Mössbauer Spectra of Some Low-spin Iron(II) Complexes with Ditertiary Phosphines

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The Mössbauer spectral data for a range of low-spin iron(II) complexes [FeX(Y)(diphosphine)$_2$]$^{n+}$ (n = 0 or 1), where X and/or Y = Cl, Br, MeNC, MeCN, H, N$_2$, H$_2$, CO, etc., are reported. The isomer shifts and quadrupole splittings have been analysed in terms of ligand partial values assuming that additivity holds, and the partial values are discussed in terms of the bonding properties of the ligands. It is concluded that the partial isomer shifts are of limited use because of the small range of values. Partial quadrupole splittings (p.q.s.) are more informative, and are best computed with reference to p.q.s. (H) =0.00.

We have recently prepared a series of low-spin octahedral iron(II) complexes generally of the form trans-[FeX(Y)(dmpe)$_2$]$^{0/+}$ [dmpe = 1,2-bis(dimethylphosphino)ethane], where X may or may not be equal to Y, and some of the form cis-[Fe(L$_2$)(dmpe)$_2$], where L$_2$ is a bidentate monoanionic ligand.[1] Mössbauer spectra at 77 K were obtained for all these species, and the data are presented in Table 1. Most of the complexes are new, but several homologues of the related diphosphine depe [= 1,2-bis(diethylphosphino)ethane] complexes were described some years ago.[3] Their Mössbauer spectra were analysed in terms of the point-charge model,[3-5] and partial isomer shifts and quadrupole splittings were derived. The validity of this kind of analysis has recently been supported by work of Silver[6] on a large range of iron(II) compounds. Here we apply the same model to our dmpe complexes, and derive partial shifts and splittings for less usual ligands such as H$_2$, H$^-$ and N$_2$.

Results and Discussion

In the point-charge model the observed isomer shift (i.s.) is simply the sum of the partial isomer shifts (p.i.s.) of the individual ligands, summed arithmetically [equation (1)].

$$\text{i.s.} = \sum_{\text{L}} \text{p.i.s.} \qquad (1)$$

However, the quadrupole splitting (q.s.) (which may be positive or negative) is broken down to partial values (p.q.s.) in a fashion dependent upon structure. For trans-[FeA$_2$B$_4$] and trans-[FeACB$_4$] the derived formulae are, respectively, (2) and (3). We now apply these equations to our data. However, it must

$$\text{q.s.}_{trans} = +4\text{p.q.s.(A)} - 4\text{p.q.s.(B)} \qquad (2)$$

$$\text{q.s.}_{trans} = +2\text{p.q.s.(A)} + 2\text{p.q.s.(C)} - 4\text{p.q.s.(B)} \qquad (3)$$

be appreciated that the isomer shifts are not absolute values since they are referred to an arbitrary standard (in our case, natural iron at 298 K). Consequently analysis has tended to neglect partial values in the past. In contrast, the quadrupole splittings are apparently absolute, and these have received much more attention. In general, the approach used has been to fix some partial value by general considerations and then use this to calculate a series of partial values by considering data from available, appropriate compounds. This has the objection that it has built-in assumptions and may yield different values if

another series of compounds is used. There are no reliable criteria of errors. We have chosen a different approach to the data, which are presented in Table 1, which includes some selected data from the literature.

The set of equations linking the partial values to the experimental data are simultaneous and linear. By use of appropriate programs, we should be able to obtain approximate mathematical solutions which are related to all the compounds and all the data. They should not depend upon the particular sequence of data used in the calculations. This has been achieved relatively easily, and the two sets of partial values so obtained are now considered.

(i) Partial Isomer Shifts (p.i.s.).—The partial isomer shifts calculated by our method, together with values presented in the literature, are given in Table 2. For the purposes of calculation, where our determinations differ from literature data, we have used a mean value, after making appropriate corrections for reference and temperature differences.

It will be seen that the p.i.s. values are all rather small, with a small range of values. The relative order of values is only roughly in accord with that of the literature values but it is to be noted that these values were often obtained by consideration of single compounds. Four of the first five values (the exception is Br) refer to bidentate ligands in cis complexes, and these data are therefore not really comparable to those for monodentate ligands.

Bancroft et al.[3-5] inferred that p.i.s. values are a measure of ($\sigma + \pi$) electron donation from ligand to metal, with more positive values suggesting least donation and therefore the most ionic character. Our values appear to fit this pattern. Vinylidene is a very strong π acceptor, and gives by some way the most negative value of p.i.s. Dinitrogen and H$_2$ are intermediate and similar, and Cl and Br are poor ($\sigma + \pi$) donors. Table 1 shows the observed isomer shifts and those calculated by summing appropriate p.i.s. values. The data were fitted to a straight line by a least-squares method, with correlation coefficient 0.987. Closer examination reveals that the best agreement between observed and computed shifts is found for compounds containing a ligand which appears only once in the series.

The conclusion must be that the basic assumptions of the point-charge model are valid only to a first approximation. This only becomes clear when more than minimal data are used. A single compound used to establish a p.i.s. will always give a good fit. The fit then deteriorates as more compounds are included, before improving with large numbers of data. The

Table 1   Mössbauer spectra of some low-spin octahedral iron(II) complexes[a]

Compound	i.s./mm s⁻¹ Experimental	i.s./mm s⁻¹ Computed	q.s./mm s⁻¹ Experimental	q.s./mm s⁻¹ Computed p.q.s.(Cl) = −0.27	q.s./mm s⁻¹ Computed p.q.s.(H) = 0.00	Γ/mm s⁻¹
1 [Fe(CNMe)₆][HSO₄]₂	−0.11[b]	−0.11	0			s, n.r.
2 [FeCl(CNMe)(dmpe)₂][BPh₄]	0.11	0.12	0.85	0.74	0.70	0.18
3 [FeCl₂(depe)₂]	0.41,[c] 0.37	0.39	1.42,[c] 1.44	1.43	1.41	0.16
4 [FeCl₂(dmpe)₂]	0.37,[c] 0.37	0.37	1.61,[c] 1.70	1.68	1.64	0.14
5 [FeH(Cl)(depe)₂]	0.20[c]	0.23	≤ ±0.12[c]	−0.22 (calc.)	−0.20 (calc.)	n.r.
6 [FeH(CNMe)(dmpe)₂][BPh₄]	−0.02	−0.03	−1.05	−0.92	−0.90	0.20
7 [FeH(CNBuⁱ)(depe)₂][BPh₄]	−0.04[d]	−0.04	−1.13[d]	−1.13	−1.13	n.r.
8 [FeH₂(depb)₂]	−0.02[c]	−0.02	−1.78[c]	−2.00	−1.96	n.r.
9 [FeCl₂(depb)₂]	0.39[c]	0.34	1.16[c]	1.30	1.24	n.r.
10 [FeBr₂(depe)₂]	0.47[c]	0.45	1.45[c]	1.42	1.48	n.r.
11 [FeBr₂(depb)₂]	0.39[c]	0.40	1.21[c]	1.24	1.30	n.r.
12 [FeBr(N₂)(dmpe)₂][BPh₄]	0.25	0.27	1.68	1.80	1.62	0.19
13 [FeBr(CO)(dmpe)₂][BPh₄]	0.05	0.04	1.08	0.92	0.92	0.17
14 [Fe(CCPh)Br(depe)₂]	0.22	0.23	0.32	0.25	0.29	0.16
15 [Fe(CCPh)Cl(depe)₂]	0.21	0.19	≤ ±0.15	0.26 (calc.)	0.24 (calc.)	0.15
16 [Fe(CCPh)Cl(dmpe)₂]	0.16	0.17	0.44	0.51	0.47	0.16
17 [Fe(CCHPh)Cl(dmpe)₂][BPh₄]	−0.04	−0.04	±1.32	+ve (calc.)	+ve (calc.)	0.19
18 [FeH(H₂)(dmpe)₂][BPh₄]	0.06	0.06	−0.16	−0.07	−0.08	0.17
19 [FeH(H₂)(depe)₂][BPh₄]	0.08	0.08	−0.23	−0.32	−0.31	0.18
20 [FeH(N₂)(dmpe)₂][BPh₄]	0.10	0.08	≤ ±0.11	0.14	0.00	0.11
21 [FeH(N₂)(depe)₂][BPh₄]	0.07,[d] 0.10	0.10	−0.33,[d] −0.29	−0.10	−0.23	0.20
22 [FeCl(N₂)(dmpe)₂][BPh₄]	0.24	0.24	1.61	1.81	1.59	0.22
23 [FeH(CO)(depe)₂][BPh₄]	−0.12[d]	−0.13	−1.00[d]	−0.97	−0.94	n.r.
24 [FeCl(CO)(dmpe)₂][BPh₄]	−0.09	−0.03	0.86	0.93	0.89	0.13
25 [FeH(CO)(dmpe)₂][BPh₄]	−0.09	−0.15	−0.79	−0.72	−0.72	0.18
26 [FeH(C₂H₄)(dmpe)₂][BPh₄]	0.10	0.10	−0.72	−0.72	−0.72	0.19
27 [FeH(NCMe)(dmpe)₂][BPh₄]	0.11	0.10	−0.32	−0.26	−0.28	0.21
28 [FeH(NCMe)(depe)₂][BPh₄]	0.10[d]	0.11	−0.46[d]	−0.52	−0.50	n.r.
29 [Fe(O₂CH)(dmpe)₂][BPh₄]	0.26	0.26 (calc.)	±1.33			0.21
30 [Fe(SSCH)(dmpe)₂][BPh₄]	0.17	0.17 (calc.)	±0.62			0.24
31 [Fe{CH=C(O)OMe}(dmpe)₂][BPh₄]	0.17	0.17 (calc.)	±1.62			0.20
32 [Fe(HCH₂C=CMe₂)(dmpe)₂][BPh₄]	0.20	0.20 (calc.)	±1.93			0.25

[a] Values computed using a computer program written by Dr. J. G. Stamper and run on a MicrovaxII (or, where indicated, calculated using appropriate p.i.s. or p.q.s. values). Experimental errors normally ±0.01 mm s⁻¹. All values for Γ (width at half height) are from the present work. depb = C₆H₄(PEt₂)₂-1,2. n.r. = Not reported, s =singlet. [b] Ref. 2. [c] Ref. 3. [d] Ref. 4.

Table 2   Partial isomer shifts (mm s⁻¹) calculated in this work, and in the literature

Ligand	This work	Literature[*]
OOCH	+0.34	—
CHC(O)OMe	+0.28	—
Br	+0.26	+0.13
HCH₂C=CMe₂	+0.25	—
SSCH	+0.25	—
Cl	+0.22	+0.10
C₂H₄	+0.12	—
MeCN	+0.11	—
N₂	+0.09	—
H₂	+0.08	—
H	+0.07	−0.08
CCPh	+0.03	—
depe/2	−0.02	+0.06
MeNC	−0.02	0.00
dmpe/2	−0.02	+0.05
depb/2	−0.03	+0.06
BuⁱNC	−0.04	—
CO	−0.13	0.00
CCHPh	−0.18	—

[*] Refs. 3 and 4. All values are quoted relative to stainless steel at 295 K.

calculated isomer shifts are nevertheless good enough to enable the p.i.s. values to be used for estimating isomer shifts of new species.

(*ii*) *Partial Quadrupole Splittings* (*p.q.s.*).—The quadrupole splittings span a larger range than the isomer shifts, and the p.q.s. values should be more discriminatory than the partial isomer shifts. We used the analysis cited above, ignoring lattice contributions.[4] We have little option but to do this, and the results suggest we are justified, though lattice effects on quadrupole splittings are clearly demonstrable.[7] We believe that the neglect is justified because we are working with large cations and a common large anion. In the past [3–5] care has been taken to work only with neutral or with charged compounds in order to avoid assumptions about lattice contributions.

At first sight the solution of the linear equations should be straightforward and give absolute values, since no external references are required. In fact this is untrue, because there is no way to determine an isolated p.q.s. for our compounds, and consequently the equations are not independent. There are an infinite number of solutions. What must characterise all the solutions is that the differences between p.q.s. values for given ligands should be constant. As an arbitrary reference, −0.27 mm s⁻¹ has been selected for Cl.[4,6] One set of data in Table 3 has been calculated on this basis. However, because the smallest (most negative) value we have is associated with H, which can be considered to be a pure σ-bonder to the iron, then it makes sense to adopt its p.q.s. (= σ − π contribution according to Bancroft *et al.*[4]) as zero. Few (if any) p.q.s. values should then be negative. The numbers so determined are also in Table 3. In our computations we used values of Bancroft *et al.*[4] to determine the signs of the quadrupole splittings. Where we could not make

Table 3 Partial quadrupole splittings (mm s^{-1}) and literature data

Ligand	Computed p.q.s. (Cl) = -0.27^a	Literature values^b p.q.s. (Cl) = -0.27	Computed p.q.s. (H) = 0.00
Br	-0.27	-0.26	0.82
Cl	-0.27	-0.27	0.80
H$_2$	-0.32	—	0.74
N$_2$	-0.21	-0.37	0.78
MeCN	-0.41	—	0.64
depb/2	-0.60	-0.54	0.49
depe/2	-0.63	-0.62	0.45
CO	-0.65	-0.74	0.43
C$_2$H$_4$	-0.64	—	0.42
dmpe/2	-0.69	-0.70	0.39
CNBu^t	-0.72	—	0.33
CNMe	-0.74	—	0.33
CCPh	-0.86	—	0.22
H	-1.10	-1.04	0.00

^{a} Values for CCPh were calculated using these p.q.s., giving -0.45 [p.q.s. (Cl) = -0.27] and 0.64 [p.q.s. (H) = 0.00] mm s^{-1}. ^{b} Ref. 6, discusses these values at some length. Other values are found in references 3, 4 and 5.

reasonable assignments, the compounds were ignored. In addition, where the q.s. values themselves were too small reliably to be determined, these values were omitted from the computations. The calculated values for these compounds from the computed p.q.s. are also presented in Table 1, based both on values of -0.27 for Cl and 0.00 for H. The correlation coefficients are 0.996 and 0.997, respectively. The standard errors are significantly less for p.q.s. (H) = 0.00 compared to p.q.s. (Cl) = -0.27, a reflection no doubt of the fact that the calculations involve only seven compounds containing Cl but 11 containing H. We regard the former [p.q.s. (H) = 0.00] values as more satisfactory. The calculated (or computed) and the experimental values are in reasonable agreement. This also enables us to calculate a p.q.s. for the vinylidene ligand, and assign the sign of the q.s. for [FeCl(CCHPh)(dmpe)$_2$][BPh$_4$] as positive.

(iii) Significance of the Data.—Our results extend the literature data for low-spin iron(II) octahedral complexes to a new set of compounds, primarily based upon dmpe. The extra ligands include H$_2$, C$_2$H$_4$ and CCPh, and we have modified the literature data for ligands such as CO and N$_2$. Our data have generally been obtained by considering several comparable compounds, whereas the literature value for CO, for example, was obtained using less appropriate materials, such as [Fe(SnCl$_3$)$_2$(CO)$_4$] and [FeH$_2$(CO)$_4$].[5]

Bancroft *et al.*[3–5] interpret the isomer shifts for iron in terms of a measure of σ donation and π-back bonding of the ligands (σ + π), both of which lead to an increase in s-electron density at the nucleus and a decrease in isomer shift. Expressed alternatively, p.i.s. = $-k(\sigma + \pi)$. On this basis, Br and Cl (Table 2) are probably poor σ donors, their bonds to iron being largely ionic. Phenylvinylidene must be a very strong π acceptor, comparable to NO$^+$ for which a value of -0.20 mm s^{-1} has been reported.[3] Hydrogen (H) must be a pure σ donor, the effect of which is comparable to the combined (σ + π) effects of N$_2$ and H$_2$. Ethylene is probably a better σ donor in these compounds than might have been expected, and CO is clearly a better (σ + π) donor than N$_2$, in agreement with current dogma.[8] The other data in Table 2 are much as one might expect.

Again using the analysis of Bancroft *et al.*,[3–5] the p.q.s. values, which also have a lattice component which we have ignored,

become more negative with increased σ bonding but more positive with increased π-back bonding. This can be expressed formally as p.q.s. = $-q_{\text{lattice}} - C(\sigma - \pi)$. We did attempt to introduce a single constant q_{lattice} term into our calculations of the p.q.s. data involving ionic complexes in Table 3, but this produced worse fits. Consequently, we feel justified in making $q_{\text{lattice}} = 0$.

It is clear that the p.q.s. values do not parallel the p.i.s. values discussed above. Indeed they could only do so were the π contributions to the metal–ligand bond to be zero, although σ effects on p.i.s. and p.q.s. values are believed to predominate over π influences.[5] It is reassuring that H has by far the most negative p.q.s., and is presumably a pure σ-bonder. At the other end, Cl and Br are both poor σ and π donors, which agrees with their positions. Dinitrogen and H$_2$ again come close together, suggesting not only that their summed σ and π contributions are similar, but that the absolute contributions are similar, too. This is also consistent with displacement of H$_2$ by N$_2$ postulated in nitrogenases and observed in many metal hydrides.[9] The CO value suggests that CO is a better σ donor than N$_2$ or H$_2$, and that this effect predominates over its π-bonding acceptance, since the latter would tend to make the p.q.s. more positive.

Finally, it is worth noting the position of CCPh and the calculated value for CCHPh. The former is presumably primarily a σ donor. The latter gives a calculated value of 0.64 [p.q.s. (H) = 0.0]. This is consistent with it being a poor σ donor and a good π acceptor, which is what we also infer from the p.i.s. values.

In summary, therefore, our new extended list of partial values for low-spin, octahedral, iron(II) complexes is more reliable than that in the literature. It also shows reasonable consistency with the generally accepted properties of ligands, whether the complexes considered are charged or not, and should therefore have some predictive value for new hitherto uninvestigated complexes.

Experimental

The compounds were prepared as described in the literature.[1] Mössbauer spectra were determined on an ES Technology MS-105 Mössbauer spectrometer with a 25 mCi ^{57}Co source in a rhodium matrix. Spectra were recorded at 77 K and referenced against iron foil at 298 K.

Acknowledgements

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