Simultaneous Determination of Ligand-Field Parameters of Isostructural Lanthanide Complexes by Multidimensional Optimization

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A new approach is proposed for the determination of the ligand-field (LF) parameters of a set of isostructural lanthanide complexes, and this approach is examined in terms of uniqueness and accuracy of the solutions. The method employs a multidimensional optimization algorithm to find a set of parameters that gives a least-squares fit to either or both of two types of experimental data, namely ^{1}H NMR paramagnetic shifts and the temperature dependence of the magnetic susceptibility. To produce an overdetermined situation, each LF parameter is approximated as a linear function of the atomic number of the lanthanide ion. Simultaneous use of the experimental data sets of multiple lanthanide complexes under this restriction efficiently reduces the range of possible solutions from that determined when using a data set of a single lanthanide complex. The use of either NMR or magnetic susceptibility experimental data does not give a complete conversion, although it can provide an approximate estimate of the LF parameters. It is demonstrated that a search for parameters that satisfy both types of experimental data sets is essential to obtain the unique solution.

Introduction

Studies of the magnetic properties of lanthanide compounds are often based exclusively on the LS-coupling scheme, with an implicit presumption that the ground electronic state with a total angular momentum J is $(2J + 1)$ degenerate. Lifting of the degeneracy by the ligand field is, however, not quite negligible in many lanthanide complexes, because the splitting can reach the order of 10^1-10^2 cm^{-1}. In such cases, information regarding the sublevel structure of the ground multiplet is vital in the study of their magnetic properties. Determination of the sublevel structure is, nevertheless, a difficult task, both experimentally and theoretically, in many cases.

The traditionally used approach to determine sublevel structures and ligand-field (LF) parameters is through analysis of the f−f absorption or luminescence spectrum. The energies of the f−f electronic spectral bands in the region from near-IR to UV, if they are available, are similar to those of free ions. The fine structure in each band is ascribed to LF splitting of the ground and excited multiplets and, therefore, contains direct information of the sublevel structures. In the cases where the fine structures are sharp enough to be separated from each other, it is possible to determine sublevel structures and LF parameters. The problem of this approach is obviously that it cannot be applied for the cases where neither a sharp absorption nor an emission spectrum is available.

Recently, Ishikawa et al. reported a study of interactions between the two f-electronic systems in a series of triple-decker phthalocyanine complexes that contained two lanthanide ions.[1,2] In the course of the research, LF parameters for the lanthanide ions in the complexes were determined by a different approach, using ^{1}H NMR and magnetic susceptibility data. The new approach is based on the following conjecture: for a series of isostructural lanthanide complexes, each LF parameter varies regularly as the atomic number of the lanthanide ion increases

and can be approximated as a linear function of the atomic number. A simplex multidimensional minimization algorithm was employed to find the set of LF parameters that reproduce both ^{1}H NMR paramagnetic shifts and the temperature dependence of the magnetic susceptibility. This approach turned out to be quite successful in determining such parameters, which led to elucidation of the nature of the f−f interaction within the dinuclear complexes.[2]

In this paper, a detailed description of the implementation of the new method for determination of the sublevel structures of trivalent ions of the later half of the lanthanide series is presented. Particular emphasis is placed on how the accuracy and uniqueness of the solution are improved through increases of the size of the experimental data set to be used. Experimental data for ^{1}H NMR paramagnetic shifts and the temperature dependence of magnetic susceptibility of $(Pc)_2Ln^-TBA^+$ (Ln = Tb, Dy, Ho, Er, Tm, or Yb; TBA^+ = tetra(*n*-butyl)ammonium cation), which are published in a separate paper,[3] are used for the demonstration. The $(Pc)_2Ln^-$ complexes have approximately D_{4d} symmetry, in which a lanthanide ion is sandwiched between two Pc ligands.[4] The number of LF parameters needed for each complex of this symmetry is three, which is the minimum number possible in the operator-equivalent formalization. Because of the small number, the present example has an important advantage over lower symmetry cases, in terms of the ease of graphical illustration of the distribution of determined parameter sets.

Method

Figure 1 illustrates the flow of the process. The first step is to generate an initial guess for the LF parameters. In the present paper, random numbers within a specific range were used. The next step enters the minimization procedure, which searches a set of parameters that give a local minimum for the root-mean-square (RMS) error from preprovided experimental data: that is, both or either of the ^{1}H NMR paramagnetic shifts $\Delta\delta$ and/or the temperature dependence of the $\chi_M T$ value (where χ_M

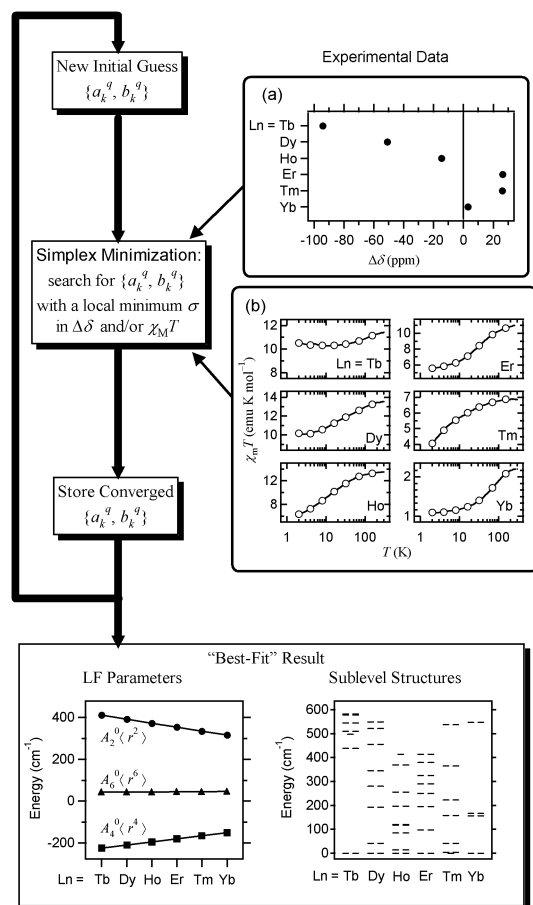* Author to whom correspondence should be addressed. E-mail: ishikawa@chem.titech.ac.jp.

Figure 1. Flowchart of the determination process of LF parameters. Experimental data shown on top right are (a) $\Delta\delta$ values and (b) $\chi_M T$ vs T plots of Ln(Pc)$_2^-$TBA$^+$ actually used in this paper. Details of the experimental data are described in ref 3.

is the molar magnetic susceptibility and T is the temperature, in Kelvin). As the minimizer, the standard simplex algorithm[5] was used. Thus-obtained parameters are stored, and the entire process is repeated with a new initial guess each time until the global minimum or the point regarded as such is reached. The "best-fit" result is the set of LF parameters to be determined, with which energies and wave functions of the sublevels of the ground multiples of the complexes are specified.

The computer program was written with MATLAB programming language,[6] and calculations were performed on a COMPAQ model AlphaServer GS320 system at the Global Scientific Information and Computing Center at the Tokyo Institute of Technology.

The $\Delta\delta$ and $\chi_M T$ values are calculated as follows. The trivalent ions in the later half of the lanthanide series with f^8−f^{13} electronic systems have the ground state with the total angular momentum $J = L + S$. The Hamiltonian for the $2J + 1$ substates of the ground multiplet under an external magnetic field is

$$\hat{H} = \beta(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{H} + \mathbf{F}$$

The first and second terms of the right-hand side are the Zeeman effect and the LF interaction, respectively.

The LF term is expressed by the operator equivalent in the notation by Abragam and Bleaney[7] as

$$\mathbf{F} = \sum_{q=0}^{2} A_2^q \langle r^2 \rangle \alpha \mathbf{O}_2^q + \sum_{q=0}^{4} A_4^q \langle r^4 \rangle \beta \mathbf{O}_4^q + \sum_{q=0}^{6} A_6^q \langle r^6 \rangle \gamma \mathbf{O}_6^q$$

The coefficients α, β, and γ are constants that were tabulated by Stevens.[8] The $\mathbf{O}_k^q$ matrices are the polynomials of J^2, J_z, J_-, and J_+, and their definitions are described in ref 7. The choice of which terms are included in the summation is dependent on the symmetry of the ligand field. The (Pc)$_2$Ln$^-$ complexes have a ligand field of D_{4d} symmetry, in which only three terms— $A_2^0\langle r^2 \rangle$, $A_4^0\langle r^4 \rangle$, and $A_6^0\langle r^6 \rangle$—are nonzero.

The coefficients $A_k^q \langle r^k \rangle$ are the parameters to be determined in the minimization calculation. To generate an overdetermined system, a restriction is imposed on the parameters so that each is expressed as a linear function of the number of f electrons, n:

$$A_k^q\langle r^k \rangle(n) = a_k^q + b_k^q(n - n_0) \qquad \text{(for } n = 8, 9,..., 13) \quad (1)$$

In the present paper, the value of n_0 is set at 10.5, which is the mean value of n. Under the restriction, a set of parameters that simultaneously reproduces experimental data of more than one lanthanide complex is sought. From the Hamiltonian, three principal values of the magnetic susceptibility per molecule are obtained: χ_{xx}, χ_{yy}, and χ_{zz}. The observed molar magnetic susceptibility χ_M for a powder sample is the product of the Avogadro number and the average of the three principal values χ_{xx}, χ_{yy}, and χ_{zz}:

$$\bar{\chi} = \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz})$$

The dipolar contribution in the ^{1}H NMR paramagnetic shift gives the relation of the axial anisotropy in the magnetic susceptibility and the geometric parameters:

$$\Delta\delta = \frac{3\cos^2\theta - 1}{2R^3}(\chi_{zz} - \bar{\chi})$$

Here, R is the distance between the paramagnetic center and the proton and θ is the azimuthal angle, with respect to the quantization axis.[9] For the calculations in this study, θ and R were estimated from the X-ray data for (Pc)$_2$Lu$^-$TBA$^+$, (Pc)$_2$Ho$^-$TBA$^+$, and (Pc)$_2$Gd$^-$TBA$^+$.[4]

Results and Discussion

1. Determination of LF Parameters Using an Experimental Data Set of a Single Compound. Before examining the method utilizing multiple data sets, this section tests the case where an experimental data set of a single complex is used. Figure 2 shows two examples: that is, the results for Tb (f^8) and Tm (f^{12}) complexes. Panel (1) in Figure 2 shows the set of $A_k^0\langle r^k \rangle$ parameters that gives a relative error of <3% from the observed $\Delta\delta$ value for the Tb complex. Each point has been obtained as a local minimum in the $A_k^0\langle r^k \rangle$ space. Not surprisingly, the points are spread over a wide range in the $A_k^0\langle r^k \rangle$ space, which indicates that the system is underdetermined.

The case that uses $\chi_M T$ values is shown in panel (2) of Figure 2. The relative RMS error from the selected experimental data points at 2, 4, 8, 15, 30, 70, and 150 K was minimized. The actual experimental data are shown in Figure 1b as open circles. The relative RMS error for a lanthanide complex is defined as

$$\sigma_{\chi T}^{Ln} = \sqrt{\frac{1}{m_T}\sum_T \left(\frac{\chi_{calc}^{Ln}T - \chi_{obs}^{Ln}T}{\chi_{obs}^{Ln}T}\right)^2}$$

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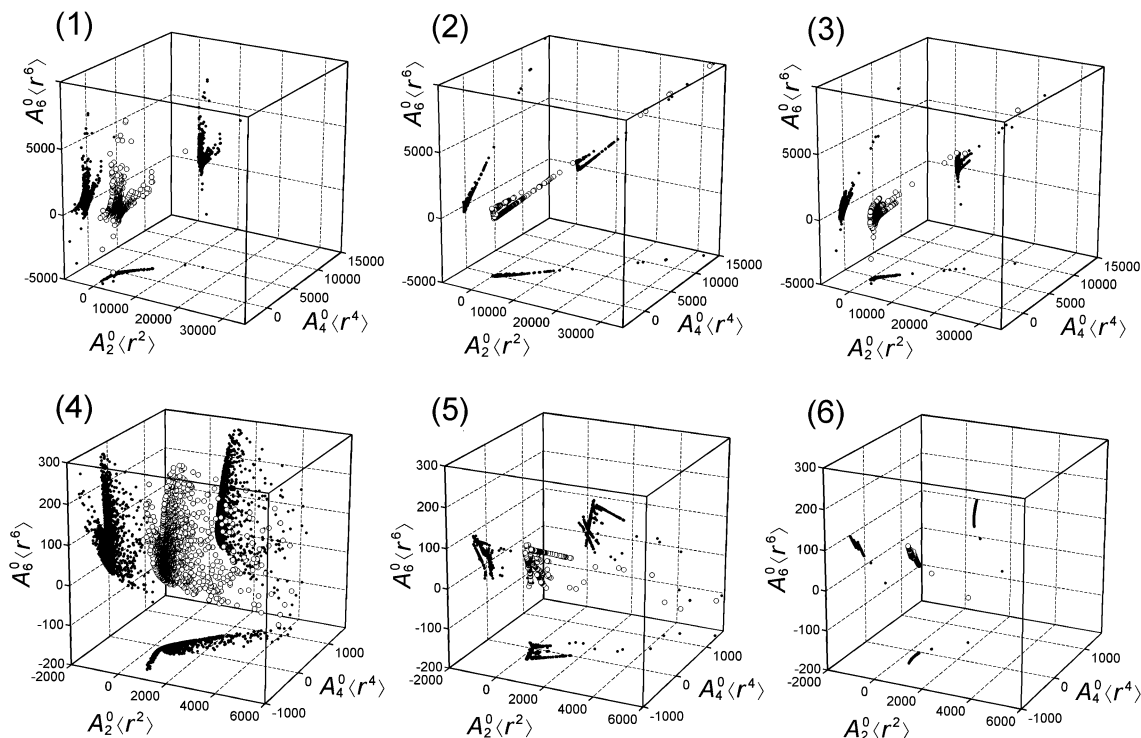
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Figure 2. LF parameters $A_2^0\langle r^2\rangle$, $A_4^0\langle r^4\rangle$, and $A_6^0\langle r^6\rangle$ (given in cm^{-1}) determined by simplex algorithm for Tb(Pc)$_2$$^-TBA^+$ (panels 1, 2, and 3) and Tm(Pc)$_2$$^-TBA^+$ (panels 4, 5, and 6). Open circles represent the parameters giving (1 and 4) an $\Delta\delta$ value within a relative RMS error of 3%, (2 and 4) $\chi_M T$ vs T plots within 3% error, and (3 and 6) both sets of experimental data within 3% error. Dots on the walls of the cubes are the projection of the data points onto the $A_2^0\langle r^2\rangle$–$A_4^0\langle r^4\rangle$, $A_4^0\langle r^4\rangle$–$A_6^0\langle r^6\rangle$, and $A_2^0\langle r^4\rangle$–$A_6^0\langle r^6\rangle$ planes.

Here, m is the number of the data points (in this paper, $m = 7$) and χ_{calc}^{Ln} and χ_{obs}^{Ln} are the calculated and experimental χ_M values for the lanthanide, respectively. Again, the points are spread over a broad region.

Panel (3) in Figure 2 shows the points that reproduce both the experimental data obtained by minimizing the sum of the two types of relative RMS errors. No significant narrowing of the range is observed.

A better improvement, through the use of both RMS errors, is observed in the Tm complex case (see panels (4), (5), and (6) in Figure 2). This indicates that the simultaneous use of the two different experimental data sets can narrow the range of the parameters.

2. Simultaneous Determination of the LF Parameters of the Six Lanthanide Complexes Using $\Delta\delta$ Data. The main reason for the impossibility in finding the unique solution is that the number of parameters to be determined (N_{para}) is greater than the number of experimental values to be fit (N_{obs}). Reduction of the relative ratio of N_{para} to N_{obs} is made possible by imposing a suitable restriction on the LF parameters of multiple lanthanide complexes and treating them simultaneously. In this section, the restriction that is defined by eq 1 is applied for the case where $\Delta\delta$ values of the six complexes are given.

The relative RMS error to be minimized is a function of the six LF parameters—that is, $\boldsymbol{a} = \{a_2^0, a_4^0, a_6^0, b_2^0, b_4^0, b_6^0\}$—and is defined as Here, N is the number of the complexes considered,

$$\sigma_{\Delta\delta}(\boldsymbol{a}) = \sqrt{\frac{1}{N}\sum_{Ln=Tb}^{Yb}\left(\frac{\Delta\delta_{calc}^{Ln}(\boldsymbol{a}) - \Delta\delta_{obs}^{Ln}}{\Delta\delta_{obs}^{Ln}}\right)^2}$$

and $\Delta\delta_{calc}^{Ln}$ and $\Delta\delta_{obs}^{Ln}$ are the calculated and experimental $\Delta\delta$ values of the lanthanide complex, respectively. The $A_k^0\langle r^k\rangle$

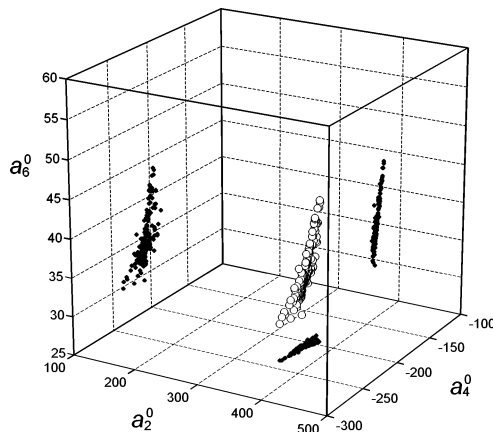**Figure 3.** LF parameters a_2^0, a_4^0, and a_6^0 (given in cm^{-1}) determined by the simplex algorithm with the NMR data for six Ln(Pc)$_2$$^-TBA^+$ complexes (Ln = Tb, Dy, Ho, Er, Tm, or Yb). Open circles are the a_k^q parameters reproducing the observed $\Delta\delta$ values within an relative RMS error of 3.5%. Dots are the projections onto the corresponding planes.

values for each complex are calculated by eq 1 with the parameter set $\boldsymbol{a}$.

Figure 3 shows the LF parameters thus obtained. The coordinates of each point represent a_2^0, a_4^0, and a_6^0 values of a parameter set $\boldsymbol{a}$. The b_k^0 values associated with each point are not shown in the figure. The region where the points are located is significantly reduced from the cases where only single NMR data are used. This indicates that the restriction that is defined by eq 1 efficiently narrows the range of possible parameters.

Interestingly, the figure illustrates that such a small number of the experimental values, six in the present case, gives an approximate estimate of the LF parameters with a decent quality.
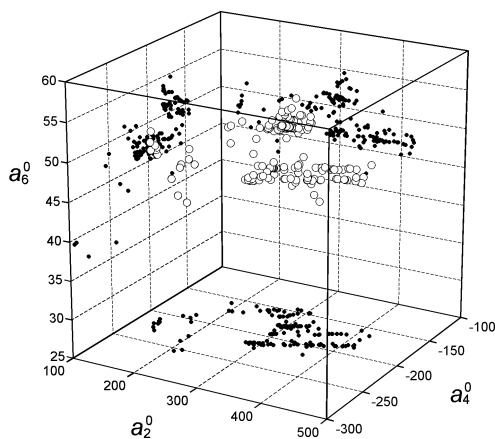
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Figure 4. LF parameters a_2^0, a_4^0, and a_6^0 (given in cm^{-1}) determined by the simplex algorithm for six Ln(Pc)$_2^-$TBA$^+$ complexes (Ln = Tb, Dy, Ho, Er, Tm, or Yb). Open circles are the a_k^q parameters reproducing the observed $\chi_M T$ vs T plots within an RMS error of 3.5%. Parameters b_2^0, b_4^0, and b_6^0, which have been determined with each a_k^q set, are not shown.

This example indicates that analysis using only NMR data at room temperature can provide a great deal of preliminary information of the sublevel structure of the ground multiplets.

3. Simultaneous Determination of the LF Parameters of the Six Lanthanide Complexes Using $\chi_M T$ Data. The next case to be examined is that in which the $\chi_M T$ values of the six lanthanide complexes are used simultaneously. The function to be minimized is the relative RMS error from the observed $\chi_M T$ values for the six lanthanide systems:

$$\sigma_{\chi T}(\boldsymbol{a}) = \sqrt{\frac{1}{N}\sum_{Ln=Tb}^{Yb}(\sigma_{\chi T}^{Ln}(\boldsymbol{a}))^2}$$

Figure 4 shows the LF parameter sets with a relative RMS error of <3.5% as a point in the a_k^0 space with the same scale as the preceding figure for the NMR case. Although the extent of the reduction is rather small, compared to the NMR case, the region of the points is considerably narrowed from the case using a data set of a single lanthanide complex. The efficiency of the restriction by eq 1 is also high in this case.

It should be noted here that the LF parameters obtained from the $\chi_M T$ values have been found in a similar range to that obtained from the $\Delta\delta$ values. This indicates that the model employed consistently accounts for the two different experiments. Comparison of the two separate calculations is also important in checking whether the NMR paramagnetic shift is actually of a magnetic—dipolar nature.

4. Simultaneous Determination of the LF Parameters of the Six Lanthanide Complexes Using Both $\Delta\delta$ and $\chi_M T$ Data. The difference in the distribution pattern of the a_k^0 points between Figures 3 and 4 suggests that combining the two cases can further narrow the range of the possible solutions. This can be done by minimizing the sum of the two types of RMS errors:

$$\sigma_{both}(\boldsymbol{a}) = \sigma_{\Delta\delta}(\boldsymbol{a}) + \sigma_{\chi T}(\boldsymbol{a})$$

The parameter sets giving a local minimum of σ_{both} are shown as points in the a_k^0 space by open circles in Figure 5. At each point, the two relative RMS errors—namely, $\sigma_{\Delta\delta}$ and $\sigma_{\chi T}$—are both <3.5%. The scale of the figure is the same as that of Figures 3 and 4.
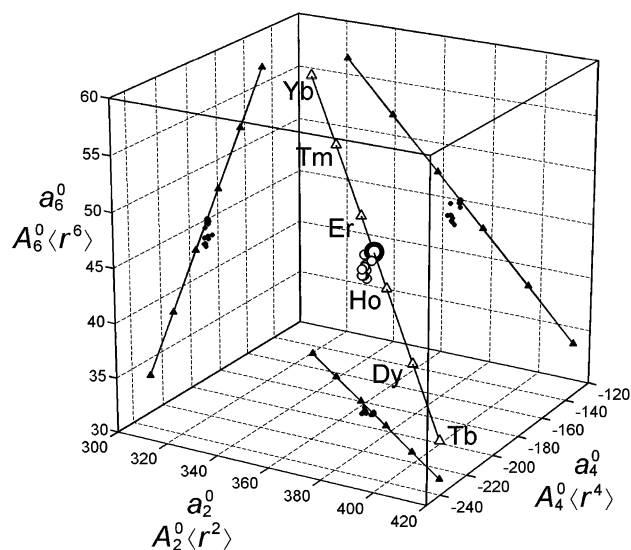

Figure 5. LF parameters a_2^0, a_4^0, and a_6^0 (given in cm^{-1}) determined using both $\Delta\delta$ and $\chi_M T$ data for six Ln(Pc)$_2^-$TBA$^+$ (Ln = Tb, Dy, Ho, Er, Tm, or Yb). Open circles are the a_k^q parameters reproducing the observed $\Delta\delta$ values and $\chi_M T$ vs T plots within a relative RMS error of 3.5%. Triangles connected by the straight line are the "best" parameters $A_2^0\langle r^2\rangle$, $A_4^0\langle r^4\rangle$, and $A_6^0\langle r^6\rangle$ for the six complexes.

Clearly, the range of the LF parameters has been narrowed significantly. The best-fit parameter set, which is drawn by a thick line in Figure 5, has been found to give relative RMS errors of 3.1% for the NMR data and 3.3% for the susceptibility data. The corresponding $A_2^0\langle r^2\rangle$, $A_4^0\langle r^4\rangle$, and $A_6^0\langle r^6\rangle$ parameters for the six complexes are shown by triangles that are connected by a straight line. Considering the uncertainties contained in the experimental data, it can be said that sufficient uniqueness of the solution has been achieved.

The increase of the uniqueness by the combination of the two experimental data is probably because a χ_M value of a powder sample is the average of the principal components of anisotropic magnetic susceptibility, whereas $\Delta\delta$ values represents the deviation of the axial component from the average. Particularly, when the system has axial symmetry, as in the present case, a pair of χ_M values and $\Delta\delta$ values completely determines both the axial and transverse components of the magnetic susceptibility.

Conclusion

(1) The restriction that each ligand-field (LF) parameter be a linear function of the atomic number of the lanthanide ion has been demonstrated to be essential for finding the unique solution.

(2) The use of either experimental $\Delta\delta$ or $\chi_M T$ vs T data sets for multiple lanthanide complexes can narrow the range of the possible solutions. Although the level of conversion is incomplete, it can provide an approximate estimate of the LF parameters. In particular, NMR measurement at room temperature seems to be a very good starting point, because spectrometry is one of the most common tools for chemists.

(3) To obtain the unique solution, a search for the parameter sets that satisfy both experimental data sets is required. Improvement of the uniqueness of solution occurs because two experiments give mutually complementary information for the anisotropic components of the magnetic susceptibility of a lanthanide complex.

LF Parameters of Isostructural Lanthanide Complexes

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