On correlating the frequency of the $^7F_0 \to {}^5D_0$ transition in Eu^{3+} complexes with the sum of 'nephelauxetic parameters' for all of the coordinating atoms [☆]

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Abstract

The frequency of the $^7F_0 \to {}^5D_0$ transition of Eu^{3+} is found to correlate with the sum of derived nephelauxetic parameters of the ligating atoms in Eu^{3+} complexes. Parameters for nine distinct coordinating atom types are obtained via a multiple linear regression method applied to experimental $^7F_0 \to {}^5D_0$ transition frequencies of twenty-seven 9-coordinate Eu^{3+} complexes with known ligand constituents. The linear correlation coefficient is 0.99. Addition of data from 7-, 8-, 10-, and 11-coordinate complexes and use of a multiplicative constant, characteristic of each coordination number, produces a second linear correlation covering thirty-seven systems with a correlation coefficient of 0.98. The present approach seeks to understand the factors which influence the $^7F_0 \to {}^5D_0$ transition frequency and to make predictions of this quantity for particular ligand environments. It is completely empirical in nature; however, the results may be understood in terms of an underlying theoretical cause. The parameters obtained here correlate roughly with the nephelauxetic h-values of Jørgensen for the few cases where appropriate ligand matches are available. The $^7F_0 \to {}^5D_0$ term separation will decrease from its free-ion value of 17 374 cm^{-1} with increasing Eu^{3+}–ligand covalency, and the presently derived parameters are consistent with this idea. The correlation presented here is clearly superior to our earlier attempt to identify a relationship between the $^7F_0 \to {}^5D_0$ transition frequency and the total formal charge on the ligands in a complex.

Keywords: Europium complexes; Luminescence; Nephelauxetic effect; Covalency

1. Introduction

Methods based largely on laser excitation of Eu^{3+} and the ability of this ion to luminesce in solution at room temperature have been developed in this laboratory over the past eighteen years to exploit this luminescence phenomenon in characterizing the metal-ion-binding properties of proteins [1–6], nucleic acids [7–9], viruses [10], and small chelating ligands [11–15]. The experiment of most utility in this regard is the excitation of Eu^{3+} from its $^7F_0$ ground state to the $^5D_0$ excited level, from which luminescence is emitted, with the most intense being the $^7F_0 \to {}^5D_2$ transition at 612 nm. Both the ground ($^7F_0$) and excited ($^5D_0$) states are nondegenerate and therefore, in principle, only a single excitation transition can be observed for each unique

Eu^{3+} environment. A relatively narrow range of transition frequencies has been observed for different Eu^{3+} complexes ($\approx 17\,225$ to $\approx 17\,280$ cm^{-1}). However, since the excitation bands are generally quite narrow, often with full widths at half maximum (fwhm) of less than 10 cm^{-1}, individual Eu^{3+} environments may often be resolved in excitation experiments and the transition frequencies can be measured with good accuracy. Some typical $^7F_0 \to {}^5D_0$ excitation spectra are shown in Fig. 1. A wealth of information can be obtained from the luminescence experiments, including the number of species present [16,17], complex stoichiometries [11–15] and binding constants [18], binding constants for other metal ions (through competition experiments) [16,18], distances between metal ion binding sites [1,19], and ligand exchange rates [20]. Since the $^7F_0$ and $^5D_0$ levels arise from different terms of the $4f^6$ configuration, their separation is a function of interelectronic repulsion parameters. The $^7F_0 \to {}^5D_0$ transition involves the pairing of two of the previously unpaired electrons in the $4f$ orbitals. Variation in the energetic separation of terms

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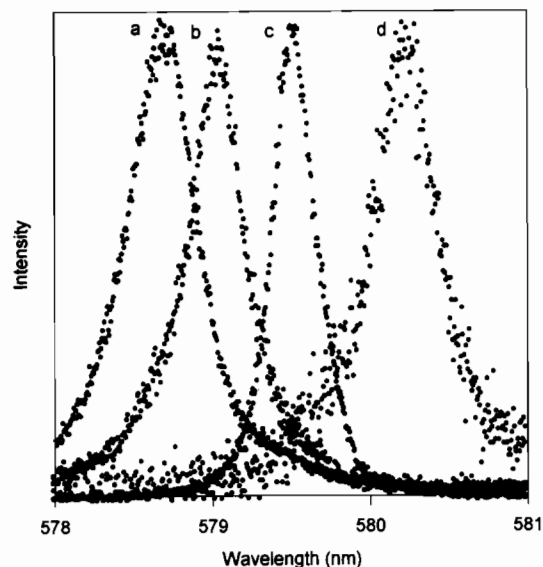
Fig. 1. $^7F_0 \rightarrow {}^5D_0$ spectra of (a) $Eu(H_2O)_9{}^{3+}$, (b) $Eu(imda)(H_2O)_6{}^+$, (c) $Eu(edta-dam)(H_2O)_3$, and (d) $Eu(dpa)_3{}^{3-}$. For abbreviations see Table 1. Spectra were recorded at pH 7, 25 °C. Intensities are normalized to a common value.

of an ion as a function of the ligands involved in different complexes is a well-known phenomenon, especially for transition metal ions. The degree to which the term separation decreases from that of the free gaseous ion as a function of various ligand environments has been termed the *nephelauxetic effect* [21]. In an attempt to understand this effect for the $^7F_0 \rightarrow {}^5D_0$ energy separation, it was noted by workers in this laboratory several years ago that the frequency of the transition appears to correlate with the total formal charge on the ligands coordinated to the Eu^{3+} [22]. An empirical equation relating the frequency ν (in cm^{-1}) to the total formal ligand charge p on the ligands was found in a study of 36 well-characterized Eu^{3+} complexes [15] as given in Eq. (1):

$$\nu = -0.76p^2 + 2.22p + 17\,273 \tag{1}$$

It was concluded from this study that the observed nephelauxetic effect was not due to covalency, but to a decrease in the effective nuclear charge of the Eu^{3+} ion upon binding to a negatively charged ligand. This relationship between formal ligand charge and $^7F_0 \rightarrow {}^5D_0$ transition frequency holds well for many complexes, but many exceptions have been noted in this laboratory [14] and elsewhere [23–25], including a series of amide-based macrocycles recently studied by Eu^{3+} luminescence and molecular modeling [26]. In the last-mentioned study it was noted that the observed shifts were better correlated to the sum of the partial charges on the ligand atoms than to the total formal charge.

Our objective here is to discover what features of the ligand environment of Eu^{3+} are most responsible for the $^7F_0$-$^5D_0$ separation. To this end, the present study utilizes multiple linear regression to develop parameters characteristic of each type of coordinating atom such that, when these are summed over all atoms in the first coordination sphere, a quantity is obtained which allows one to predict the frequency of the $^7F_0 \rightarrow {}^5D_0$ transition for various Eu^{3+} complexes. Importantly, the individual ligand atom parameters so obtained appear to correlate with the ranking of the ligands in the nephelauxetic series developed by Jørgensen [21] for transition metal ions, and thus have some basis in theory.

2. Experimental

2.1. Materials

Hydrated $EuCl_3$, iminodiacetic acid, and dipicolinic acid were purchased from Aldrich. N-2-hydroxyethyl-piperazine-N'-ethanesulfonic acid (HEPES) was purchased from Sigma. Rhodamine 590 and 610 dyes were purchased from Exciton and Kodak, respectively. The water used was distilled and deionized. All chemicals were used without further purification.

2.2. Methods

Eu^{3+} excitation spectra of $Eu(H_2O)_9{}^{3+}$, $Eu(imda)$-$(H_2O)_6{}^+$, and $Eu(dpa)_3{}^{3-}$ were recorded with a Continuum YG-581C pulsed (10 Hz) Nd:YAG laser pumped tunable TDL-50 dye laser, as an excitation source. A mixture of rhodamine 590 and 610 dyes was used to access the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} (577–581 nm) while monitoring the $^7F_0 \rightarrow {}^5D_2$ emission at 614 nm. The data acquisition system was identical to that which has been described previously [26]. The samples were prepared containing 10 μM Eu^{3+} with an appropriate amount of ligand in 50 mM HEPES at pH 7, and the spectra were recorded at 25 °C.

The coordination numbers of $Eu(CH_3OH)_x$ and $EuCl(H_2O)_x$ were determined by means of molecular mechanics calculations carried out on an IBM RISC 6000 graphics workstation running QUANTA (version 3.3) and CHARMm (version 2.2) (Molecular Simulations Inc.) molecular mechanics/dynamics software. The details of these calculations are identical to those described previously [26]. For each complex, models were constructed with varying amounts of coordinated solvent molecules. These models were then minimized to determine whether their structure was energetically favorable. In extreme cases, one or more solvent molecules were liberated from the first coordination sphere during the energy minimization. Using this analysis, the maximum number of coordinated solvent molecules was determined. The bond distances calculated for these maximally solvated structures compare well with

known bond distances. Matrix calculations were performed using Mathcad (version 4.0) software.

3. Results and discussion

3.1. Total formal ligand charge

We have reexamined our previously proposed correlation of the frequency ν of the $^7F_0 \rightarrow {}^5D_0$ transition with the total ligand formal charge, restricting our attention to a series of thirty-seven Eu^{3+} complexes, each of which exhibits a single $^7F_0 \rightarrow {}^5D_0$ excitation band and for which we have a reasonably good idea of the constitution of the first coordination sphere. The data set contains complexes that are 7-, 8-, 9-, 10-, and 11-coordinate with a reasonably diverse array of coordinating atoms. Most of the ligands in this study are small chelates. However, one biological macromolecule is included, namely the satellite tobacco necrosis virus (stnv), which has a particularly well-characterized Eu^{3+} binding site [10]. Many of these systems, which are listed in Table 1, were considered in our earlier study [15]. The frequencies of the $^7F_0 \rightarrow {}^5D_0$ transition, hereafter referred to as ν-values, are plotted versus the total formal ligand charge on the ligands in Fig. 2. As observed in our previous study, the points fit best to a quadratic function with a correlation coefficient of 0.72. The quality of the fit is not particularly satisfying. Furthermore, there is no theoretical reason why a greater formal charge should produce a larger nephelauxetic effect. For instance, the F^- ion lies at the low end of the nephelauxetic series, while I^- is at the other end, producing the largest effect. For these reasons we feel that the apparent correlation of ν-values with formal ligand charge may be fortuitous.

3.2. The sum of partial charges on ligand atoms

A recent study in this laboratory examined several amide-based macrocyclic ligands with carboxylate-containing side arms, which are of potential interest in the magnetic resonance imaging contrast agent field [26]. Eu^{3+} luminescence spectroscopy was used in conjunction with molecular mechanics calculations to achieve a detailed characterization of these systems, all of which have ligands with -3 formal charge. It was observed in that study that the ν-values, which ranged from 17 244 to 17 262 cm^{-1}, correlated moderately well with the sum of the partial charges on the atoms in the first coordination sphere. Unfortunately, this correlation also breaks down when a larger, more diverse data set is considered. Furthermore, since an exact knowledge of the partial charges on various ligand atoms is difficult to obtain in general, and because there is no apparent underlying theoretical justification

for the observed correlation, we here explore an alternative and more general approach to the problem as described below.

3.3. Nephelauxetic parameters

Since there is no apparent reason why the total formal ligand charge, or partial charge sum, should be proportional to the nephelauxetic effect, we sought a parameter, characteristic of the atoms in the first coordination sphere, that might have a more fundamental relationship to the nephelauxetic effect than the aforementioned quantities. It was reasoned that multiple linear regression could be used to develop parameters for the individual coordinating atom types that would be descriptive of their ability to produce a nephelauxetic effect. This technique, which utilizes matrix algebra to solve a system of equations, has been discussed at length recently [31–33]. It is particularly useful when the number of equations is greater than the number of unknown parameters. For the present data set (Table 1) there are thirty-seven Eu^{3+} complexes and nine distinct coordinating atom types. The experimentally determined ν-value and the number of coordinating atoms of each type are listed for every complex in Table 1. A series of equations was generated as follows:

$$\nu = \nu_0 + n_1 \cdot \delta_1 + n_2 \cdot \delta_2 + \cdots + n_j \cdot \delta_j \quad (2)$$

where δ_j is the parameter for atom type j and n_j is the number of atoms of type j in the first coordination sphere of the complex. The constant ν_0 in these equations represents the ν-value of the gaseous Eu^{3+} ion (Eu^{3+} with no coordinating atoms). We have chosen a ν_0-value of 17 374 cm^{-1}, the value of the gaseous Eu^{3+} ion which was calculated from energy matrices that take into account electrostatic (interelectronic repulsion) and spin–orbit interactions [34]. Theoretically this should be the largest ν-value, and therefore the calculated atom parameters, δ_j, should each be negative such that the act of an atom coordinating the Eu^{3+} ion decreases its ν-value relative to that of the gaseous Eu^{3+} ion, in accordance with the nephelauxetic effect. To simplify the multiple linear regression, the constant (ν_0) was subtracted from both sides of Eq. (2) to give

$$\nu - \nu_0 = n_1 \cdot \delta_1 + n_2 \cdot \delta_2 + \cdots + n_j \cdot \delta_j \quad (3)$$

We first considered all of the 9-coordinate complexes, which account for the large majority in our data set. Since there are twenty-seven 9-coordinate complexes and nine atom types, a 27×1 matrix ([C]) was generated that includes all of the $(\nu - \nu_0)$-values, hereafter referred to as $\Delta\nu$. As well, a 27×9 matrix ([B]) was generated that contains the number of coordinating atoms of each atom type for each of the twenty-seven complexes, where each column represents a different atom type. According to matrix algebra then,

Table 1
Complexes studied, coordination number (CN), estimated coordinating atoms, $^7F_0 \rightarrow ^5D_0$ transition energy, and formal ligand charge

Complex [a]	CN	Coordinating atoms [b]	$^7F_0 \rightarrow ^5D_0$ (cm^{-1})	Formal charge	Ref.
Eu(dbm)$_3$(H$_2$O) (s)	7	6 Oβ, 1 OW	17 259	-3	[15]
Eu(stnv)$^{3+}$ (aq)	8	5 O, 3 OW	17 254	0	[10]
Eu(pa)$_4$(ClO$_4$)$_3$ (s)	8	4 O, 4 NT	17 259	0	[27]
[Eu(acac)$_3$(H$_2$O)$_2$]·H$_2$O (s)	8	6 Oβ, 2 OW	17 262	-3	[15]
Eu(nic)$_3$(H$_2$O)$_2$ (s)	8	3 OT, 3 NT, OW	17 262	-3	[15]
EuCl$_2$(H$_2$O)$_6$]Cl (s)	8	2 Cl, 6 OW	17 263	-2	[15]
Eu(dpa)$_3$$^{3-}$ (aq)	9	6 OT, 3 NT	17 232	-6	[22]
Eu(chel)$_3$$^{6-}$ (aq)	9	6 OT, 3 NT	17 235	-6	[15]
Eu(imda)$_3$$^{3-}$ (aq)	9	6 OT, 3 NT	17 235	-6	[22]
Na$_3$[Eu(oda)$_3$]·6H$_2$O (s)	9	6 OT, 3 OE	17 235	-6	[15]
Eu(oda)$_3$$^{3-}$ (aq)	9	6 OT, 3 OE	17 238	-6	[22]
Eu(dtpa)(H$_2$O)$^{2-}$ (aq)	9	5 OT, 3 NT, OW	17 240	-5	[15]
Eu(bis(dtpa-eam))(H$_2$O) (aq)	9	3 OT, 2 O, 3 NT, 1 OW	17 244	-3	[26]
Eu(dtpa-oam)(H$_2$O) (aq)	9	3 OT, 2 O, 3 NT, 1 OW	17 244	-3	[26]
Eu(deu)$_3$(NO$_3$)$_3$ (s)	9	3 O, 6 ON	17 247	-3	[27]
Eu(do3a-dimer)(H$_2$O) (aq)	9	3 OT, 1 O, 4 NT, 1 OW	17 247	-3	[26]
Eu(dota)(H$_2$O)$^-$ (aq)	9	4 OT, 4 NT, 1 OW	17 247	-4	[15]
Eu(dpa)$_2$(H$_2$O)$_3$$^-$ (aq)	9	4 OT, 2 NT, 3 OW	17 249	-4	[22]
Eu(chel)$_2$(H$_2$O)$_3$$^{3-}$ (aq)	9	4 OT, 2 NT, 3 OW	17 251	-4	[15]
Na[Eu(edta)(H$_2$O)$_3$]·5H$_2$O (s)	9	4 OT, 2 NT, 3 OW	17 251	-4	[15]
Eu(imda)$_2$(H$_2$O)$_3$$^-$ (aq)	9	4 OT, 2 NT, 3 OW	17 252	-4	[22]
Eu(edta-dam)(H$_2$O)$_3$ (aq)	9	3 OT, 1 O, 2 NT, 3 OW	17 253	-3	[26]
Eu(oda)$_2$(H$_2$O)$_3$$^-$ (aq)	9	4 OT, 2 OE, 3 OW	17 253	-4	[22]
Eu(dpm)$_3$(terp) (s)	9	3 NT, 6 Oβ	17 254	-3	[28]
Eu(hedta)(H$_2$O)$_3$ (aq)	9	3 OT, 2 NT, 1 OH, 3 OW	17 255	-3	[22]
Eu(nta)(H$_2$O)$_5$ (aq)	9	3 OT, 1 NT, 5 OW	17 263	-3	[22]
Eu(dpa)(H$_2$O)$_6$$^+$ (aq)	9	2 OT, 1 NT, 6 OW	17 264	-2	[22]
Eu(chel)(H$_2$O)$_6$ (aq)	9	2 OT, 1 NT, 6 OW	17 265	-2	[15]
Eu(oda)(H$_2$O)$_6$$^+$ (aq)	9	2 OT, 1 OE, 6 OW	17 266	-2	[22]
Eu(imda)(H$_2$O)$_6$$^+$ (aq)	9	2 OT, 1 NT, 6 OW	17 267	-2	[22]
EuCl(H$_2$O)$_8$$^{2+}$ (aq)	9 [c]	1 Cl, 8 OW	17 270	-1	[29]
Eu(MeOH)$_9$ $^{3+}$ (aq)	9 [c]	9 OH	17 270	0	[30]
Eu(H$_2$O)$_9$$^{3+}$ (aq)	9	9 OW	17 280	0	this work
[Eu(18-C-6)(NO$_3$)$_2$]NO$_3$ (s)	10	6 OE, 4 ON	17 257	-2	[25]
Eu(NO$_3$)$_3$(H$_2$O)$_4$ (s)	10	6 ON, 4 OW	17 262	-3	[15]
Eu(eda)$_2$(H$_2$O)$_3$ $^-$ (aq)	11	4 OE, 4 OT, 3 OW	17 257	-4	[16]
Eu(eda)(H$_2$O)$_7$ $^+$ (aq)	11	2 OE, 2 OT, 7 OW	17 271	-2	[16]

[a] Abbreviations: dbm = dibenzoylmethane; stnv = satellite tobacco necrosis virus; pa = picolinamide; acac = acetylacetonate; nic = nicotinate; dpa = dipicolinate; chel = chelidamate; imda = iminodiacetate; oca = oxydiacetate; dtpa = diethylenetriaminepentaacetate; bis(dtpa-eam) = 1,4,7,16,19,22-hexa(carboxymethyl)-9,14,24,29-dioxa-1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane; dtpa-oam = 1,4,7-tris(carboxymethyl)-9,14-dioxo-13,16-dioxa-1,4,7,10,19-pentaazacycloheneicosane; deu = diethylurea; do3a-dimer = 1,4-bis(1-acetyl-4,7,10-tris(carboxymethyl)-1,4,7,10-tetraazacyclododecane)piperazine; dota = 1,4,7,10-tetraazacyclododecane-N,N',N'',N'''-tetraacetate; edta = ethylenediaminetetraacetate; edta-dam = 4,10,13-tris(carboxymethyl)-8,15-dioxo-1,4,7,10,13-pentaazacyclopentadecane; dpm = dipivolylmethane; terp = terpiridine; hedta = N'(2-hydroxyethyl)ethylenediaminetriacetate; nta = nitrilotriacetate; MeOH = methanol; eda = (1,2-ethanedioxydiyl)diacetate; s = solid state; aq = aqueous.

[b] Abbreviations: OT = charged carboxylate oxygen; OE = ether oxygen, O = amide carbonyl oxygen; NT = amine nitrogen; OW = water molecule oxygen; Cl = chloride ion; Oβ = β-diketonate oxygen; ON = nitrate oxygen; OH = hydroxyl oxygen.

[c] Coordination number estimated from molecular mechanics calculations (see Experimental).

$$[B] \cdot [A] = [C] \tag{4}$$

where matrix A is a 9×1 matrix that includes the nine atom parameters. Matrix A can be solved for by the following equation:

$$[A] = ([B'] \cdot [B])^{-1} \cdot ([B'] \cdot [C]) \tag{5}$$

where $[B']$ is the transpose of matrix B. Table 2 shows the atom types and atom parameters that were calculated

in this manner for the 9-coordinate complexes. A matrix $[C_p]$ containing predicted $\Delta\nu$ values can then be calculated as follows:

$$[C_p] = [B] \cdot [A] \tag{6}$$

Fig. 3 shows a plot of predicted ν-values versus actual ν-values for all of the 9-coordinate complexes. An excellent linear correlation is observed, with a correlation coefficient of 0.99. Surveying the residuals (ac-
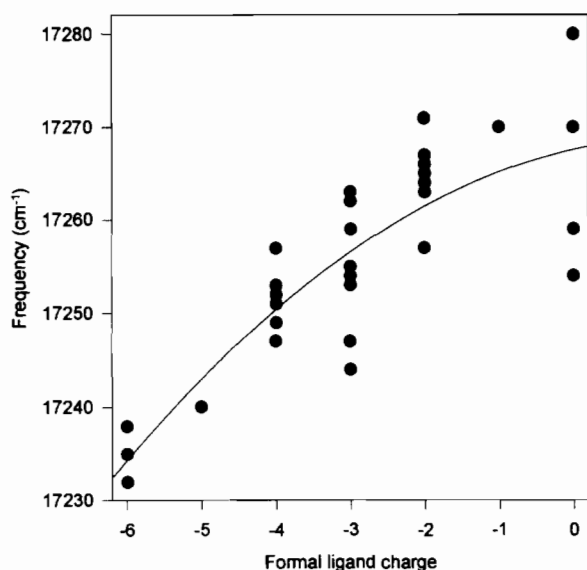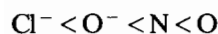
Fig. 2. Plot of the frequency of the $^7F_0 \rightarrow {}^5D_0$ transition vs. the formal charge of the ligands for each complex in the present study. The solid line represents a quadratic fit to the data ($\nu = -0.63p^2 + 1.78p + 17\,267$, where $p=$ formal ligand charge) with a correlation coefficient of 0.72. Several of the points are coincidental.

tual − predicted) suggests an uncertainty of ± 2 cm^{-1} in this calculation.

The generated atom parameters (δ_j) for 9-coordinate complexes cover a reasonable range of values (Table 2), the most negative being -21.2 for Cl$^-$ and the least negative being -10.4 for the oxygen atom of a water molecule, indicating that each atom type is distinct in its ability to lower the ν-value of Eu^{3+} in a particular complex. One can therefore rank these atoms in their ability to produce a nephelauxetic effect with Eu^{3+} as follows:

$$Cl^- > OT > O > O\beta > ON > NT > OH > OE > OW$$

This trend is essentially opposite to that of the expected electronegativities of these atoms or ions:

$$Cl^- < O^- < N < O$$

Since the covalency of the ligand–metal bond can be expected to increase with a decrease in the electronegativity (the atom becomes more willing to share

its electrons), this suggests that these calculated δ-values are a measure of the tendency of a particular atom to bond covalently with the Eu^{3+} ion. Although this covalent contribution to bonding is undoubtedly very small in relation to the ionic character of the bond, it nonetheless appears to have a measurable consequence on the $^7F_0 \rightarrow {}^5D_0$ transition. To establish further the legitimacy of these atom parameters, we note a rough linear correlation between those few of our computed nephelauxetic parameters that correspond to ligands involving the same donor atoms for which Jørgensen has presented nephelauxetic h-values [21] (Fig. 4).

There have been a number of reports in the literature which describe the nephelauxetic effect on the spectra of various lanthanide ions (Ln^{3+}) [35–39]. In each case the effect is attributed to variations in covalency among the complexes. Based on our analysis, we too believe that covalency is responsible for decreasing the parameters of interelectronic repulsion in the Eu^{3+} complexes studied here. If this is the case, one might expect that the nephelauxetic effect that an atom produces would vary among complexes of different coordination number. The average M–L distance is known to increase with coordination number, and hence the degree of covalency would decrease in the same manner. Indeed, this has been suggested previously in a study of Pr^{3+} and Nd^{3+} complexes [37]. For the present study, if the nephelauxetic parameters δ_j generated for the 9-coordinate complexes are used to predict the ν-values of the 7-, 8-, 10-, and 11-coordinate complexes, poor agreement with the experimental ν-values is obtained. Therefore, in order to adjust the nephelauxetic parameters to accommodate differences in coordination numbers, we returned to the multiple linear regression technique.

In this case an equation was written for each complex in the full data set (Table 1) as follows:

$$\text{actual } \Delta\nu = (\text{CN coefficient}) \cdot (\text{predicted } \Delta\nu) \qquad (7)$$

where CN coefficient is the nephelauxetic parameter adjustment coefficient associated with the coordination number of the particular complex, and the predicted ν-value is derived from the parameters determined for

Table 2
Coordination number coefficient (CN coeff.) and calculated nephelauxetic parameters for the 9 atom types [a] with various coordination numbers (CN)

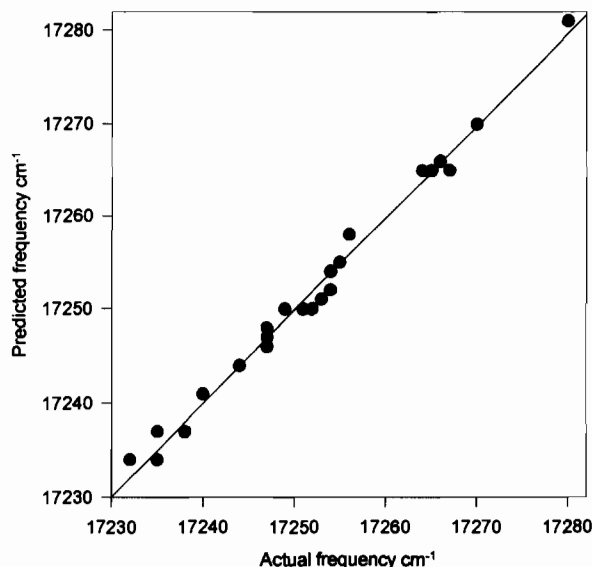| CN	CN coeff.	OT	OE	O	NT	OW	Cl	Oβ	ON	OH
7	1.22	−21.0	−13.5	−19.2	−14.8	−12.7	−25.9	−17.0	−16.2	−14.2
8	1.06	−18.2	−11.8	−16.6	−12.8	−11.0	−22.5	−14.7	−14.1	−12.3
9	1.00	−17.2	−11.1	−15.7	−12.1	−10.4	−21.2	−13.9	−13.3	−11.6
10	0.95	−16.3	−10.5	−14.9	−11.5	−9.9	−20.1	−13.2	−12.6	−11.0
11	0.80	−13.8	−8.4	−12.6	−9.7	−8.3	−17.0	−11.1	−10.6	−9.3

[a] For abbreviations see Table 1.

Fig. 3. Plot of predicted ν-values vs. ν-values for the twenty-seven 9-coordinate Eu^{3+} complexes listed in Table 1. The solid line represents a linear fit to the data with a correlation coefficient of 0.99. Several of the points are coincidental.
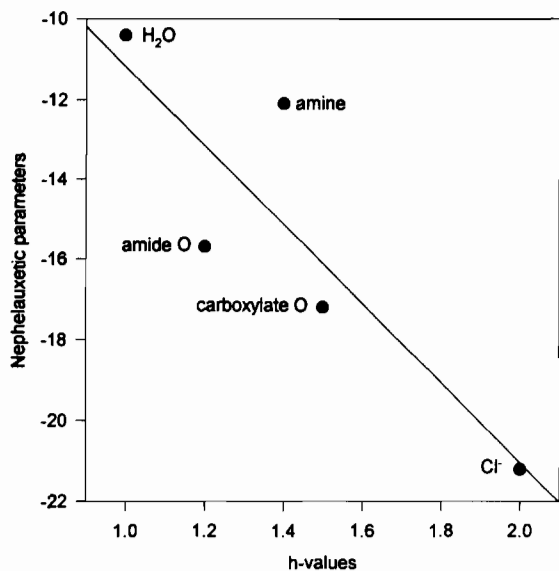

Fig. 4. Plot of nephelauxetic parameters developed in this study for 9-coordinate complexes vs. Jørgensen's [21] nephelauxetic h-values derived from studies on transition metal complexes for coordinating atoms that are common to both studies. The solid line represents a linear fit to the data.

the 9-coordinate complexes. A matrix [C] was generated as a 37×1 matrix containing all of the actual $\Delta\nu$ values. A matrix [B] was generated as a 37×5 matrix containing the predicted $\Delta\nu$ values in the appropriate column, wherein each column represents a particular coordination number. All other elements in matrix B were set equal to 0. Using Eq. (5), a 5×1 [A]-matrix was calculated which contains the adjustment coefficients (CN coefficients) for the various coordination numbers. The adjustment coefficients and the adjusted nephe-

lauxetic parameters so obtained are listed for each coordination number in Table 2. Once again, we calculate a matrix [C_p] that contains predicted ($\nu - \nu_0$)-values from Eq. (6). A plot of predicted ν-value versus actual ν-value for all thirty-seven complexes is shown in Fig. 5. The points fit very well to a straight line with a correlation coefficient of 0.98. Surveying the list of residuals for this correlation (actual − predicted) suggests that the uncertainty in the calculation is ±3 cm^{-1}. However, the $Eu(stnv)(H_2O)_3^{3+}$ complex falls 5 cm^{-1} from the line. Plotting CN coefficient versus coordination number (Fig. 6) produces a sigmoidal
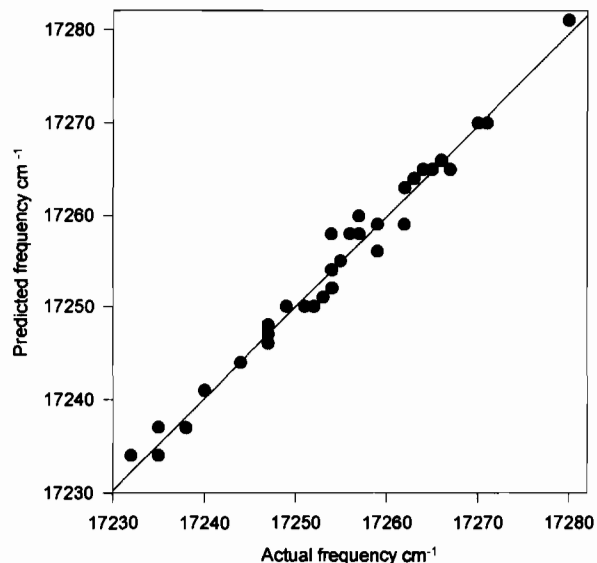

Fig. 5. Plot of predicted ν-values vs. actual ν-values for all of the thirty-seven Eu^{3+} complexes listed in Table 1. The solid line represents a linear fit to the data with a correlation coefficient of 0.98. Several of the points are coincidental.
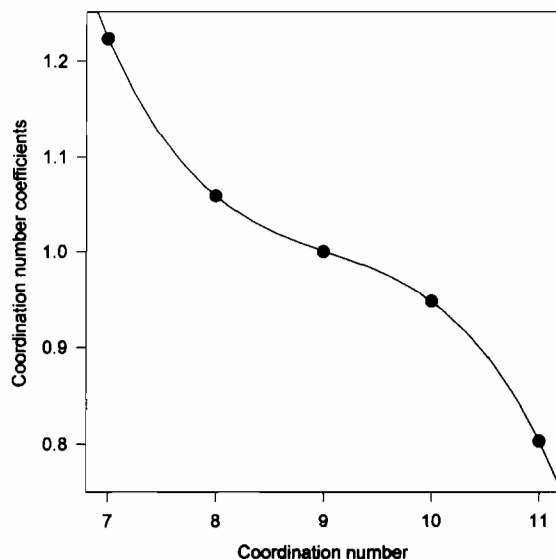

Fig. 6. Plot of coordination number coefficients determined in this study vs. coordination number. The solid line represents a cubic fit to the data.

curve whereby the coefficients increase exponentially going from coordination number 9 down to coordination number 7, and decrease exponentially going from coordination number 9 up to coordination number 11. The trend of increasing CN coefficient with decreasing coordination number in this curve reflects the sensitivity of covalent bonding to the internuclear distance. It should be noted, however, that there are very few data points for coordination numbers 7, 10, and 11. Thus their CN coefficients must be considered somewhat uncertain.

The thirty-seven Eu^{3+} complexes in our data set fit remarkably well to the line described by Eq. (2) when the appropriate coordination-number-adjusted nephelauxetic parameters (Table 2) are used. The Eu^{3+}–cryptate complex, $[Eu^{3+} \subset 2.2.1]Cl_3 \cdot 2H_2O$, provides a notable exception to the above-described correlation. In aqueous solution the complex coordinates 5 ether oxygens and 2 amine nitrogens from the cryptand, as well as 3 water-molecule oxygens [24]. According to Eq. (2), a ν-value of 17 269 cm^{-1} is predicted for this complex. However, the actual ν-value is 17 240 cm^{-1} [24]. It is likely, therefore, that the rigid, constraining environment created by the cryptand ligand encapsulating the Eu^{3+} ion causes the average internuclear distance to be shorter in this complex than it might otherwise be, bolstering the degree of covalency beyond that which is expected for other 10-coordinate complexes.

In the same light, we note the minor discrepancy with the complex $Eu(stnv)(H_2O)_3{}^{3+}$. Satellite tobacco necrosis virus is an icosahedral virus that contains a fivefold binding site for Ca^{2+} which consists of 5 backbone amide carbonyl oxygens. In a recent study [10], Eu^{3+} was used to replace Ca^{2+} in stnv and the system was thoroughly characterized by Eu^{3+} luminescence spectroscopy. The $^7F_0 \rightarrow {}^5D_0$ excitation spectrum revealed a single narrow (full width at half maximum equal to 6.5 cm^{-1}) band at 17 254 cm^{-1}. The sharp band, which is very unusual in biological systems, indicates a rigid homogenous environment, which is also revealed by a remarkable size selectivity among the Ln^{3+} ions. In this study it was also determined that the Eu^{3+} binds 3 water molecules. According to Eq. (2), the predicted ν-value is 17 259 cm^{-1}. While this is close to the actual ν-value, it does fall further off the line than any other complex in the data set, and this is likely due to the rigid metal ion environment in the virus. There are undoubtedly other systems like the cryptand and this virus that impose a rigid environment upon the Eu^{3+} ion, causing a heightened nephelauxetic effect.

In addition to the rigidity of the Eu^{3+} environment, geometric constraints may also cause certain complexes to deviate from the above-described correlation. In fact, it has been noted elsewhere that heterocyclic nitrogens tend to produce a greater nephelauxetic effect than do their aliphatic counterparts [24,25]. Although we see no evidence for this in the present study, it seems likely that directionality of bonding, imposed by geometric constraints, may be an important factor in some cases. For instance, the angle at which the Eu^{3+} ion bonds to a nitrogen atom may affect how well the metal orbitals can overlap with the lone-pair orbital of the nitrogen atom. Perhaps in many macrocyclic complexes the lone-pair orbitals of the heterocyclic nitrogens are better directed towards the Eu^{3+} ion, causing greater covalency.

We point out one anomalous system which cannot be understood in terms of the present correlation. The geometric isomers of solid tris(dipivaloylmethanato)-(2,9-dimethyl-1,10-phenanthroline)europium(III) are reported to have ν-values of 17 305 and 17 270 cm^{-1} (corrected to room temperature) [23]. This separation of 35 cm^{-1} is unprecedented for geometric isomers. Using the nephelauxetic parameters for 8-coordinate complexes derived in this study, a ν-value of 17 260 cm^{-1} is predicted for both of these isomers. The cause of this unusual behavior is not understood.

4. Conclusions

The $^7F_0 \rightarrow {}^5D_0$ transition energies for various Eu^{3+} complexes cover a range of only ≈ 55 cm^{-1}. Fortunately, owing to their narrow line widths (< 10 cm^{-1}), one can measure these energies very precisely. The energy of this transition is related to the interelectronic repulsion parameters for the Eu^{3+} ion, which are reduced from their free-ion values by the degree of covalency for a particular complex, according to the nephelauxetic effect. This effect is very subtle for Eu^{3+} complexes, as the f orbitals are well shielded from the ligand field, and covalency is expected to be minimal. Nonetheless, the effect is observable and allows the frequency of the $^7F_0 \rightarrow {}^5D_0$ transition to be used to diagnose the Eu^{3+} ion environment. Moune and Caro [40] have shown, using crystal field calculations involving large matrices and holding the interelectronic repulsion parameters constant, that the $^7F_0 \rightarrow {}^5D_0$ splitting may be affected by variations in $B_0{}^2$ and $B_2{}^2$, but not by other crystal field parameters. This effect arises from interactions between the split $^7F_1$ level and the ground $^7F_0$ state. Their phenomenological approach is not useful in low-symmetry complexes; however, crystal field differences from complex to complex may have minor influences on the ν-values and account to some degree for the imperfection in our correlation.

Nephelauxetic parameters have been deduced in this study for nine distinct coordinating atom types found in thirty-seven Eu^{3+} complexes. Importantly, these parameters can be understood in terms of expected dif-

ferences in the covalency of their bonds to Eu^{3+}. Furthermore, these parameters are shown to depend on the coordination number of the various complexes, such that coordinating atoms produce a greater nephelauxetic effect in complexes of lower coordination number than in complexes of higher coordination number. Since the internuclear distance is expected to decrease with decreasing coordination number, the trend in the nephelauxetic parameters is reflective of the sensitivity of covalency to internuclear distance.

Our future efforts will be aimed at extending the data set presented in this work to include more 7-, 8-, 10-, and 11-coordinate complexes as well as complexes that contain a greater variety of coordinating atoms, such as fluorine, bromine, iodine, and sulfur. As more data becomes available (i.e., X-ray crystallographic structure determinations of various Eu^{3+} complexes) we plan to focus our attention on the effect that internuclear distance has on covalency.

Acknowledgements

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