Correlation between Ligand Coordination Number and the Shift of the $^7F_0-^5D_0$ Transition Frequency in Europium(III) Complexes

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The relative shift of the Eu(III) $^7F_0-^5D_0$ transition toward lower energies due to the formation of inner-sphere Eu(III) complexes is shown to be linearly proportional to the total ligand donor number of the ligand bound to Eu(III) for 40 organic ligand complexed species in both water and DMSO solvents. Such a correlation allows estimation of the donor number, CN_L, of organic ligands coordinated to Eu(III) from the relative frequency, $\Delta\nu$, of the Eu(III) $7F_0-^5D_0$ transition by the equation of $CN_L = 0.237\Delta\nu + 0.628$. The validity of the method has been confirmed by using shift data of other Eu(III) complex systems from the literature. The nature of the shift of $^7F_0-^5D_0$ band upon complexation is discussed as possibly due to a small degree of covalency in the Eu−L bond of the complexes with organic ligands.

Introduction

Trivalent lanthanides exhibit variable and often large coordination numbers in complexes. For example, the lanthanide coordination number in crystals is as low as 3 in complexes with such bulky ligands as $N(SiCH_3)_3$[1] and as high as 12 with the small nitrate ligand.[1] The stereochemistries in these lanthanide complexes are determined primarily by the electrostatic and spatial requirements of the ligands and are frequently difficult to predict. This is particularly true for lanthanide complexes in solution.[2]

Although many techniques have been used for the determination of the coordination number of lanthanide ions in complexes (*e.g.*, conductivity,[3] measurement of entropies and enthalpies of complexation,[4−7] luminescence[8,9] and UV−visible spectroscopy,[10,11] and X-ray diffraction[12,13]), only the last one can give definite answers. Unfortunately, this technique is generally limited to crystalline complexes. Most often, the coordination numbers for lanthanide cations complexed in solution have been deduced from spectroscopic and conductance measurements. Recently, Eu(III) luminescence spectroscopy has been applied increasingly to the study of the coordination chemistry of lanthanides.[14−18]

In aqueous solution, the quenching of Eu(III) luminescence is due primarily to the hydroxyl group vibrations of solvated water. It has been shown that the luminescence-quenching effect is directly proportional to the number of water molecules in the inner coordination sphere.[19] Similar results were also observed for N−H vibrators.[20] The ground state manifold of Eu(III) ($4f^6$) is ^7F_i ($i = 0, 1, ..., 6$), and the excited state manifold is ^5D_j ($j = 0, 1, ...$). Though the higher excited states, such as $^5D_1$, are capable of luminescing, usually the strongest observed emission is from the transitions between $^5D_0$ and levels of the ground state manifold, ^7F_i ($i = 0, 1, ..., 6$) due to efficient energy transfer from higher excited states to $^5D_0$. Both of the shapes and the luminescence intensities of the excitation spectra and emission spectra of Eu(III) are sensitive to their environment and thus informative about the coordination structure.[21]

An interesting aspect of Eu(III) luminescence involves the $^7F_0-^5D_0$ excitation spectra. Since the excited state and ground state are both nondegenerate and cannot be split further by the ligand field, each peak in the spectrum must correspond to a distinct Eu(III) environment. Previous work[14−17,22] has shown that for Eu(III), the frequency of the $^7F_0-^5D_0$ excitation spectra shift upon complexation decreases as the coordination of the complex increases. This observation suggests that the $^7F_0-^5D_0$ frequency of Eu(III) may have a correlation with the ligand coordination number. This paper reports the results of a study of such a correlation in Eu(III) complexes with organic ligands. The symbols used for the ligands are listed in Table 1.

Experimental Section

Reagents. Samples of europium oxide (99.99%, Aldrich Chemical Co.) were dissolved in perchloric acid to prepare aqueous solutions of the europium perchlorate. The concentrations of europium were determined by complexometric titration with EDTA using 20% hexaethyltetramine as a buffer and xylenol orange as an indicator.[23]

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Table 1. Ligands Involved in This Work and Their Abbreviations

ligand	abbreviation
acetate	Ac
benzoate	BA
phthalate	PHA
isophthalate	IPA
terephthalate	TPA
hemimellitate	HMA
trimellitate	TMA
trimesate	TSA
pyromellitate	PMA
mellitate	MA
malonate	MAL
succinate	SUC
glutarate	GLU
adipate	ADI
pyridinedicarboxylate	DPA
diglycolate	DGA
iminodiacetate	IDA
N-methyliminodiacetate	MIDA
diethylenetriaminepentaacetate	DTPA
(diethylenetriaminepentaacetato)bis(methoxylamide)	DTPA-BMEA
1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetate	DOTA
4-hydroxypyridine-2,6-dicarboxylate	Chelid
ethylenediamine-N,N′,N″,N‴-tetraacetate	EDTA
nitrilotriacetate	NTA
ethylene glycol bis(β-aminoethyl ether) *N*,*N*,*N*′,*N*′-tetraacetate	EGTA
1,3-diphenyl-1,3-propanedione	DBM
4,4,4-trifluoro-l-(2-thienyl)-1,3-butanedione	TTA
4,4,4-trifluoro-l-phenyl-1,3-butanedione	btfa
enthylenediamine	en
1,10-phenanthroline	phen
dimethyl sulfoxide	DMSO

Diethylenetriaminepentaacetate-bis(methoxyethylamide) (DTPA-BMEA) was provided by Mallinckrodt Medical Corp. Reagent grade benzoic and acetic acids were purchased from Fisher Chemical Co. Anhydrous dimethylsulfoxide, DMSO, was purchased from Aldrich. The water content in the DMSO was less than 0.005%. All other ligands and the organic solvents were reagent grade from Aldrich and used without further purification. Distilled, deionized water was used in all experiments.

Stock solutions of the ligands with concentrations between 0.05 and 0.2 M were prepared by dissolving appropriate amounts of the acid ligand with adjustment of the pH with 1.0 M NaOH solution as necessary to achieve solution. The final pH of the stock solutions was adjusted to pH 5−6 with solutions either of sodium hydroxide or perchloric acid. Working solutions of the organic acids were prepared by dilution of the stock solution using distilled and deionized water. An appropriate amount of sodium perchlorate was added to maintain the ionic strength of the solutions at 0.1 M.

DMSO-solvated europium perchlorate was prepared by the published method.[24] A sample of europium oxide was dissolved in reagent grade perchloric acid with excess europium oxide. The mixture was heated to 50−80 °C for 4−5 h and the undissolved oxide removed by filtration. An excess of anhydrous DMSO was added to the filtrate solution after which the water was removed by evaporation under vacuum. The solid, with a formula of $Eu(ClO_4)_3 \cdot 7.5DMSO$, was obtained by precipitation with benzene. After filtration, the crystals were dried under vacuum at 50 °C for several days. The DMSO content was obtained by elemental carbon and hydrogen analysis and the europium content by EDTA titration using xylenol orange as an indicator. Solutions of europium perchlorate in DMSO was prepared by dissolving a weighed amount of this material in anhydrous DMSO.

The ethylenediamine reagent, its solutions, and DMSO were stored in the presence of powdered P_2O_5 in a glovebox with a dry nitrogen atmosphere. Except during manipulations, the glovebox was kept dark to prevent the reagents and solutions from possible photolytic effects.

The EDTA solution was prepared by dissolving reagent grade disodium salt (Aldrich) in distilled water. Hexamethylenetetramine solution (20%) was prepared by dissolution of the reagent in distilled water. Xylenol orange was prepared as a 1:100 solid dispersion in NaCl.

Solutions of the complexes were prepared by mixing the europium perchlorate solution and the corresponding ligand solution. The pH of these solutions were adjusted as needed using NaOH or perchloric acid. Speciation calculations using the program SPECIES[17] were performed to ensure that, under the solution conditions, a significant amount of complex was formed.

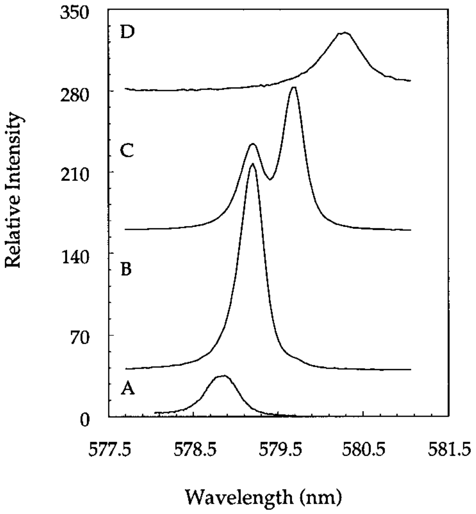

Figure 1. $^7F_0-^5D_0$ selective excitation spectra of Eu(III) complexes with dipicolinic acid. [Eu(III)] = 0.01 M; [DPA]:[Eu(III)] = 0:1 (A), 0.9:l (B), 1.8:1 (C), and 3.5:1 (D); λ_{em} = 618 nm. Offset to the intensity: curve A, 0; curve B, 40; curve C, 160; curve D, 280.

Apparatus. The $^7F_0-^5D_0$ selective excitation spectra of Eu(III) were measured in 1 cm quartz fluorimeter cells using an instrumental setup described elsewhere.[20] Spectral deconvolutions were performed for overlapping spectral peaks using the program SPECTRA written in this laboratory.[16] The precision of the spectral measurement is <0.2 cm^{-1} (<0.0067 nm).

The excitation spectra were recorded by scanning the dye laser monochromator throughout the $^7F_0-^5D_0$ band while monitoring the luminescence intensity at 616 nm. The luminescence decay curves were obtained after excitation at the maximum absorption of the $^7F_0-^5D_0$ band by monitoring the luminescence intensity at 616 nm.

Both of the monochromators were calibrated using the emissions lines of a mercury lamp at 404.656, 435.840, and 546.074 nm. The laser dye was a 50:50 (v/v) mixture of Rhodamine 590 and Rhodamine 610 (Exciton Chemical), and the dye was pumped by the second harmonic output of an Nd:YAG laser at 532 nm, which gave a laser power of *ca.* 30 mJ at 580 nm.

The pH measurements were performed with a Corning 130 pH meter equipped with a Corning Semi-Micro combination electrode filled with saturated sodium chloride solution. Standard buffer solutions at pH 7.00 and 4.00 (Fisher) were used for the calibration of the pH meter.

Results and Discussion

Twenty aqueous systems as well as a nonaqueous amine system in DMSO were studied. The aqueous ligands included mono-, di-, tri-, tetra-, and hexacarboxylic acids, aminocarboxylic acids, and oxocarboxylic acids. Figure 1 shows examples of typical excitation spectra of Eu(III), in this case complexed with pyridine-2,6-dicarboxylic acid, $Eu(DPA)_i$ ($i = 1, 2, 3$). As seen in the figure, formation of Eu(III) complexes with DPA causes a shift of the $^7F_0-^5D_0$ peak toward longer wavelengths. The luminescence decay constants for the complexes was decreased as *i* increased, *e.g.*, from *ca.* 9.0 ms^{-1} for $Eu(H_20)_9{}^{3+}$ to 0.6 ms^{-1} for $[Eu(DPA)_3]^{3-}$. The spectral shifts and the changes in the luminescence lifetimes for the other complexed systems are similar to those for the Eu(III)−DPA system.

Table 2 lists the $^7F_0-^5D_0$ frequencies, the shifts of the $^7F_0-^5D_0$ frequency relative to that of aquated Eu(III), $\Delta\nu$, and the maximum ligand coordination number, CN_L.

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Table 2. Frequency of $^7F_0-^5D_0$ Bands of Eu(III) Complexes at 25 °C and Total Ligand Coordination Numbers

complex	ν	$\Delta\nu$	CN_L	CN_c	ΔCN
$Eu(III)_{aq}{}^{3+}$	17 276.00	0.00	0	0.93	0.53
$EuAc^{2+}$	17 273.24	2.76	1	1.44	0.44
$Eu(Ac)_2{}^+$	17 271.15	4.85	2	1.91	−0.09
$Eu(Ac)_3$	17 265.19	10.81	3	3.22	0.22
$EUBA^{2+}$	17 271.75	4.25	1	1.77	0.77
$Eu(BA)_2{}^+$	17 264.75	11.25	2	3.32	1.32
$EUIPA^{2+}$	17 271.50	4.50	1	1.83	0.83
$Eu(IPA)_2{}^+$	17 265.50	10.50	2	3.1	1.15
$EuTPA^{2+}$	17 271.50	4.50	1	1.83	0.83
$EuPHA^+$	17 270.40	5.60	2	2.07	0.07
$Eu(PHA)_2{}^-$	17 262.15	13.85	4	3.89	−0.10
$EuMAL^+$	17 275.60	0.40	2	0.92	−1.08
$Eu(MAL)_2{}^-$	17 267.55	8.45	4	2.70	−1.30
$EuSUC^+$	17 271.60	4.40	2	1.81	−0.19
$Eu(SUC)_2{}^-$	17 264.25	11.75	4	3.43	−0.57
$EuGLU^+$	17 271.60	4.40	2	1.81	−0.19
$Eu(GLU)_2{}^-$	17 264.60	11.40	4	3.35	−0.65
$EuADI^+$	17 272.20	3.80	2	1.67	−0.33
$Eu(ADI)_2{}^-$	17 264.95	11.00	4	3.26	−0.74
EuHMA	17 270.25	5.75	2	2.10	0.15
EuTMA	17 270.50	5.50	2	2.05	0.04
EuTSA	17 271.50	4.50	1	1.83	0.83
$EuPMA^-$	17 271.00	5.00	2	1.94	−0.06
$EuMA^{3-}$	17 271.00	5.00	2	1.94	−0.06
$EuDPA^+$	17 265.19	10.81	3	3.22	0.22
$Eu(DPA)_2{}^-$	17 250.89	25.11	6	6.38	0.38
$Eu(DPA)_3{}^{3-}$	17 233.95	42.05	9	10.13	1.13
$EuDGA^+$	17 269.06	6.96	3	2.37	−0.63
$Eu(DGA)_2{}^-$	17 257.14	18.86	6	5.00	−0.99
$Eu(DGA)_3{}^{3-}$	17 244.94	35.83	9	8.75	−0.24
$EuIDA^+$	17 267.87	8.13	3	2.63	−0.37
$Eu(IDA)_2{}^-$	17 254.17	21.83	6	5.66	−0.34
$Eu(IDA)_3{}^{3-}$	17 238.11	37.89	9	9.21	0.21
$Eu(MIDA)_3{}^{3-}$	17 246.30	29.70	9	7.40	−1.60
$EuDTPA^{2-}$ [a]	17 240.00	36.00	8	8.79	0.79
Eu(DTPA-BMEA)[a]	17 244.00	32.00	8	7.91	0.09
$Eu(DMSO)_x{}^{3+}$	17 265.00	0.00	0	0.00	0.00
$Euen^{3+}$ in DMSO	17 259.50	5.50	2	2.05	0.05
$Eu(en)_2{}^{3+}$ in DMSO	17 252.00	13.00	4	3.71	−0.29
$Eu(en)_3{}^{3+}$ in DMSO	17 243.00	22.00	6	5.70	−0.30

[a] From ref 25.

For the Eu−en complexes, the shifts are relative to the frequency of the solvated Eu(III) in DMSO. The maximum ligand coordination numbers were obtained from literature data of X-ray diffraction studies of the solid complexes or of solid complexes of chemically similar ligands. For complexes for which no X-ray diffraction data are available, the maximum ligand coordination numbers were obtained by subtraction of the hydration number obtained in luminescence lifetime measurements from the total coordination number of Eu(III), *i.e.*, 9.0. For most of the ligands in this work, these maximum ligand coordination numbers coincide with the number of potential donor atoms of the ligand. For some ligands (*e.g.*, mellitate) luminescence lifetime measurement indicated that, among the six binding donors, only two carboxylates can bind simultaneously, presumably because of the steric hindrance. Therefore, a maximum ligand coordination number of 2 was listed. In all our systems, replacement of coordinated solvent molecules by a ligand causes the peak maxima to be shifted toward lower energies.

The shift, $\Delta\nu$, of the $^7F_0-^5D_0$ band of each of the complexes listed in Table 2 is plotted against the maximum ligand coordination number, CN_L, in Figure 2. Assuming linearity for this plot, linear regression analysis was used to obtain the equation

$$CN_L = 0.237\Delta\nu + 0.628 \qquad (1)$$

The correlation coefficient was 0.97. Such a good linear correlation supports the use of eq 1 to estimate the ligand coordination number of Eu(III) in complexes.

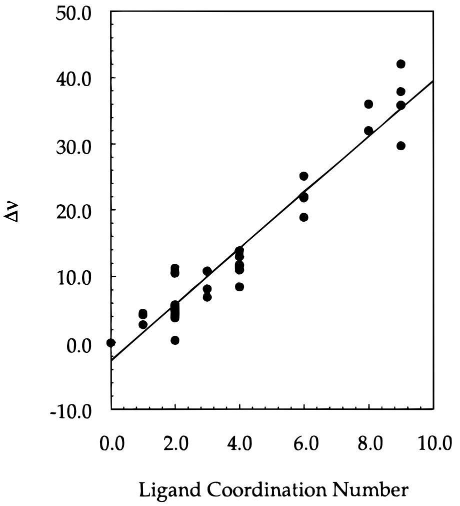

Figure 2. Correlation between the shift of the $^7F_0-^5D_0$ band frequency in Eu(III) complexes *vs* the total ligand coordination number, CN_L.

Table 3. Frequency of $^7F_0-^5D_0$ Bands of Eu(III) Complexes at 25 °C and Total Ligand Coordination Numbers Cited from Literature

complex	ν	$\Delta\nu$	CN_L	CN_c	ΔCN	ref
$Eu(DOTA)^-$	17247.00	29.00	8	7.50	−0.50	22
$Eu(chelid)_3{}^{6-}$	17235.00	41.00	9	10.34	1.34	22
$Eu(chelid)_2{}^{3-}$	17251.00	25.00	6	6.55	0.55	22
Eu(chelid)	17265.00	11.00	3	3.24	0.24	22
$Eu(EDTA)^-$	17251.00	25.00	6	6.55	0.55	22
EU(NTA)	17263.00	13.00	4	3.71	−0.29	22
$Eu(NO_3)^{2+}$	17269.00	7.00	2	2.29	0.29	22
$Eu(NO_3)_2{}^+$	17261.00	15.00	4	4.18	0.18	22
$Eu(DBM)_3(phen)$	17244.35	31.65	8	8.13	0.13	26
$Eu(TTA)_3(phen)$	17243.75	32.25	8	8.27	0.27	26
$Eu(btfa)_3(phen)$	17244.64	31.36	8	8.06	0.06	26
$Eu(EGTA)^-$	17244	32	8	8.21	0.21	27

The ligand coordination number calculated, CN_c, using eq 1 and the difference between these values and that of CN_L, ΔCN, are also listed in the Table 2. The values of CN_c are within ±1.5 of CN_L for 98% of the complexes, within ±1.0 for 88% of the complexes, and within ±0.5 for 58% of the complexes.

To further test the validity of eq 1, comparisons were made between the coordination numbers for complexes not used in Figure 2 or Table 2 in which the ligand coordination number can be estimated with good confidence and the coordination number calculated from the frequency of $^7F_0-^5D_0$ excitation spectra reported for the complex system in other studies.[22,25−27] The values in Table 3 indicate that the calculated values of the ligand coordination numbers are in good agreement with the reported values.

The shift of the absorption maxima of the $^7F_0-^5D_0$ excitation spectra of Eu(III) to lower energies upon complex formation has been studied by several authors[16,22,28−30] and is attributed commonly to a nephelauxetic effect. This shift can reflect either an increase of the metal−ligand bond covalency or a decrease of the effective nuclear charge on the metal ion upon complexation. From examination of the $^7F_0-^5D_0$ band frequency and

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the ligand charge of a number of complexes, Albin and Horrocks[15] correlated the frequency of the $^7F_0-^5D_0$ band and the total formal negative charge of the ligands by eq 2,

$$\nu = -0.76p^2 + 2.29p + 17\,273 \qquad (2)$$

where ν is the frequency of the $^7F_0-^5D_0$ band in inverse centimeters and p is the formal negative charge. This correlation attributes the shift of the frequency of the $^7F_0-^5D_0$ band of Eu(III) upon complexation to a decrease in the effective nuclear charge on the lanthanide as the negative charge of the ligands is increased. This relationship has been used to interpret the nature of metal ion binding in proteins.[22] Calculation of the ligand formal charge in these complexes studied[22] yields values with errors of ±1.4 charge units. This relationship seems to hold for ligands in which most of the donor groups are negatively charged but not for those in which most of the donor groups are neutral or a large number of the anion groups are not bound *(e.g.,* amines, β-diketones, and crown ethers). For example, with eq 2, the frequency shift of the $^7F_0-^5D_0$ bands of Eu−en complexes indicate that each en acts as though its charge was ≥ -2.0 even though en is a neutral ligand. A similar problem with eq 2 is found in the DTPA and DTPA-BMEA complexes in which the ligands coordinate to Eu(III) as octadentate ligands. The five carboxylate groups of DTPA results in a formal charge of −5 while DTPA-BMEA, with three carboxylate groups, has a formal charge of −3. However, Eu(III) complexes of both ligands show very similar shifts of the $^7F_0-^5D_0$ band frequencies.[18] The binary complex of Eu(III) with 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane-*N*,*N′*-diacetic acid (K22DA)[19] and the ternary complex of Eu(III) with β-diketones and 1,10-phenanthroline (phen) have total charges of −2 and −3, respectively. From the frequencies of the $^7F_0-^5D_0$ bands, the total ligand charges of both are calculated to exceed −5 by eq 2.

The data in Tables 2 and 3 suggest that correlation of the shift of the $^7F_0-^5D_0$ band frequencies of Eu(III) complexes and the maximum ligand coordination number can be applied over a wider range of complexes than the relationship between the frequency and formal negative charge.

From the correlation of the nephelauxetic effect in Pr(III) and Nd(III) complexes with average metal−ligand distances determined by X-ray crystallography, Davidenko and Yatsimirskii[28] suggested that there might be a correlation between the electronic transition frequency with the total coordination number of the metal. From the data for a limited number of complexes, Albin and Horrocks[22] reported finding no such correlation. Our more extensive data support such a linear correlation but with the actual number of bound ligand donor groups, CN_L, rather than the total metal coordination number, *(i.e.,* ligand + inner-sphere solvent).

If the shift of spectral maxima toward lower energy in lanthanides is due to a decrease in the parameters of interelectronic repulsion arising from either covalency of the metal−ligand bond or a decrease in the effective nuclear charge of the metal ion,[22] the fact that neutral ligands have effects of similar magnitude as negatively charged donors in inducing the spectral shift might imply a relatively important role for covalency (assuming that the neutral ligands have neutral donor atoms). Nevertheless, it is important to assess this implication properly as the great majority of evidence is that the covalent contribution to Eu(III)−L bonding is minor. For example, among all of the complexes listed in Tables 2 and 3, the largest shift of the $^7F_0-^5D_0$ frequency is only 43 cm^{-1}. Compared with the energy of the $^7F_0-^5D_0$ band, 17 276 cm^{-1}, this is 0.25% of the energy of the band, indicating minor covalent perturbation at best. Also, shifts of the absorption spectra toward lower energies were observed in the complexes of Nd(III) and Ho(III).[31−33] Unfortunately, the *J* multiplicity of both the ground states and the excited states of these two metal ions prevent developing quantitative relationships between the frequencies of the absorption spectra of complexes and properties of the ligands or of the complexes. Both the ground and excited states split further in a ligand field and result in a large number of overlapping absorption bands that cannot be separated. This prevents assignment of the frequency of the electronic transition of a single *J* sub level.

The present results show that, for pure solvated Eu(III) in H_2O and in DMSO, the $^7F_0-^5D_0$ band appears at different frequencies, which indicates that the energy of the band is affected by the solvent. Similar effects have been reported for the absorption spectra of lanthanide ions. For example, a study of Nd(III) absorption spectra in a series of organic solvents and H_2O by Bai et al.[34] found that the oscillator strength of the hypersensitive band of Nd(III) at 575 nm increases from 9.68 $\times 10^{-6}$ in H_2O to 19.62 $\times 10^{-6}$ in acetonitrile and shifts toward longer wavelengths. Misra and Sommerer[35] showed that, for Nd(III) complexed with β-diketonates, alkoxides, and Schiff base derivatives and in mixed ligand complexes in DMSO solvent, the sequences of the oscillator strengths of the five visible bands for transitions from the $^4I_{9/2}$ to the $^4G_{7/2}$, $^4G_{5/2}$, $^4F_{7/2}$, $^4F_{5/2}$, and $^4F_{3/2}$ levels are always higher than in other solvents. Because of this solvent effect, eq 2 is valid only when $\Delta\nu$ is calculated from the complexed and solvated Eu(III) in the same solvent (unless the effect of solvent has been property corrected).

The relative frequency shift of Eu(III) between DMSO and H_2O indicates DMSO is the stronger solvator as had been shown previously.[36] The frequency shift caused by a single inner-sphere DMSO solvate molecule is much smaller than that by a strong chelating ligand.

Even with the uncertainty reflected in Tables 2 and 3, the linear relationship derived in the present work could be quite useful in the exploration of lanthanide coordination chemistry and of ligand binding behavior toward Ln(III), since direct measurement of the $^7F_0-^5D_0$ spectra of the complex allows determination of the ligand coordination number in the inner sphere of Eu(III). Combined with the determination of the residual hydration number by Eu(III) luminescence lifetime measurement,[19] this allows evaluation of the total coordination structure of complexed Eu(III) in aqueous systems. An advantage of eq 1 is that it is not solvent limited. Further, the very small temperature dependence of the peak frequency simplifies the measurement of the frequency. The data in Table 3 does indicate that, while this general correlation can be useful, there are other factors which perturb the correlation. For example, comparison of $\Delta\nu$ values for $Eu(Ac)_2$, Eu(MAL), and Eu(SUC) reflects the effect of a stable five-member chelate ring.

Note added in proof: We note that since the initial submission of this paper, a correlation between frequency of the $^7F_0-^5D_0$ transition in Eu(III) complexes with the sum of the nephelauxetic parameters of the coordinating atoms has been published.[37]

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