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On the Use of Ligand Field Parameters in the Study of Coordinated Water Molecules in Eu^{3+} Complexes

R. Q. Albuquerque,*,† R. O. Freire,‡ and O. L. Malta‡

Department of Chemistry and Biochemistry, Universität Bern, Freiestr. 3, 3012 Bern, Switzerland, and Departamento de Química Fundamental, CCEN, UFPE, Cidade Universitária, 50670-901, Recife-PE, Brazil

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A new methodology is proposed by which the number of coordinated water molecules, n, can be estimated in Eu^{3+} complexes. It is based on a comparison between the theoretical and experimental Stark levels, the former being calculated by assuming that n varies from 0 to 4 and predicting the so-called ligand field parameters, B^k_q. The methodology, initially developed in the study of the $Eu(pya)_3 \cdot nH_2O$ complex, has been applied successfully to β-diketonate complexes of Eu^{3+}, for which crystallographic and luminescence data are available.

I. Introduction

Lanthanide coordination compounds play a very important role in the design of new luminescent systems, such as UV dosimeters, thin films for optical devices, and luminescent labels in fluoroimmunoassays.[1−3] In these systems, it is desirable to use lanthanide complexes that exhibit high emission quantum yields. The luminescence of such complexes can usually be improved by the use of organic ligands, which strongly absorb UV radiation and transfer energy to the lanthanide ion. In this process, the emitting level of the lanthanide ion is usually more efficiently populated, in comparison with the direct excitation of excited 4f levels.[4] However, luminescence can also be quenched if the first coordination sphere of the lanthanide ion contains water molecules. In this case, the emitting level can be strongly depopulated through coupling with the excited vibrational levels of the OH oscillator of the water molecules.[5] Because of this quenching, the knowledge of the number of coordinated water molecules becomes crucial if one is interested in the design of new luminescent compounds.

Horrocks and Sudnick have proposed an experimental procedure through which the number of coordinated water molecules can be determined by comparing the luminescence decay time of a given lanthanide complex in solutions of H_2O and D_2O.[6] In this procedure, the luminescence lifetimes of the complex must be measured in both solvents and special care must be taken to avoid contamination of the D_2O solution by H_2O.

In this paper, we propose a semiempirical methodology to determine the number of coordinated water molecules in Eu^{3+} complexes. We have applied this new methodology to the $Eu(pya)_3$ complex initially, which contains 3 bidentate pyrazine ligands.[7] This methodology is based on a comparison between experimental Stark levels, obtained from the emission spectrum, and the theoretical Stark levels, obtained from ligand field calculations. These calculations involve the optimization of the geometry of the Eu^{3+} complex using the Sparkle model,[8] the calculation of the ligand field parameters using the simple overlap model (SOM),[9] and the prediction of Stark levels by diagonalizing the ligand field Hamiltonian within the ground ^7F term.[10] In each calculation, a different number of water molecules, n, is adopted ($n = 0-4$). A comparison between the theoretical and experimental Stark levels is then used to find the best n. The methodology has also been applied to some β-diketonate complexes for which crystallographic structures are available.

II. Methodology

The following complexes were investigated: $Eu(pya)_3$,[7] $Eu(acac)_3$,[11] $Eu(tta)_3$,[12] and $Eu(btfa)_3$,[13] where pya = pyrazine-2-carboxylic acid, acac = 2,4-pentanedione, tta = tris(thenoyltrifluoroacetonate), and btfa = tris(4,4,4-trifluoro-1-phenyl-1,2-butanedione).

For the complexes studied, n has been varied from 0 to 4, which is a range chemically acceptable for Eu^{3+} complexes. This chemical reasoning is based on both the availability of experimental data found for Eu^{3+} complexes already having three bidentate ligands and the fact that in geometry optimizations the 5th water molecule added is generally expulsed from the first coordination sphere of the Eu^{3+} ion because of the great repulsion with the bulky β-diketonate ligands.

For each value of n, the geometry was optimized using the semiempirical Sparkle model implemented on the MOPAC program.[8] The uncertainties in the geometry optimizations of Eu^{3+} complexes using the Sparkle model have shown to be comparable with the ones obtained using ab initio calculations,[14] and therefore this semiempirical model has proven to be appropriate to be used in the present work.

In these calculations, the spherical coordinates of the ligating atoms and the force constants between them and the Eu^{3+} ion were obtained. In a second step, the ligand field parameters, B^k_q, have been calculated using the SOM,[9] with the charge factors, g, being given by the ionic specific valence (ISV) as defined in ref 15. These B^k_q values have been used to predict the energy of the Stark levels,[10] which were then compared to the experimental Stark levels in order to find the best n for each complex.

Geometry Optimization. The geometries of the complexes have been optimized using the following MOPAC keywords: GNORM = 0.25 (in order to guarantee the energy minimum), SCFCRT = 1·D − 10 (in order to increase the SCF convergence

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* Corresponding author. Tel: +41 31 631-4225. Fax: +41 31 631-3994. E-mail: rodrigo@iac.unibe.ch.

† Universität Bern.

‡ Cidade Universitária.

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criterion), and XYZ (the geometry optimizations were performed in Cartesian coordinates).

After each optimization, another calculation was carried out in order to obtain the force constants, which have been calculated using the FORCE keyword in the MOPAC input line.

Ligand Field Calculations. The R, Θ, and Φ spherical coordinates of the ligating atoms, obtained from the optimized geometries, were used in the expression of the ligand field parameters as given by the SOM[9]

$$B_q^k = e^2\langle r^k\rangle \sum_j g_j\rho_j(2\beta_j)^{k+1}\left(\frac{4\pi}{2k+1}\right)^{1/2}\frac{Y_q^{k*}(\Theta_j,\Phi_j)}{R_j^{k+1}} \tag{1}$$

where the summation runs over the ligating atoms and $k = 2$, 4, and 6. In eq 1, e is the electron charge, $\langle r^k\rangle$ is a 4f radial integral, Y_q^k is a spherical harmonic of rank k, ρ_j is the overlap between the lanthanide ion and the jth ligating atom valence shells, β is given by $(1 + \rho)^{-1}$, and g is a charge factor. The following expression for the charge factors was used[16]

$$g_j \equiv \mathrm{ISV} = R_j\sqrt{\frac{K_j}{2\Delta E_j}} \tag{2}$$

where K_j is the force constant of the jth bond (lanthanide ion − ligating atom). In eq 2, ΔE is the energy difference between the valence orbitals of the ligating atoms and the lanthanide 4f orbitals, given by[16]

$$\Delta E_j = \epsilon\cdot\exp\left(\frac{R_0}{R_j}\right) \tag{3}$$

In eq 3, R_0 is the smallest among the distances, R_j, and ϵ is a constant for each ligating atom considered, being interpreted as the energy difference between the valence shells of the isolated ligand atoms and the isolated Eu^{3+} ion. The ϵ values of 0.6281 and 0.69153 au for the nitrogen and oxygen ligating atoms, respectively, have been adopted.

The B_q^k values obtained from the above equations were then used to predict the energy of the Stark levels through the diagonalization of the ligand field Hamiltonian with matrix elements $\langle\Psi|\sum C_q^k B_q^k|\Psi'\rangle$, where C_q^k is a Racah tensor operator of rank k and Ψ and Ψ' constitute the 49 basis functions (in the intermediate coupling scheme) of the ^7F_J multiplets of the Eu^{3+} ion. The theoretical Stark levels obtained have been compared to the experimental ones through the expression

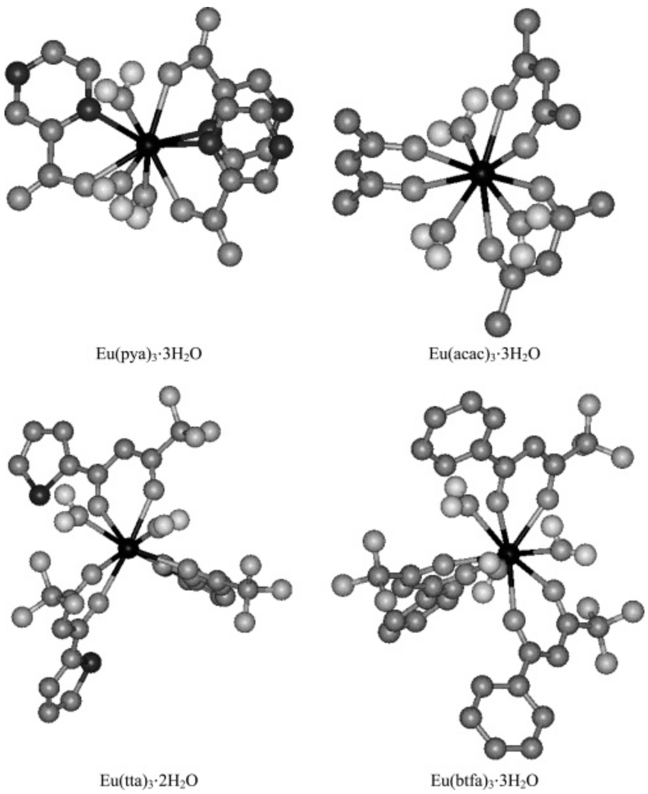
$$\sigma = \left[\sum_i^l \frac{1}{l}\left(\frac{E_i^{\mathrm{exptl}} - E_i^{\mathrm{calcd}}}{E_i^{\mathrm{exptl}}}\right)^2\right]^{1/2}\cdot 100\% \tag{4}$$

where E_i^{exptl} and E_i^{calcd} are the experimental and theoretical energies of the Stark levels, respectively, and l is the total number of experimental Stark levels. The σ parameter was calculated for each number, n, of water molecules.

Finally, σ has been plotted versus n in order to determine the minimum in the curve that should correspond to the most probable number of coordinated water molecules.

III. Results

The optimized geometries of the Eu^{3+} complexes that gave the smallest σ are shown in Figure 1. In all of the geometries, the symmetry point group achieved was C_1 and the coordination number (CN) varied from 6 to 10. For the $Eu(pya)_3$ complex, each pyrazine was found to be coordinated to the Eu^{3+} through one carboxylic oxygen and one nitrogen from the ring, in agreement with previous studies.[7] The convergence of the calculations has shown to be dependent on the initial guess of the structures and mainly on the number of water molecules added to the first coordination sphere. For the cases where n was higher, a higher number of different initial guesses has shown to be necessary in order to achieve the convergence criterion and the stability of the structure, that is, to keep the water molecules coordinated to the Eu^{3+} ion. The Cartesian coordinates of the ligating atoms of the optimized complexes are shown in the Supporting Information.



$Eu(pya)_3\cdot 3H_2O$ $Eu(acac)_3\cdot 3H_2O$

$Eu(tta)_3\cdot 2H_2O$ $Eu(btfa)_3\cdot 3H_2O$

Figure 1. Optimized geometries of the $Eu(pya)_3\cdot 3H_2O$, $Eu(acac)_3\cdot 3H_2O$, $Eu(tta)_3\cdot 2H_2O$, and $Eu(btfa)_3\cdot 3H_2O$ complexes using the Sparkle model.

TABLE 1: Values of the Real Part of the Ligand Field Parameters (B_0^2, B_1^2, and B_2^2, in cm^{-1}), the Ligand Field Strength Parameter (N_v, in cm^{-1}), and the Mean Charge Factors for the Oxygens of the Water ($g_{\mathrm{O-water}}$) and for the Other Ligating Atoms (g_L) Predicted for the $Eu(L)_3\cdot nH_2O$ Complexes[a]

complex	B_0^2	B_1^2	B_2^2	N_v	g_L	$g_{\mathrm{O-water}}$
$Eu(pya)_3\cdot 3H_2O$	−175.89	−249.29	577.59	1474.10	0.80	0.91
$Eu(acac)_3\cdot 3H_2O$	0.80	164.83	−357.86	1057.80	0.85	0.90
$Eu(tta)_3\cdot 2H_2O$	110.57	−116.58	107.15	730.75	0.84	0.89
$Eu(btfa)_3\cdot 3H_2O$	203.65	−76.14	261.99	969.60	0.85	0.91

[a] L = pya, acac, tta and btfa.

The real part of the ligand field parameters and the mean charge factors calculated from eqs 1 and 2, respectively, are shown in Table 1 for the best n value for each complex. The values of B_q^2 have been used to predict the ligand field strength parameter, N_v, which is a measure of the ligand field strength around the lanthanide ion.[17] The values of N_v are also shown in Table 1. The results show the existence of a strong ligand field in the case of the $Eu(pya)_3\cdot 3H_2O$ complex and a weak one for the $Eu(tta)_3\cdot 2H_2O$ complex.

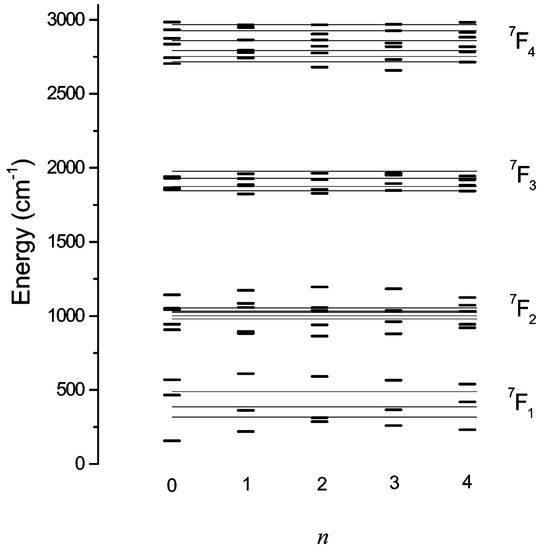


Figure 2. Comparison between theoretical (black lines) and experimental (full gray lines) Stark levels for the Eu(pya)$_3$·nH_2O complex.

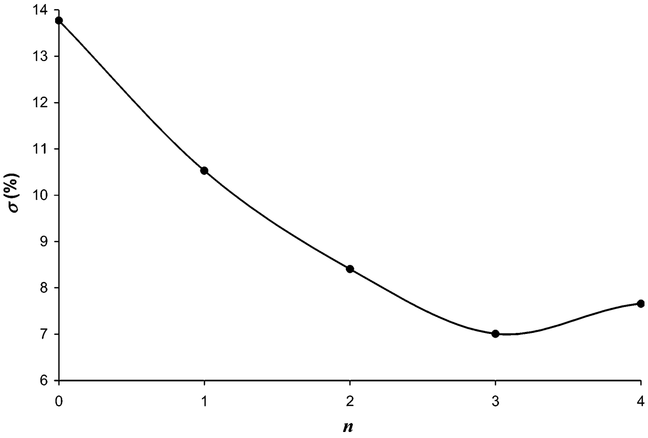


Figure 3. Plot of the error in the prediction of the Stark levels, σ (in %), versus the number of coordinated water molecules, n, for the Eu(pya)$_3$·nH_2O complex.

On average, the mean charge factors of the oxygens of the water molecules for all of the complexes were 0.90, whereas those for the other ligating atoms were slightly smaller (0.84). The larger distance commonly found between the water molecules and the Eu^{3+} ion is the main reason their charge factor values are higher (eq 2). For the Eu(pya)$_3$·3H_2O complex, the value of g_L shown in Table 1 is the average between the values for the oxygens and nitrogens of the pyrazine: 0.86 and 0.73, respectively.

The theoretical and experimental Stark levels for the Eu(pya)$_3$·nH_2O complex are presented in Figure 2. The experimental Stark levels (full gray lines) have been obtained from the emission spectrum found in ref 7. The plot σ versus n for this complex is shown in Figure 3. The curve presents a smooth behavior with a global minimum at $n = 3$. This result is in agreement with a previous determination of n.[7]

The calculated σ values for the four complexes used in the present work are shown in Table 2 and are plotted (except for Eu(pya)$_3$) against n in Figure 4. For the Eu(acac)$_3$ complex[11] (Figure 4, circles), the best σ value was obtained for $n = 3$, which is in agreement with the crystallographic data.[18] In the solid state, this complex shows three water molecules around the Eu^{3+} ion, one of which is at a rather large distance (R = 5.61 Å). For the Eu(tta)$_3$ complex[12] (Figure 4, squares), there is only one minimum located at $n = 2$, in agreement with the crystallographic data.[19]

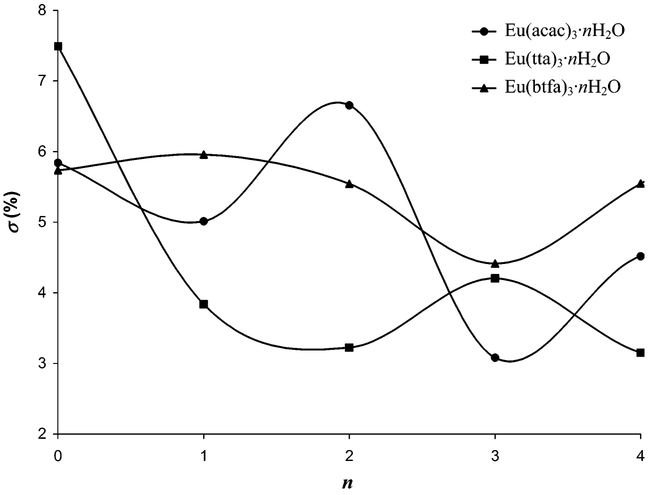


Figure 4. Plot of the error in the prediction of the Stark levels, σ (in %), versus the number of coordinated water molecules, n, for the Eu(acac)$_3$·nH_2O, Eu(tta)$_3$·nH_2O, and Eu(btfa)$_3$·nH_2O complexes.

TABLE 2: Calculated Values of σ for Complexes Eu(pya)$_3$·nH_2O, Eu(acac)$_3$·nH_2O, Eu(btfa)$_3$·nH_2O, and Eu(tta)$_3$·nH_2O

	σ (%)				
complex	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
Eu(pya)$_3$·nH_2O	13.77	10.53	8.40	7.01	7.66
Eu(acac)$_3$·nH_2O	5.84	5.01	6.65	3.08	4.52
Eu(btfa)$_3$·nH_2O	5.73	5.96	5.54	4.41	5.55
Eu(tta)$_3$·nH_2O	7.49	3.84	3.22	4.21	3.15

The σ versus n curve for the Eu(btfa)$_3$ complex[13] also shows a smooth behavior (Figure 4, triangles) with a minimum at $n = 3$. Although this is not corroborated by the crystallographic data,[20] from which $n = 2$, it is interesting that, in this case, the value of n determined from the experimental measurements of luminescence lifetimes and intensities, in solutions of H_2O and D_2O, lies between 2 and 3.[21] Because our theoretical calculations refer to the isolated complex unit, the result is expected to be closer to that obtained in solution, particularly for complexes with larger ligands, such as the btfa one, where steric effects might be more pronounced in the solid state.

IV. Summary and Final Comments

A semiempirical procedure has been proposed by which the number, n, of coordinated water molecules in Eu^{3+} complexes can be determined. This procedure is based on a comparison between the theoretical and experimental Stark levels by assuming different n values for the complexes. The values of n for the β-diketonate complexes have shown an overall satisfactory agreement with the crystallographic data. The result obtained for the Eu(btfa)$_3$ complex suggests that, in solution, there are three coordinated water molecules.

The proposed methodology has the advantage of needing only one experimental measurement, that is, the ligand field Stark levels from emission or absorption spectra, and may be extended to other complexes with different lanthanide ions. Besides, because it involves a direct comparison between theory and experiment, it constitutes a further test for the reliability of ligand field models. In this sense, the SOM, with the charge factor values given by the analytical expression in eq 2, has shown to provide a satisfactory description of the ligand field in these Eu^{3+} compounds.

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Supporting Information Available: Cartesian coordinates of the ligating atoms of the optimized Eu^{3+} complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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