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A Simple and General Method to Determine Reliable Pseudocontact Shifts in Lanthanide Complexes

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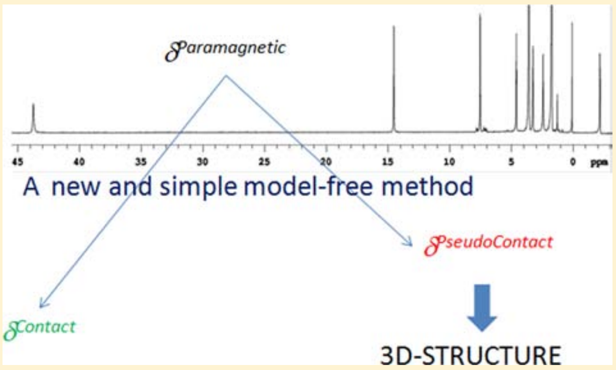
ABSTRACT: Pseudocontact shifts (PCS) contain a wealth of geometric information, which makes paramagnetic NMR one of the best methods for accurate geometric determinations in solution. It is well-known that PCS are intrinsically linked to Fermi contact (FC) shifts, and the separation of the two terms is achieved through linearization methods, which heavily rely on (a) isostructurality (even concerning a labile axial site) and (b) the validity of Bleaney's constants. Recently we proposed a method that circumvents both assumptions in the case of axially symmetric complexes, and presently we generalize it to lower symmetry. Our method is model-free and thus does not rely on any structural hypothesis. Our results compare very well with recently published data obtained through an accurate ab initio approach.



INTRODUCTION

Interest in small- to medium-size lanthanide complexes has constantly been renewed. One or two decades ago, these compounds would mostly find application as contrast agents (CAs) in magnetic resonance imaging (MRI)[1,2] or as selective Lewis acid catalysts in organic synthesis. Nowadays, one may cite organic light-emitting diodes (OLEDs),[3−5] chemical and bio probes (lanthanide luminescent bioprobes, LLBs),[6−9] lasers,[10,11] photovoltaics,[12−14] and single-molecule magnets (SMM).[15] This variety of uses primarily stems from the extraordinary optical and magnetic properties of these ions: (i) long excited-state lifetime and large Stokes shift;[5] (ii) sharp absorption and emission lines; and (iii) paramagnetism for most elements of the series.[16,17] For structural investigation, X-ray diffraction in the solid state can be complemented by very accurate solution studies made possible by paramagnetic NMR.[16−19]

Paramagnetism is responsible for two contributions that add to the conventional (diamagnetic) chemical shift of any NMR-active nucleus, called Fermi contact (FC) and pseudocontact shift (PCS). The latter (PCS) brings about a wealth of structural information, which is the basis for accurate solution geometry determination. The separation of PCS and FC contributions to the total shift can be achieved through several methods, whose true merit has been impossible to assess so far due to the lack of independent sources of PCS or FC. Only the quality of the fit (e.g., RMS or reasonable structural parameters) of the set of PCS′ to some geometry would provide a test of the reliability of the separation protocol.[16,20] Unfortunately, this procedure is largely tautological, because in principle one would use the PCS to determine the geometry, and the "accuracy" of the geometry itself to validate the PCS: in such a way the two objects are strongly correlated. Only in cases of largely overdetermined systems may one claim internal consistency as a valid parameter.[21,22]

Recently, Platas-Iglesias and co-workers[23] published a density functional theory (DFT) calculation of FCs from first principles, which provides a benchmark set of FC values to test separation methods and which indeed revealed some inconsistency in previously reported data.[24]

We proposed a variation of the popular so-called Reilley protocol to determine PCS and FC, which avoids the somewhat unnatural assumption intrinsic in the original method,[25,26] and we wish to test whether it performs better by comparing our FCs with those reported by Platas-Iglesias and co-workers.[23] We shall demonstrate that our method allows one to separate Fermi contact and pseudocontact shifts quite reasonably (i.e., in good to excellent agreement with the FCs obtained through ab initio methods) while avoiding any assumption on the structure of the complex. We have already demonstrated that our method is robust in the case of axially symmetric complexes (containing a C_3 or higher symmetry axis), and here we shall see that it can be extended also to a system with lower symmetry (following NMR data it is apparently D_2).

OUR MODEL-FREE METHOD

In a mononuclear lanthanide complex based on the ion Ln^{3+}, the observed shift of a nucleus i can be written as the sum of two contributions: one is the diamagnetic shift, δ^{dia}, which is the part that does not depend on the additional local field determined by the anisotropic distribution of unpaired electrons in the f orbitals; the remaining part is called

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paramagnetic shift, δ^{para}. The paramagnetic shift can be further partitioned into a Fermi contact (FC or δ^{FC}) and a pseudocontact shift (PCS or δ^{PC}). The FC rapidly loses importance with increasing number of bonds between i and Ln. In most cases, FC is strongly reminiscent of scalar (J) couplings between $^1/_2$ spins (notably ^{1}H) in ordinary diamagnetic spectra, and it is relevant only for nuclei 2−4 bonds away from the lanthanide. In the common case of three bonds, a Karplus-type trend has been observed, whereby vicinal nuclei antiperiplanar to Ln exhibit the largest FC.[17] For the PCS, it is commonly assumed that the unpaired spin density is localized on the Ln^{3+} nucleus (metal-centered point−dipole-point-dipole approximation), which is justified by the compact radial function of f orbitals[18] and bears relevant geometric information.

The paramagnetic term vanishes for Ln = La or Lu, which are diamagnetic, and the PCS would be negligible for Gd, on account of its f^7 configuration (which lacks the necessary anisotropy), but its FC cannot be measured because of the extensive line broadening brought about by the long electronic relaxation time of this ion. In the hypothesis of isostructurality, one can write

$$\delta_{i,\text{Ln}}^{\text{obs}} = \delta_{i,\text{Ln}'}^{\text{dia}} + \delta_{i,\text{Ln}}^{\text{para}} \tag{1}$$

where Ln′ = La or Lu. Taking advantage of a well-established treatment, one can write

$$\begin{aligned}\delta_{i,\text{Ln}}^{\text{para}} &= \delta_{i,\text{Ln}}^{\text{FC}} + \delta_{i,\text{Ln}}^{\text{PCS}}\\ &= \frac{A_i}{\hbar\gamma B_0}\langle S_z\rangle_{\text{Ln}} + \frac{1}{2N_A r_i^3}\Bigg[\left(\chi_{zz}^{\text{Ln}} - \frac{1}{3}\text{Tr}(\chi^{\text{Ln}})\right)\\ &\quad (3\cos^2\theta_i - 1) + (\chi_{xx}^{\text{Ln}} - \chi_{yy}^{\text{Ln}})(\sin^2\theta_i \cos 2\varphi_i)\Bigg]\\ &\quad + \frac{1}{N_A r_i^3}\Big[\chi_{xy}^{\text{Ln}} \sin^2\theta_i \sin 2\varphi_i + \chi_{xz}^{\text{Ln}} \sin 2\theta_i \cos\varphi_i\\ &\quad + \chi_{yz}^{\text{Ln}} \sin 2\theta_i \sin\varphi_i\Big]\end{aligned} \tag{2}$$

where A_i and γ_i are respectively the hyperfine coupling constant and magnetogyric ratio of the resonant nucleus i, B_0 is the applied magnetic field, $\langle S_z\rangle_{\text{Ln}}$ is the expectation value of the S_z operator for the specific lanthanide, N_A is Avogadro's number, χ^{Ln} is the Ln^{3+} magnetic susceptibility tensor, and r_i, θ_i, and φ_i are the spherical coordinates of the resonating nucleus in a polar system centered on the lanthanide metal ion.

In the principal system of the magnetic susceptibilty tensor χ^{Ln}, the off-diagonal components of type χ_{xy}^{Ln} vanish and one can write a simplified equation, which reduces to

$$\delta_{i,\text{Ln}}^{\text{para}} = F_i\langle S_z\rangle_{\text{Ln}} + [D_{1,\text{Ln}}G_i + D_{2,\text{Ln}}H_i] \tag{3}$$

The expressions for the various terms are as follows, expressed in the principal axes systems of the tensor χ^{Ln}:

$$D_{1,\text{Ln}} = \frac{1}{2N_A r_i^3}\left[\chi_{zz}^{\text{Ln}} - \frac{1}{3}\text{Tr}(\chi_{zz}^{\text{Ln}})\right]$$

$$D_{2,\text{Ln}} = \frac{1}{2N_A r_i^3}(\chi_{xx}^{\text{Ln}} - \chi_{yy}^{\text{Ln}})$$

$$F_i = \frac{A_i}{\hbar\gamma_i B_0}$$

$$G_i = (3\cos^2\theta_i - 1)$$

$$H_i = (\sin\theta_i \cos 2\varphi_i)$$

The terms D_1 and D_2 are also called axial and rhombic terms of the magnetic susceptibility.

Most separation methods rely on Bleaney's theory, which relates PCS, through the terms D_1 and D_2, to the crystal field parameters $B_0{}^2$ and $B_2{}^2$, which are independent of the lanthanide but only on the complex through the expressions

$$\begin{aligned}D_{1,\text{Ln}} &= C_{\text{Ln}}B_0{}^2\\ D_{2,\text{Ln}} &= \sqrt{6}\,C_{\text{Ln}}B_2{}^2\end{aligned} \tag{4}$$

the factors C_{Ln} (Bleaney's factors) are tabulated.[16,17] Validity of Bleaney's theory has been discussed,[27,28] with the evidence that other crystal field terms may contribute to eq 4 and moreover the constant may differ from theoretical Bleaney's values. Our treatment does not rely on eq 4 but we admit only that the terms D_1 and D_2 remain proportional ($D_{1,\text{Ln}} = rD_{2,\text{Ln}}$) to one another throughout the series, which permits us to write

$$\delta_{i,\text{Ln}}^{\text{para}} = F_i\langle S_z\rangle_{\text{Ln}} + D_{1,\text{Ln}}[G_i + rH_i] \tag{5}$$

The proportionality constant r is unknown.

Following ref 25, in the first step of our separation protocol one must choose one compound as the reference and, for each of the other Ln compounds, one must plot all the $\delta_{i,\text{Ln}}^{\text{para}}$ values versus those of the reference, $\delta_{i,\text{ref}}^{\text{para}}$, which yields the slopes m_{Ln} (forcing the fit through the origin).

At this point, it is possible to follow eq 5, replacing $D_{1,\text{Ln}}$ with the product $m_{\text{Ln}}D_{1,\text{ref}}$ and to plot, for each nucleus i, $\delta_{i,\text{Ln}}^{\text{para}}/\langle S_z\rangle_{\text{Ln}}$ versus $m_{\text{Ln}}/\langle S_z\rangle_{\text{Ln}}$. These data are again linearly interpolated (this time not forcing the fit through the origin): the slopes M_i and the intercepts Q_i are the FC and PCS of the nucleus i in the reference complex. In mathematical terms, this approach can be translated as

$$m_{\text{Ln}} \approx \frac{D_{1,\text{Ln}}}{D_{1,\text{ref}}} \tag{6}$$

$$\frac{\delta_{i,\text{Ln}}^{\text{para}}}{\langle S_z\rangle_{\text{Ln}}} = F_i + m_{\text{Ln}}D_{1,\text{ref}}[G_i + rH_i] \tag{7}$$

$$\begin{aligned}Q_i &= F_i = \delta_{i,\text{ref}}^{\text{FC}}/\langle S_z\rangle_{\text{ref}}\\ M_i &= D_{1,\text{ref}}[G_i + rH_i] = \delta_{i,\text{ref}}^{\text{PCS}}\end{aligned} \tag{8}$$

Or equivalently

$$\begin{aligned}\delta_{i,\text{Ln}}^{\text{FC}} &= Q_i\langle S_z\rangle_{\text{Ln}}\\ \delta_{i,\text{Ln}}^{\text{PCS}} &= M_i m_{\text{Ln}}\end{aligned} \tag{9}$$

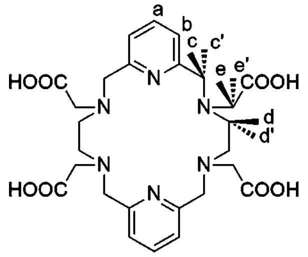
In such a way we can obtain the FC and PCS terms without assuming a structure, although we must admit isostructurality throughout the series. This latter may not be correct if there is a variable coordination number, for example, because of solvent, water, or other ancillary ligands. In the case of axially symmetric complexes, we demonstrated that this does not introduce a problem and that our treatment is perfectly fit to treat it. In rhombic systems, this may not be the case, because the terms D_1 and D_2 are likely to be differently affected by the occupancy of a further site. This implies that the term r in eqs 5 and 8 may not be constant. In this case the whole treatment would fail.

We must also recall that eq 6 is only approximate and may not be valid, which has been discussed in our previous work.[25]

■ RESULTS

We presently reanalyze the data published by Geraldes and co-workers[24] in 2002, relative to a series of Ln^{III} complexes (Ln = La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Lu^{3+}) with 3,6,14,17,23,24-hexaazatricyclo[17.3.1.1]tetracosa-1(23),8(24),9,11,19,21-hexaene-3,6,14,17-tetraacetic acid (H_4L or $Py_2N_6Ac_4$), displayed in Chart 1.

Chart 1



$Py_2N_6Ac_4$ (L)

They published an almost complete set of ^1H shifts for all complexes and we were thus able to extract the slopes of the linear plots $\delta_{i,Ln}^{para}$ versus $\delta_{i,Pr}^{para}$: we chose Pr^{3+} as the reference compound, because all the shifts were available and it has one of the lowest FC/PCS ratios.[25] We discarded Sm^{3+}, because of its very small value of $\delta_{i,Sm}^{para}$ (they are intrinsically small because of the Bleaney's factor). The results are displayed in Table 1.

Table 1. Slopes m_{Ln} of Linear Plots of $\delta_{i,Ln}^{para}$ versus $\delta_{i,Pr}^{para}$

	Ln						
	Ce	Nd	Eu	Tb	Dy	Ho	Er
m	0.58	0.47	−0.77	5.61	5.31	1.73	−4.4
R	0.99	0.79	0.82	0.94	0.96	0.52	0.89

The fact that we obtain good linear fits (with the exception of Ho and to a lesser extent Nd) for all $[Ln(Py_2N_6Ac_4)]^-$ can be taken as a good indication of isostructurality in solution.

With these slopes m_{Ln} we built the plots $\delta_{i,Ln}^{para}/\langle S_z\rangle_{Ln}$ versus $m_{Ln}/\langle S_z\rangle_{Ln}$ shown in Figure 1 and summarized in Table 2.

The data for protons b and a are heavily scattered, and consequently they show a poor correlation coefficient *R*. Considering their rather small paramagnetic shifts, we suspect that some inconsistency may have occurred in their assignment in the various spectra. Luckily, this has very little consequence in the present treatment, because poorly shifted signals do not contribute to the determination of the first slopes *m*.

The data reported in Table 2 allow one to calculate the PCS and FC contributions to the paramagnetic shift of any lanthanide compound, through eq 9, and we chose Tb-$(Py_2N_6Ac_4)$, because we aim at comparing our results with those obtained by means of ab initio calculations (by Platas-Iglesias and co-workers[23]) and by the conventional Reilley method (by Geraldes and co-workers[24]), as displayed in Table 3.

Platas-Iglesias and co-workers[23] calculated the PCS values as the difference from the total paramagnetic shift and the FC contribution they had obtained from ab initio calculations starting from the crystal structure of $[Tb(Py_2N_6Ac_4)]^-$. We may immediately appreciate that there is a remarkable similarity between the PCS values obtained by our method and those obtained through computations. On the contrary, the difference with standard Reilley separation is striking for most protons.

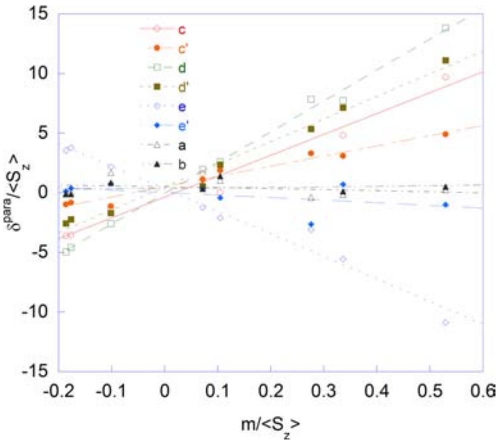


Figure 1. Linear plots $\delta_{i,Ln}^{para}/\langle S_z\rangle_{Ln}$ vs $m_{Ln}/\langle S_z\rangle_{Ln}$, as described in the text. The reference compound is the Pr complex (which by definition has slope m = 1).

Table 2. Intercepts, Slopes, and Correlation Coefficients of the Linear Fits Shown in Figure 1

proton	*Q*	*M*	*R*
c	−0.35	17.5	0.98
c′	0.50	8.61	0.98
d	−0.031	25.8	0.99
d′	0.46	19.0	0.99
e	0.35	−18.9	0.98
e′	0.015	−2.15	0.49
a	0.48	0.79	0.29
b	0.40	0.43	0.21

As we mentioned in the Introduction, the main reason for dealing with pseudocontact shifts is for accurate geometric determination in solution. Geraldes and co-workers[24] used the PCS separated through the Reilley method to testify to the persistence of the crystal structure of $[Ln(Py_2N_6Ac_4)]^-$ in solution. To this end, they analyzed their PCS through the program Shift Analysis, which produced a questionable result: the principal axes of the magnetic anisotropy tensor are very far from the C_2 axes of the D_2-symmetric complex, which is against a fundamental requirement (Neumann's principle). On the contrary, the values obtained via the protocol suggested by Platas-Iglesias and co-workers[23] completely reconcile the crystal structure with paramagnetic NMR: not only has the agreement factor improved but also there is coincidence between the tensor and the symmetry axes.

Our values are very close to these latter ones and, not surprisingly, they also fit very well the crystal structure with a symmetry-conserving magnetic susceptibility tensor. We interpreted the PCS for $[Tb(Py_2N_6Ac_4)]^-$ with our program PERSEUS,[19,29] and by keeping the geometry rigidly frozen to the XRD data, we obtained the excellent agreement factor AF = 3% (Table 4), with principal axes of the magnetic anisotropy tensor coincident (within less than 5°) with the symmetry axes.

The quality of the fit (in terms of the agreement factor) and the magnetic anisotropy parameters D_1 and D_2 compare very well with those reported in ref 23. This result confirms the

Table 3. Comparison between FC and PCS Contributions to the Paramagnetic Shift $\delta_{i,\mathrm{Tb}}^{\mathrm{para}}$ for $[\mathrm{Tb(Py_2N_6Ac_4)}]^{-}$ [a]

	exptl[24]	Reilley method[24]		ab initio[23]		this work	
proton	$\delta_{i,\mathrm{Tb}}^{\mathrm{para}}$	$\delta_{i,\mathrm{Tb}}^{\mathrm{PC}}$	$\delta_{i,\mathrm{Tb}}^{\mathrm{FC}}$	$\delta_{i,\mathrm{Tb}}^{\mathrm{PC}}$	$\delta_{i,\mathrm{Tb}}^{\mathrm{FC}}$	$\delta_{i,\mathrm{Tb}}^{\mathrm{PC}}$	$\delta_{i,\mathrm{Tb}}^{\mathrm{FC}}$
c	112.8	85.7	27.0	108.1	4.7	98.2	11.1
c′	26.2	−12.2	38.5	55.1	−28.9	48.3	−15.9
d	145.9	103.9	42.0	147	−1	144.7	1.0
d′	70.8	9.7	61.0	118.1	−47.3	106.6	−14.6
e	−120.1	−96.2	−23.8	−129.9	9.8	−106.0	−11.1
e′	−12.2	−28.5	16.2	−0.1	−12.1	−12.1	−0.5
b	3.2	16.3	−13.0	6.2	−2.6	4.4	−15.3
a	−3.7	18.1	−21.9	−1.2	−2.9	2.4	−12.7

[a] From references 24 (here labeled Reilley method) and 23 (labeled ab initio).

Table 4. Results of Optimization of the Magnetic Anisotropy Tensor through PERSEUS[a]

proton	$\delta_{i,\mathrm{Tb}}^{\mathrm{PC\ exptl}}$ [b]	$\delta_{i,\mathrm{Tb}}^{\mathrm{PC\ calcd}}$ [c]	
a	2.4	−0.99	
b	4.4	9.29	
c	98.2	96.51	AF = 0.03[d]
c′	48.3	49.65	
d	144.7	142.92	D_1 = 5460 (50)
d′	106.6	108.33	D_2 = −5420 (70)
e	−106.0	−107.11	
e′	−12.1	−10.49	

[a] Based on the XRD structure of $[\mathrm{Tb(Py_2N_6Ac_4)}]^{24-}$ and the values of PCS determined through our separation method and reported in Table 3. [b] As experimental values we took the result of our separation method, as described in the text and shown in Table 3. [c] Calculated through the routine PERSEUS. [d] Agreement factor is calculated as

$$\mathrm{AF} = \left[\sum_i \delta_i^{\mathrm{PC,exp}} - \delta_i^{\mathrm{PC,calc}} / \sum_i (\delta_i^{\mathrm{PC,exp}})^2\right]^{1/2}$$

similarity between PCS values obtained in the present work and in Platas-Iglesias's works.

CONCLUSIONS

With this work we demonstrated that our double-linearity method to separate PCS and FC contributions to the paramagnetic shift in $\mathrm{Ln^{III}}$ complexes can be extended to non-axially symmetrical systems. This is a simple model-free method, purely based on the numerical analysis of experimental data, without the necessity to know or hypothesize the geometry of the complex. It provides results in very good agreement with a set of values obtained by means of a sophisticated DFT approach, which by necessity relies upon a precise knowledge of the geometry. The set of pseudocontact shifts fits very well the XRD geometry, demonstrating that it persists in solution.

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Notes

The authors declare no competing financial interest.

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