₂ linkage to be about -1.2 mm/sec . We then take the total quadrupole splitting in the chloride compounds as

$$\Delta E_{Q_{\text{total}}} = -1.2 \text{ mm/sec} + \Delta E_{Q_{\text{valence}}},$$

where the valence contribution arises from the bonding properties of the neutral ligands and can be expressed for the trans compounds FeCl₂L₄ as

$$q_{\text{valence}} = K[n_{xy} - \frac{1}{2}(n_{xy} + n_{yz})] + K[n_{x^2-y^2} - \frac{1}{3}n_{z^2}], \quad (5)$$

where the n are the "effective" populations of the various d orbitals and $K = (4/7) \langle r^{-3} \rangle (1 - R)$.

σ donation by the neutral ligand in the trans compounds will be effectively into $d_{x^2-y^2}$ † which will create a positive q in opposition to the "chloride only" value. However, π back-donation in the trans chloride compounds can have a dual effect. If L withdraws electrons mostly of d_{xy} type, then n_{xy} becomes smaller than $\frac{1}{2}(n_{xz} + n_{yz})$ and q_{valence} will be negative, enhancing the field gradient from the chlorides. If, on the other hand, the d_{xy} orbital is essentially non-bonding, as has been suggested for cyanide complexes,¹⁶ then π bonding via d_{xz} , d_{yz} will decrease the magnitude of the Q.S.

* It seems highly unlikely that contributions from other than nearest neighbours would be 2 : 1.

† We neglect donation to the $4p$ orbitals which will give a smaller contribution to q_{valence} .

For any compound of the type FeA_2B_4 , ΔE_Q can be expressed as

$$\Delta E_{Q\text{trans}} = 4(\text{P.Q.S.})_A - 4(\text{P.Q.S.})_B,$$

and

$$\Delta E_{Q\text{cis}} = -2(\text{P.Q.S.})_A + 2(\text{P.Q.S.})_B.$$

Using the P.Q.S. value for $\text{Cl}^- = -0.30$, the P.Q.S. value for some other ligands have been derived (table 4). The P.Q.S. values are useful in assigning the stereochemistry of a compound containing any of the ligands we have studied. They appear to be much more sensitive than the P.C.S. values to the other ligands present; yet, there is reasonable agreement between predicted and observed values, and the geometry can be usually assigned with confidence.⁵

TABLE 4.—PARTIAL QUADRUPOLE SPLITTINGS

Br^-	-0.32	depb/2	-0.02
I^-	-0.31	depe/2	+0.02
Cl^-	-0.30	RNC	+0.09
SnCl_3^-	-0.17		
CN^-	-0.06		

Using eqn. (5) and the P.C.S. values for ArNC , depe and depb, we now comment on the trend in Q.S. of the dichlorides $\text{trans-FeCl}_2(\text{ArNC})_4$, $\text{trans-FeCl}_2(\text{depe})_2$ and $\text{trans-FeCl}_2(\text{depb})_2$. The P.C.S. values indicate that ArNC is an appreciably better σ donor and/or π acceptor than depe or depb. The larger Q.S. value for $\text{trans-FeCl}_2(\text{ArNC})_4$ indicates that either the d electron density withdrawn by ArNC has more d_{xy} character than for the phosphorus ligands and/or that ArNC is a poorer σ donor. The former explanation is more consistent with the P.C.S. values. The two phosphine ligands have similar P.C.S. values, yet different P.Q.S. values. This suggests that depb is a poorer acceptor of d_{xy} electrons than depe and/or that it is a better σ donor, while the total σ donor + π accepting capacity is similar for both.

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