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First direct calculation of the partial quadrupole splitting of ligands for the prediction of Mössbauer spectra parameters in low-spin iron(II) complexes

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A semi-empirical quantum mechanics method and a cone angle conception were used to factorise partial quadrupole splitting parameters for different ligands in axially coordinated macrocyclic complexes.

The ^{57}Fe Mössbauer spectroscopy is one of the most powerful techniques for probing the metal centre in inorganic and organometallic compounds of iron.[1] In spite of large progress in the theoretical analysis of Mössbauer spectra parameters on the basis of modern quantum theory methods, such as DFT and *ab initio*,[2] the partial quadrupole splitting (p.q.s.) and partial central shift (p.c.s.) models for the prediction of Mössbauer spectra parameters are still popular and useful in the case of low-spin iron(II) compounds.[3] The p.q.s. parameters have been introduced, developed and successfully applied over the last 20 years.[3,4] The p.q.s. model is attractive because of the following: (i) tabulated p.q.s. values already contain the sum of all ligand properties on which the experimental quadrupole splitting ( ) depends; (ii) the experimental geometries of compounds are not required; (iii) experimental values can be easily estimated 'by hand' {see, for instance, equations (1) and (2) for the estimation of in *trans*-[FeA$_2$B$_4$] and *trans*-[FeACB$_4$] complexes}.[3] The application of equations (1) and (2) to the pcFeL$_2$, pcFeL′L″, nx$_2$FeL$_2$ and nx$_2$FeL′L″ complexes, where [B] is pc/4, dmg/2 or nx/2, [A] is L or L′, and [C] is L″, leads to the estimation of values for the complexes of interest.

$$= 4\,\text{p.q.s.(A)} - 4\,\text{p.q.s.(B)} \qquad (1)$$

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

The p.q.s. values can be found from experimental values[3] or from structural parameters of the corresponding complexes.[4] However, the factorisation of the p.q.s. of new ligands without a wide range of experimental data is a difficult problem. Here, we consider the relationship between the electronic and geometric structures of ligands and the p.q.s. values in low-spin iron(II) complexes. The first direct calculations† of p.q.s. given below can be easily used for the calculations of p.q.s. values of unknown ligands.

In general, the p.q.s. values include the following three main contributions:

(i) A 'lattice' contribution, which depends on the ligand charge or, more correctly, the ligand coordination atom (LCA) and on the distance between the LCA and the iron atom. This interaction leads to a change in the lattice contribution to p.q.s. Usually, for low-spin iron(II) complexes, this lattice contribution is small and can be neglected.[1] However, recent DFT calculations in a local density approximation for the oepFe(pme$_3$)$_2$ complex[2(*a*)] have shown that at least in some cases the lattice contribution can play a dominant role.

Table 1 Ligand parameters estimated from experimental data and calculated p.q.s. values.

L[a]	$-V_{\text{MEP}}$/eV	V_b/eV	$C\times10^2$	T	p.q.s. (calc.)	p.q.s. (exp.)[b] [Ref.]
nh$_3$	3.09	0.035	−1.0	93	−0.54	−0.52 [3(*b*), 4]
n-prnh$_2$	3.24	0.036	−0.65	110	−0.46	−0.48 [4]
s-bunh$_2$	3.28	0.035	−0.75	113	−0.44	−0.45 [this work[c]]
t-bunh$_2$	3.35	0.036	−0.77	129	−0.36	−0.36 [this work[c]]
phnh$_2$	2.45	0.036	1.4	110	−0.44	−0.43 [this work[c]]
mepip	3.13	0.036	−0.27	123	−0.39	−0.39 [this work[c]]
mph	3.02	0.038	−0.25	123	−0.39	−0.38 [this work[c]]
14en	3.84	0.03	−0.82	110	−0.5	−0.48 [this work[c]]
dabco	2.99	0.041	0.05	145	−0.27	−0.24 [this work[c]]
py	2.86	0.093	−0.87	100	−0.51	−0.48 [this work[c]]
4ohpy	2.99	0.091	−1.46	100	−0.51	−0.51 [this work[c]]
4chopy	2.53	0.11	−0.76	100	−0.5	−0.5 [this work[c]]
tz	2.2	0.219	−0.47	100	−0.51	−0.52 [this work[c]]
meim	3.32	0.079	−1.6	98	−0.53	−0.53 [4]
pzl	2.67	0.087	−1.4	98	−0.51	−0.51 [this work[c]]
tzl	2.91	0.096	−2.05	98	−0.51	−0.53 [this work[c]]
t-bunc	2.07	0.319	1.9	76	−0.68	−0.72 [3(*d*)]
phnc	2.04	0.362	1.6	76	−0.68	−0.7 [3(*b*)]
cn$^-$	8.59	0.165	−2.5	76	−0.86	−0.84 [4]
co	1.51	0.633	5.5	78	−0.75	−0.74 [3(*d*)]
pet$_3$	1.9	0.12	26.29	118	−0.59	−0.59 [this work[c]]
pobu$_3$	0.59	0.368	32.96	109	−0.69	−0.68 [this work[c]]
tht	1.28	0.1	8.5	122	−0.4	−0.41 [this work[c]]
pc^{2-}	11.97	0.06	−1.57	85	−0.93	−0.96 [4]
Hdmg$^-$ Hnx$^-$	12.07	0.048	−0.32	85	−0.94	−0.92 [4]

[a] Abbreviations: 14en, 1,4-diaminobutane; 4ohpy, 4-hydroxypyridine; 4chopy, pyridine-4-carbaldehyde; bu, butyl; dabco, diazabicyclooctane; meim, *N*-methylimidazole; mepip, 4-methylpiperidine; mph, morpholine; nh$_3$, ammonia; ph, phenyl; pr, propyl; py, pyridine; pzl, pyrazole; tht, tetrahydrothiophene; tz, 1,2,4,5-tetrazine; tzl, 1,2,4-triazole; . [b] p.q.s. in mm s^{-1}. The p.q.s.(Cl$^-$) = −0.27 mm s^{-1} scale has been used for all values, see ref. 3. [c] All p.q.s. values from this work are based on the pcFeL$_2$, (Hnx)$_2$FeL$_2$ and (Hdmg)$_2$FeL$_2$ complexes, where pc^{2-} is the phthalocyanine dianion, Hnx$^-$ is the nioximate anion and Hdmg$^-$ is the dimethylglioximate anion.[11]

(ii) A 'valence' contribution, which arises from the - and -interaction between iron and LCA atom orbitals and leads to a change of the effective population of iron atom orbitals. For example, the -donation of electron density by a ligand changes the effective population of 3*d* and 4*p* orbitals of the iron atom. The relationship between the - and -donor and -acceptor properties of ligands and the and p.q.s. values have been widely discussed.[3]

(iii) A 'steric' contribution of the ligand, on which the metal–ligand distance and, correspondingly, the metal–ligand interaction depends. The influence of cone angle on p.q.s. parameters for phosphorus-containing ligands was discussed recently.[3(*f*)]

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† All computations were performed using the HyperChem 5.1 Pro program (HyperCube Inc.) on a Pentium PC. All ligand structures were fully optimised by the gradient Polak–Ribiere method at the semi-empirical AM1 level.[7] The molecular electrostatic potential (V_{MEP}) and the 'molecular back-bonding potential' (V_b) were evaluated as described previously.[5] The ligand resonance integrals were calculated in the NDO formalism.[8] Steric parameters of axial ligands were evaluated from a cone angle conception.[6] The effective van der Waals radius of the -system was chosen as 1.7 Å.[9] Multiparameter regression analysis was carried out by the Powell quadratic convergence method.[10]

Thus, an increase in the cone angle of a ligand probably leads to the elongation of the Fe–LC A bond. This elongated Fe–LCA bond decreases the overlap between the lone-pair orbital of the ligand and the 3*d* and 4*p* orbitals of iron and hence leads to a change in . Note that this statement is true only for conformationally rigid ligands. From the above, we can conclude that the p.q.s. values for each ligand depend on the - and -donor and -acceptor properties, the LCA charge and the cone angle.

Recently, Fielder *et al.*[5] have developed a model for the calculation of the - and -donor and -acceptor capabilities of ligands. In this model, the - and -donor properties were evaluated from the molecular electrostatic potential function, V_{MEP}, while the -acceptor properties were derived using the second-order perturbation theory, and we adopt these two parameters (V_{MEP} and V_{b}) for factorisation of the electronic structure of ligands. The 'lattice' contribution of ligands to p.q.s. can be roughly proportional to

$$C = Z_{\mathrm{LCA}}/r^3 \qquad (3)$$

Where Z_{LCA} is the LCA charge, and r is the probe atom–LCA distance. The steric factors of ligands were evaluated using the cone angle conception.[6] The final expression for evaluating the p.q.s. values is the following:

$$\text{p.q.s. (calc.)} = a_0 + a_1 V_{\mathrm{MEP}} + a_2 V_{\mathrm{b}} + a_3 C + a_4 T, \qquad (4)$$

where T is the cone angle of the ligand,[6] C is the 'lattice' contribution of LCA and V_{MEP} and V_{b} were derived as described previously.[5] The results obtained for 25 ligands are presented in Table 1. The final parameters are $a_0 = -0.96172$ mm s^{-1}, $a_1 = -0.03752$ mm s^{-1} eV^{-1}, $a_2 = -0.20849$ mm s^{-1} eV^{-1}, $a_3 = -0.75555$ mm s^{-1} au^{-1}, $a_4 = 0.0057$ mm s^{-1} deg^{-1} with the correlation coefficient 0.995 for 25 compounds with a root-mean-square error of 0.018 mm s^{-1}. Our correlation line combines different classes of ligands (alkyl- and arylamines, six- and five-membered heterocycles, isonitriles, carbon monoxide, sulfides, phosphines and phosphites). An increase in the - and -donor or -acceptor properties of ligands leads to a decrease in the p.q.s. values, this is consistent with qualitative assumptions.[3,4] As can be concluded from the results of the above regression analysis, an increase in the steric effect of ligands leads to an increase in the p.q.s. value, in accordance with experimental data.[3(*f*)] It is interesting that the cone angle is more important for most of the ligands, as compared to V_{MEP} and V_{b}, which are important only for ligands with strong -donor and/or -acceptor properties, while C is important only for phosphorus-containing ligands with a good agreement with recent DFT calculations. The values of , both calculated from equations (1) and (2) and experimental, for macFeL$_2$ and macFeL′L′′ complexes, where mac is pc^{2-}, Hdmg$^-$ or Hnx$^-$, are presented in Table 2. The correlation coefficient $r^2 = 0.975$ with a root-mean-square error of 0.10 mm s^{-1} for 27 complexes has been observed. The computed values are lower than the experimental data. Probably, this fact suggests that the cone angle conception for pc^{2-} and Hnx$^-$ is not a good estimation. Really, the recomputed values, in which experimental p.q.s. values were used for macrocyclic ligands, are in better agreement with experimental values (Table 2).

Table 2 Calculated and experimental values for macFeL$_2$ and macFeL′L′′ complexes.

Complex	(calc.)	(calc.)[a]	(exp.) [ref.]
pcFe(*n*-prnh$_2$)$_2$	1.88	2.00	1.97 [11(*b*)]
pcFe(*s*-bunh$_2$)$_2$	1.96	2.08	2.04 [11(*c*)]
pcFe(*t*-bunh$_2$)$_2$	2.32	2.40	2.38 [11(*a*)]
pcFe(phnh$_2$)$_2$	1.96	2.08	2.11 [11(*b*)]
pcFe(mepip)$_2$	2.20	2.28	2.28 [11(*c*)]
pcFe(mph)$_2$	2.20	2.28	2.31 [11(*c*)]
pcFe(dabco)$_2$	2.68	2.76	2.89 [11(*d*)]
pcFe(14en)$_2$	1.80	1.84	1.84 [11(*c*)]
pcFe(py)$_2$	1.68	1.80	2.02 [11(*d*)]
pcFe(4chopy)$_2$	1.70	1.84	1.84 [11(*d*)]
pcFe(4ohpy)$_2$	1.72	1.84	1.80 [11(*d*)]
pcFe(tz)$_2$	1.64	1.80	1.79 [11(*d*)]
pcFe(meim)$_2$	1.60	1.72	1.71 [this work]
pcFe(pzl)$_2$	1.68	1.80	1.79 [this work]
pcFe(tzl)$_2$	1.64	1.80	1.73 [this work]
pcFe(*t*-bunc)$_2$	0.96	1.12	0.80 [11(*d*)]
pcFe(phnc)$_2$	0.96	1.12	0.68 [11(*d*)]
pcFe(co)$_2$	0.72	0.84	0.82 [11(*d*)]
pcFe(pet$_3$)$_2$	1.40	1.48	1.47 [11(*d*)]
pcFe(pobu$_3$)$_2$	0.96	1.08	1.09 [this work]
pcFe(tht)$_2$	2.12	2.24	2.20 [11(*d*)]
pcFe(nh$_3$)(co)	1.12	1.24	1.02 [11(*d*)]
pcFe(py)(co)	1.20	1.34	1.19 [11(*d*)]
(Hnx)$_2$Fe(*n*-bunh$_2$)$_2$	1.92	1.84	1.83 [11(*a*)]
(Hnx)$_2$Fe(py)$_2$	1.72	1.64	1.79 [11(*a*)]
(Hnx)$_2$Fe(4chopy)$_2$	1.76	1.68	1.68 [11(*a*)]
(Hdmg)$_2$Fe(py)$_2$	1.72	1.64	1.67 [1]

[a] Calculated using p.q.s. values of –0.96 and –0.92 for pc^{2-} and Hnx$^-$, respectively.

Thus, we have proposed a new technique for the estimation of generally usable ligand p.q.s. values. The correlation coefficient obtained with a small root-mean-square error for p.q.s. values indicates that the proposed technique is a simple and correct tool for predicting values in inorganic and organometallic compounds.

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