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Quadrupole Splittings in Trigonal-prismatic Iron(II) Complexes: the Possibility of Obtaining Absolute Partial Quadrupole Splittings

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An attempt to determine the absolute values of partial quadrupole splittings (PQS) by investigating trigonal-prismatic low-spin iron(II) complexes has been made; all PQS values obtained are positive.

The Mössbauer effect is observed for a number of elements, but only the ^{57}Fe isotope is easily used in routine work. The nature of two main Mössbauer spectral parameters, isomeric shift and quadrupole splitting (Δ), are discussed at length for iron compounds. The partial quadrupole splitting (PQS) treatment has been developed by G. M. Bancroft[1,2] for low-spin iron complexes. Three cases of distorted octahedral geometry have been discussed: $FeAB_5$ and *cis*- and *trans*-FeA_2B_4 complexes. In all these cases Δ is a function of the difference between PQS_A and PSQ_B, eqns. (1).

$$\begin{array}{ll} \Delta = 4(PQS_A - PQS_B) & trans\text{-}FeA_2B_4 \\ \Delta = -2(PQS_A - PQS_B) & cis\text{-}FeA_2B_4 \\ \Delta = 2(PQS_A - PQS_B) & FeAB_5 \end{array} \qquad (1)$$

The absolute value of PQS cannot be calculated from the experimental Δ value using these equations. In this study we discuss an attempt to find the absolute values of PQS by investigating distorted trigonal-prismatic low-spin iron(II) complexes. The quadrupole splitting for ^{57}Fe can be expressed as eqn. (2),

$$\Delta = \tfrac{1}{2}e^2qQ(1+\eta^2/3)^{1/2} \qquad (2)$$

where $q = V_{zz}/e$, $\eta = (V_{xx} - V_{yy})/V_{zz}$, and V are the components of the electric field gradient (EFG) tensor. Two assumptions from ref. 1 have been used with no changes:

1. Δ can be regarded as a sum of independent contributions, one from each ligand.
2. PQS are constants for a given electronic state.

Two subsequent Bancroft assumptions have therefore been modified:

3. The structure of a distorted trigonal-prismatic complex is determined by the bite angle α and the twist angle φ (Fig. 1).
4. The z axis corresponds to the C_3 symmetry axis. It is easy to see from symmetry reasons that $V_{xx} = V_{yy}$ and $\eta = 0$.

Applying the same approximation as in the octahedral case, Δ is expressed as eqn. (3),

$$\Delta = 6(3\cos^2\theta - 1)\,PQS, \quad \text{or } \Delta = f\cdot PQS \qquad (3)$$

where f is a function of iron atom arrangement geometry and θ is the angle between the z and the Fe–N bond.

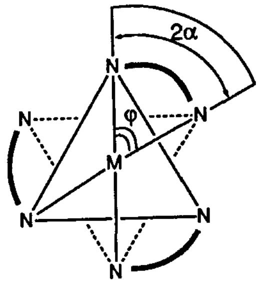


Fig. 1 Illustration of bite (α) and twist (φ) angles for trigonal-prismatic complexes

For a given bidentate ligand the value of θ is a function of both bite angle α and distortion angle φ. Simple calculations give a dependence of the f value on α and φ, eqn. (4);

$$f = 12 - 18\cos^2\alpha/\cos^2(\varphi/2) \qquad (4)$$

e.g. for an octahedron $\alpha = 45°$, $\varphi = 60°$ and $\Delta = f\cdot PQS = 0$.

Using structural data for iron complexes with known Mössbauer spectra, one can calculate the absolute PQS values for each ligand. Although PQS are probably slightly dependent on iron atom arrangement, an estimate of the Δ values for all low-spin iron complexes may be obtained from the data for trigonal prismatic ones.

The effect of cross-linking groups is lower due to the significant increase in distance from the iron atom. This phenomenon can also be described by using the PQS treatment. The capping groups are situated directly on the z axes of the complex; the contribution of these groups is $\Delta V_{zz} = (3\cos^2\theta - 1)q/r^3 = 2q/r^3$, where q is the charge on the capping group. The Δ value increases with q.

For all angles α and pseudo-octahedral iron atom arrangements ($\varphi = 50$–$60°$) the coefficient f has a negative sign. For a trigonal-prismatic iron atom arrangement the f values are comparatively high and positive. Similar results (change of Δ sign with increasing φ angle) were obtained in an early study.[3] A knowledge of both Δ and structure for some low-spin iron(II)

Table 1 Quadrupole splitting (Δ/mm s^{-1}), bite (α) and twist (φ) angles/° and PQS (mm s^{-1}) calculated from eqn. (2)

Compound[a]	Δ[b]	α	φ	f	PQS	$f\cdot$PQS[c]	$\Delta - f\cdot$PQS	Ref.
$Fe(phen)_3{}^{2+}$	−0.29	41.5	55.2	−0.85	0.35			3
$Fe(dipy)_3{}^{2+}$	−0.39	41.5	55.2	−0.85	0.45			3
$Fe(H_2Nx)_3{}^{2+}$	−0.25	39	53.4	−1.55	0.36			5, 6
$Fe(HNx)_2(H_2Nx)$	−0.61	39	53.4	−1.60	0.38			6
$FeBd_3(BF)_2$	(+)0.28	39.3	29.3	+0.49		0.25	0.0	9
$FeFd_3(BC_6H_5)_2$	≈0.0	39.2	26.4	0.60		0.30	−0.3	10
$FeGx_3(BOH)_2$	(+)0.50	39.1	23.4	+0.70		0.35	0.15	8
$FeDm_3(BF)_2$	(+)0.90	40(?)	16.7	1.18		0.60	0.3	7, 8
$FeNx_3(SnCl_3)_2^{2-}$	(−)0.19	39.5	37.5	0.04		0.02	−0.2	10, 11
$[Fe\ PccBF]^+$	+0.95	39.5	21.8	0.90		0.45	0.45	3

[a] For ligand designation, see Scheme 1. [b] The signs of the quadrupole splitting in brackets were assumed from direct measurements [$FeDm_3(BF)_2$ *and $FeGx_3(BOH)_2$[20]] or were confirmed by the temperature dependences of Δ.[21]* [c] *The value calculated using the approximate PQS = +0.5 mm s^{-1}* for uncharged macrobicyclic iron dioximates. PQS for caged molecules ought to be corrected for the effect of cross-linking groups with charge q.

Table 2 PQS values for some ligands and quadrupole splittings (mm s^{-1}) in iron(II) complexes used for PQS calculations

Compound[a]	Δ(calc.)	Δ(exp.)	Bancroft's scale	PQS[c]	Σ[d]
phen			−0.95[b]	0.35	0.35
dipy			−0.85[b]	0.45	0.45
HDm^-, HNx^-			−0.92[b]	0.38	0.38
$Fe(HNx)_2Py_2$	1.76	1.79[12]			
$Fe(HDm)_2Py_2$	1.76	1.74[13]			
HBd^-			−0.97[b]		0.33
$Fe(HBd)_2Py_2$	1.96	1.97[13]			
$Fe(HNx)_2(CNC_6H_{11})_2$	0.92	0.94[16]			
Macrocyclic			−0.86[14]		0.44
TAAB			−0.62[14]		0.68
$[Fe(TAAB)(CH_3CN)_2](BF_4)_2$	0.76	0.82[15]			
NH_3			−0.52[1]		0.78
$Fe(HNx)_2(NH_3)_2$	1.60	1.72[12]			
Py, $BuNH_2$			−0.48[b]		0.82
$Fe(HNx)_2(BuNH_2)_2$	1.76	1.83[12]			
Im			−0.53[b]		0.77
$Fe(HNx)_2(Im)_2$	1.56	1.38[12]			
CN^-			−0.84[1]		0.46
$KFe(HNx)_2(CN)(Im)$	0.94	0.93[12]			
Pc			−0.98[b]		0.32
$FePc(BuNH_2)_2$	2.0	1.94[12]			
$K_2FePc(Im)_2$	1.80	1.75[12]			
$FePc(CN)_2$	0.56	0.56[12]			
$FePc(Py)_2$	2.0	1.97[12]			
NO			+0.04[1]		1.34

[a] For ligand designation, see Scheme 1. [b] This work. [c] Calc. from eqn. (2). [d] Σ is calculated from Bancroft's PQS by addition of the difference (1.3 mm s^{-1}) between our scales and Bancroft's.

complexes[4–10] allows us to calculate f and PQS for those ligands (Table 1).

For iron tris-dioximates the range of α usually observed is comparatively narrow (39–40°). As a result, the Δ value is a function of only the φ angle and the effect of capping groups. The data for several trigonal-prismatic iron complexes and the results of the calculations are listed in Tables 1 and 2.

Most of the trigonal-prismatic iron(II) complexes studied are macrobicyclic clathrochelates, cross-linked with boron-containing groups. The charge on the boron atom q_B (obtained by CNDO/2 calculations) increases from +0.31 for BH to +0.50 for BF. A correlation between experimental Δ and q_B has been obtained for several dioximes.

For the less positive cross-linking group $SnCl_3{}^+$ the total effect is the superposition of four atomic charges (a positive one due to the tin atom and three negative ones due to chlorine atoms, which are at a distance 6 Å from the iron atom). Thus Δ values for tin halide cross-linking compounds are *ca.* −0.2 mm s^{-1} lower than the values estimated from PQS.

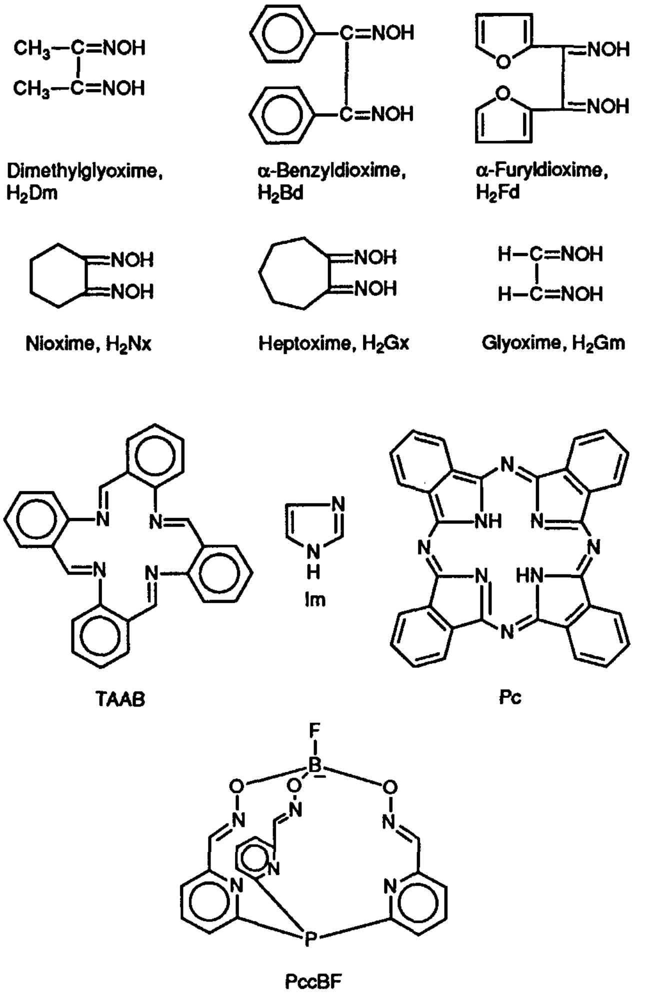
It is of interest to obtain the difference between the PQS values calculated by Bancroft and ours (Table 2).

A new PQS scale has been obtained from Bancroft's scale by adding 1.30 mm s^{-1}; this constant was obtained as the difference between the PQS values for nioxime, phenanthroline and bipyridine complexes in both Bancroft's scale and ours.

All the PQS values obtained here are positive. This result contradicts Bancroft's scale with negative PQS for all ligands except NO. Nevertheless, it is very similar to the high PQS (called 'effective point charges') for halide ions originally obtained for organotin halides.[17]

It is clear that the nature of PQS is rather different from the pure electrostatic effect of ligand atom charge. The reason for a positive PQS value is probably a decrease in electron density around the iron atom ($r < 0.5$ Å) relative to the neutral one which was observed by direct electron-density measurements[18,19] in $Na_2[Fe(CN)_5NO]$, $[Co(CN)_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$. The highest values of electron density decrease were obtained along the Fe–NO and Co–NH_3 bonds and the lowest ones along the Fe–CN and Co–CN bonds. These data correlate with the magnitude of absolute PQS for NO, NH_3 and CN (Table 2).

The PQS values we obtained have a real physical meaning and reflect the distribution of electron density in the molecule, allowing us to explain Δ for a great number of iron coordi-



Scheme 1 Some of the ligands which appear in Tables 1 and 2

nation compounds. In addition, these values make it possible to predict the structure of new compounds using the 'structure–quadrupole splitting' type of correlation dependence.

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