Calgary were supported by the Natural Sciences and Engineering Research Council Canada. We thank La Convention Intercantonale Romande pour l'Enseignement du 3^e Cycle en Chimie for a visiting professorship (to T.W.S.), D. Zbinden for chemical analyses, Drs. M. Grant and R. B. Jordan for providing us with their results in full prior to publication, and Dr. Y. Ducommun for much invaluable advice and assistance.

Registry No. $Fe(H_2O)_6^{2+}$, 15377-81-8; $Fe(H_2O)_5OH^{2+}$, 15696-19-2.

Contribution from the Departments of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514, and University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Exchange Coupling in the Hydroxo-Bridged Chromium Dimer Di-μ-hydroxo-bis(ethylenediamine-*N*,*N'*-diacetato)dichromium(III) Tetrahydrate. Observations on the Effect of Structure on Superexchange Interactions

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Received January 26, 1981

The magnetic susceptibility of the hydroxo-bridged chromium dimer di-μ-hydroxo-bis(ethylenediamine-*N*,*N'*-diacetato)-dichromium(III) has been measured in the temperature range 3.0–79 K and the data fitted by the Van Vleck equation for pairs of exchange coupled $S = {}^3/_2$ ions including a biquadratic term to yield the parameters $J = -9.3$ cm^{-1}, $j = -0.2$ cm^{-1}, and $g = 1.96$. These magnetic data for $[Cr_2(EDDA)_2(OH)_2]\cdot 4H_2O$, the complex with the smallest ratio of ϕ, the angle at the bridging oxygen atom, to r, the chromium–bridge oxygen bond distance, confirm that a correlation between the singlet–triplet splitting and ϕ/r exists. The correlation is similar to that which has been observed for di-μ-ligand-bridged copper(II) systems. The dependence of the exchange coupling mechanism on structural features is discussed in terms of molecular orbital theory.

Introduction

Following an extensive study of the effects of structural variations and chemical functional groups on exchange coupling in di-μ-hydroxo-dichromium(III) complexes of the general formula $[Cr_2L_n(OH)_2L'_m]^{q\pm}$ (where L is a bidentate or tridentate ligand and $L' = H_2O$ in complexes with tridentate ligands), Scaringe[1] observed that the singlet–triplet splitting was highly correlated with the function ϕ/r. Here ϕ is the angle at the bridging hydroxo oxygen atom and r is the chromium–bridging oxygen bond distance, or the average of the structural parameters ϕ and r, respectively, if they are crystallographically independent. The singlet–triplet splitting is given by $|\Delta E| = 2J - 6.5j$, where J is the bilinear exchange coupling constant and j is the biquadratic term from the Hamiltonian $\mathcal{H} = -2JS_1\cdot S_2 - j(S_1\cdot S_2)^2$ required for the analysis of the temperature variation of the magnetic susceptibility in most cases. Scaringe[1] provided an explanation for the correlation between structural and magnetic properties of these dimeric chromium complexes in terms of the molecular orbital formalism developed by Hoffmann and co-workers[2] and postulated that the minor deviations from the general trend between ΔE and ϕ/r were a result of other structural features, electronic effects, and intermolecular interactions. The data[3,4] for $[Cr_2(glycine)_4(OH)_2]$ suggested that ΔE had reached a maximum at a ϕ/r value of ~50°/Å, and we were lead to speculate that ΔE should decrease with further decreases in ϕ/r in a manner similar to that which has now been established for uni- and di-μ-ligand-bridged copper(II) complexes.[5] The recent report[6] of the synthesis and crystal structure of di-μ-hydroxo-bis[(ethylenediamine-*N*,*N'*-diacetato)chromium(III)] tetrahydrate has provided an excellent opportunity to verify the anticipated decrease in ΔE below ϕ/r values of 50°/Å, since the chromium–bridging oxygen bond distance in this complex is 1.964 (3) Å and the Cr–O–Cr bridging angle is 97.6 (1)°, giving $\phi/r = 49.7°/Å$, the smallest value that has been observed in this series of complexes. We have now prepared $[Cr_2(EDDA)_2(OH)_4]\cdot 4H_2O$ by an alternate synthetic route and determined its magnetic properties. The results of our work are presented in this article.

Experimental Section

$[Cr(EDDA)(acac)]\cdot 2H_2O$. The crystalline product was prepared by Shepherd's modification[7] of the synthesis reported by Fuji.[8] $CrCl_3\cdot 3H_2O$ (5.28 g) was powdered in a mortar and transferred to a 400-mL beaker. H_2EDDA (8.00 g) and 40 mL of H_2O were added, and the pH was adjusted to 3.5 with powdered $(NH_4)_2CO_3$. The solution was heated for 30 min at ca. 45 °C. Acetylacetone (Hacac) (2.00 g) was added to the solution, and the pH was adjusted to 7.0 with $(NH_4)_2CO_3$. The stirred solution was heated to 75 °C for 1 h, cooled to room temperature, and stored overnight (12 h) in a refrigerator at 4 °C. The solid crystals were collected by filtration and washed with CH_3OH which has been chilled in an ice-salt slush.

$[Cr_2(EDDA)_2(OH)_2]\cdot 4H_2O$. $[Cr(EDDA)(acac)]\cdot 2H_2O$ (3.32 g, 9.19×10^{-3} mol) was dissolved in a solution of 10.0 mL of H_2O and 10.0 mL of 1.095 M $HClO_4$ in a 50-mL beaker. The sample was heated with constant stirring for 8 h at 80 °C with the volume being maintained between 10 and 20 mL. During the reaction, which involved distillation of Hacac into the vapor phase, samples showed a decreasing absorbance at 386 nm, with the band shifting to 390 nm, and almost no change in the absorbance band at 532 nm. Acetylacetone was also detectable by its characteristic odor until the later periods of heating. After 8 h, the solution was adjusted to pH 5.96 with 0.38 g of NaOH pellets. The color changed with a shift in the long-wavelength maximum from 549 to 557 nm. The solution was heated for 1 h at 80 °C, resulting in a reduction in the volume to 10 mL by evaporation. The solution was allowed to cool to room temperature overnight, after which time a purple-pink opalescent

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Table I. Magnetic and Structural Data for Di-μ-hydroxo-Bridged Chromium(III) Complexes

	ϕ, deg	Cr–O, Å	Cr–Cr, Å	$2J$, cm^{-1}	j, cm^{-1}	ΔE, cm^{-1}	ϕ/r, deg/Å	ref
$[Cr(EDDA)(OH)]_2 \cdot 4H_2O$	97.6 (1)	1.960 (4)	2.950 (2)	−18.6	−0.2	−19.9	49.80	6, this work
$[Cr(gly)_2(OH)]_2$	98.2 (2)	1.967 (4)	2.974 (2)	−7.4	0.4	−10.0	49.92	3, 4
$Na_4[Cr(mal)_2OH]_2 \cdot 5H_2O$	99.34 (7)	1.988 (2)	3.031 (2)	+2.2	0.0	+2.2	49.95	16
$[Cr(en)_2OH]_2(S_2O_6)_2$	100.0 (2)	1.979 (5)	3.032 (3)	−2.16	0.234	−3.6	50.53	17
$Na_4[Cr(ox)_2OH]_2 \cdot 6H_2O$	99.6 (2)	1.963 (11)	3.000 (3)	−0.6	0.0	−0.6	50.74	18
$[Cr(H_2O)(HO\text{-dipic})OH]_2 \cdot 4H_2O^a$	99.5 (2)	1.953 (8)	2.981 (5)	−4.2	0.0	−4.2	50.95	19
$[Cr(H_2O)(dipic)OH]_2 \cdot 2H_2O^b$	100.7 (2)	1.947 (8)	2.997 (3)	−10.2	0.0	−10.2	51.72	20
$[Cr(H_2O)(Cl\text{-dipic})(OH)]_2{}^c$	100.7 (5)	1.947 (11)	2.999 (3)	−14	0.0	−14	51.72	19
$[Cr(en)_2OH]_2Cl_4 \cdot 2H_2O$	102.42 (5)	1.944 (5)	3.029 8 (4)	−29.4 (5)	0.3 (1)	−31.4	52.69	21
$[Cr(en)_2OH]_2Br_4 \cdot 2H_2O$	102.6 (1)	1.948 (3)	3.040 (2)	−28.6, −27.7 (8)	0.8, 0.3 (2)	−33.8, −26.8	52.7, 52.7	21
$[Cr(en)_2OH]_2(Cl)_2(ClO_4)_2 \cdot H_2O$	103.42 (8)	1.949 (4)	3.059 (2)	−26.8, −24.3 (3)	0.0, 0.4 (1)	−26.8, −26.9	53.1, 53.1	1, 21
$[Cr(phen)_2OH]_2I_4 \cdot 4H_2O$	102.1 (3)	1.919 (7)	2.986 (4)	−43.8	1.5	−53.6	53.21	22
$[Cr(phen)_2OH]_2Cl_4 \cdot 6H_2O$	102.7 (5)	1.927 (11)	3.008 (3)	−55.5	0.8	−50.3	53.3	23, 24

[a] HO-dipic is 4-hydroxopyridine-2,6-dicarboxylate. [b] dipic is pyridine-2,6-dicarboxylate. [c] Cl-dipic is 4-chloropyridine-2,6-dicarboxylate.

powder was obtained. The product, which is insoluble in acetone or DMF, was collected by filtration. The solid $[Cr_2(EDDA)_2(OH)_2] \cdot 4H_2O$ was redissolved in hot water and reclaimed from a concentrated solution by a reduction in the volume and slow cooling overnight. The resulting solid was collected by filtration.

Magnetic Measurements. Magnetic susceptibility data were collected with the use of a Princeton Applied Research Model 155 vibrating sample magnetometer.[9] The vibrating-sample magnetometer was operated at 10 kOe, and the VSM magnet (Magnion H-96), power supply (Magnion HSR-1365), and associated field control unit (Magnion FFC-4 with a Rawson-Lush model 920 MCM rotating-coil gaussmeter) were calibrated against NMR resonances (^1H and ^3Li). The field set accuracy is better than 0.15% at 10 000 G. The magnetometer was initially calibrated against $HgCo(NCS)_4$,[10] and the calibration was checked against a sample of $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$.[11] The results using these two standards agreed to within 2%, and it is felt that this represents the upper limit to the uncertainty in the measurements of the magnetic susceptibility since the field is known to a much higher degree of accuracy. Powdered samples of the calibrants and compounds used in this study were contained in precision-milled Lucite sample holders. Approximately 150 mg of each were used. Diamagnetic corrections for the constituent atoms were made with use of Pascal's constants, and a correction for temperature-independent paramagnetism was estimated from tabulated data.[12-14]

Results

Magnetic susceptibility data were collected on several samples of $[Cr_2(EDDA)_2(OH)_2]$, all of which gave excellent analytical data with the observed and calculated percentages of carbon, hydrogen, and nitrogen differing by no more than 0.2. However, all of these samples contained a small quantity of monomeric impurity, presumably $[Cr(EDDA)(OH)(H_2O)] \cdot nH_2O$, as indicated by the Curie-like behavior of the magnetic susceptibility at low temperatures.

The Van Vleck equation[15] for a pair of exchange coupled $S = {}^3/_2$ ions, including biquadratic exchange (eq 1) was fitted

$$\chi_m = (Ng^2\mu_B{}^2/kT) \times \{2\exp[(2J - 6.5j)/kT] + 10\exp[(6J - 13.5j)/kT] + 28\exp[(12J - 9j)/kT]\}/\{1 + 3\exp[(2J - 6.5j)/kT] + 5\exp[(6J - 13.5j)/kT] + 7\exp[(12J - 9j)/kT]\} \quad (1)$$

to the magnetic susceptibility data in the temperature range 20–80 K with use of a nonlinear Simplex fitting routine with

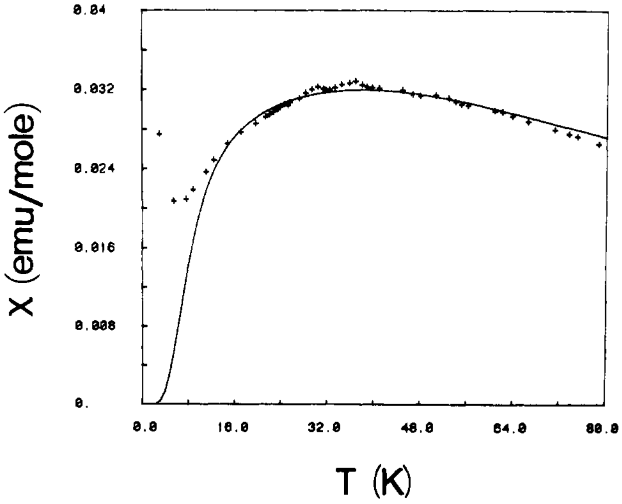

Figure 1. Temperature variation of the magnetic susceptibility of $[Cr_2(EDDA)_2(OH)_2] \cdot 4H_2O$. The solid line was generated from the Van Vleck equation for pairs of exchange coupled $S = {}^3/_2$ ions with the best fit parameters $J = -9.3$ cm^{-1}, $j = -0.2$ cm^{-1}, and $g = 1.96$.

the criterion of best fit being the minimum value of the function $\sum_n[(\chi_n{}^{obsd} - \chi_n{}^{calcd})/\chi_n{}^{obsd}]^2$. Data below 20 K were not used in the fitting process since successive calculations indicated that these data reflected the presence of the monomeric impurity, while those data above 20 K were unaffected within the experimental error of the measurements. The best fit parameters $J = -9.3$ cm^{-1}, $j = -0.2$ cm^{-1}, and $g = 1.96$ were used with eq 1 to generate the solid line in Figure 1.

Discussion

Structural and magnetic data have been collected[3,4,16-24] for a number of di-μ-hydroxo-dichromium(III) complexes of the general formula $[Cr_2L_n(OH)_2L'_m]^{q\pm}$ where L is a multidentate ligand and L′ is H_2O with $n = 2$ in complexes with tridentate

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ligands; $n = 4$ and $m = 0$ for bidentate ligands, and $n = 1$, $m = 0$ for the one example of a tetradentate ligand. The available data, including those obtained during the course of this work, are collected in Table I. The chromium–bridging oxygen bond distances are the average of two crystallographically independent values except for the complexes with 1,10-phenanthroline and oxalate ligands where all four Cr–O distances are independent. As may be seen from the entries in the table, these bond distances range from 1.92 to 1.99 Å. The chromium–oxygen–chromium bridge angels, or the mean of two independent Cr–O–Cr angles, range from 97.6 (1)° in $[Cr_2(EDDA)_2(OH)_2]\cdot 4H_2O$ to 103.42 (8)° in $[Cr(en)_2OH]_2Cl_2(ClO_4)_2\cdot H_2O$. In all cases, the chromium ions are situated in distorted octahedral coordination environments. The edge-sharing octahedral structures of the dimeric units are formed by bridging hydroxo ligands, and it has been firmly established that the pairs of chromium(III) ions in the dimers are exchange coupled by superexchange interactions propogated through the orbitals of the bridging oxygen ligands.[1,25,26]

In an extension of the treatment of superexchange interactions by Hoffmann and co-workers[2] to pairs of interacting chromium(III) ions, Scaringe[1] constructed two-center molecular orbitals from localized molecular orbitals on the chromium(III) ions. These orbitals on chromium(III) contain the unpaired electrons which are involved in the superexchange interactions and are mainly t_{2g}-like orbitals, but some ligand character is implied. The localized molecular orbitals are defined as

$$\phi_a^A \simeq d_{x^2-y^2}^A \qquad \phi_d^B \simeq d_{x^2-y^2}^B$$

$$\phi_b^A \simeq d_{xz}^A \qquad \phi_e^B \simeq d_{xz}^B$$

$$\phi_c^A \approx d_{yz}^A \qquad \phi_f^B \approx d_{yz}^B$$

Where A and B designate the two chromium(III) ions in the exchange coupled pair. The two center molecular orbitals are defined as

$$\phi = 1/2^{1/2}(\phi_a^A + \phi_d^B) \qquad \phi_2 = 1/2^{1/2}(\phi_a^A - \phi_d^B)$$

$$\phi_3 = 1/2^{1/2}(\phi_b^A + \phi_e^B) \qquad \phi_4 = 1/2^{1/2}(\phi_b^A - \phi_e^B)$$

$$\phi_5 = 1/2(\phi_c^A + \phi_f^B) \qquad \phi_6 = 1/2^{1/2}(\phi_c^A - \phi_f^B)$$

Ferromagnetic contributions arise from potential exchange integrals K_{ij}, where i and j designate the localized molecular orbitals. J_F is given by eq 2. The antiferromagnetic contribution J_{AF} is given by eq 3 where J_{ij} are the Coulomb

$$J_F = \tfrac{2}{9}(K_{ad} + K_{ae} + K_{af} + K_{bd} + K_{be} + K_{bf} + K_{cd} + K_{ce} + K_{cf}) \tag{2}$$

$$J_{AF} = -\frac{1}{18}\left[\frac{(E_2 - E_1)^2}{J_{aa} - J_{ad}} + \frac{(E_4 - E_3)^2}{J_{bb} - J_{be}} + \frac{(E_6 - E_5)^2}{J_{cc} - J_{cf}}\right] \tag{3}$$

integrals and E_i are the one-electron molecular orbital energies.

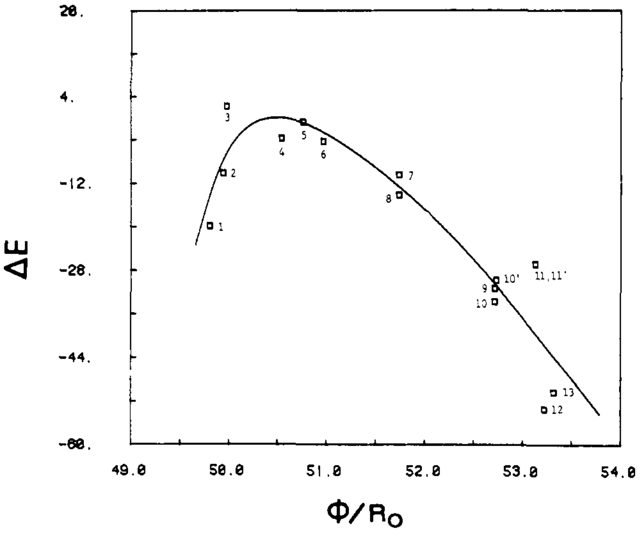

Figure 2. Plot of singlet–triplet splittings ΔE vs. the structural function ϕ/r for the series of complexes $[Cr_2L_n(OH)_2L'_m]^{q\pm}$. ϕ is the Cr–O–Cr bridge angle, and r is chromium–bridging oxygen bond distance. The numbers refer to the data points listed in Table I, and the solid line is a guide for the eye.

The potential-exchange integrals K_{ij} between orbitals largely localized on the two different metal centers are positive, and J_F is always positive although its magnitude is governed by structural and chemical variations of the specific complex. Hoffmann and co-workers[2] have presented convincing arguments that the K_{ij}'s are not affected a great deal by subtle structural variations in a series of chemically related complexes, and it is reasonable to conclude that significant changes in the sign and magnitude of the exchange coupling constant must depend on changes in the contributions to J_{AF}. Since Coulomb integrals J_{ii} between electrons localized largely on the same metal center will always be greater than those between electrons on different metal centers, J_{ij}, the denominators of the three terms in eq 3 will always be positive. Since these integrals are insensitive to minor structural variations, then variations in exchange coupling must result from changes in the energy differences of the molecular orbitals, the numerators of the three terms in eq 3. If it is assumed that the energies of the orbitals are proportional to overlap, then a qualitative discussion of the effects of chemical and structural variations on J can be based on an examination of the effect of chemical and structural features on orbital overlap.

Essentially, the overlap of the symmetric and antisymmetric combinations of the metal-based orbitals with those of the ligand bridge must be examined, where it may be expected that the p_x, p_y, p_z orbitals of the bridging hydroxo oxygen atoms are the major participants in the bonding. First, consider the in-plane orbitals: these include the symmetric and antisymmetric combinations ψ_1 and ψ_2 of the $d_{x^2-y^2}$ orbitals and like combinations of oxygen p_x and p_y orbitals. Scaringe[1] concluded that these orbitals made the dominant contribution to J_{AF} based on spectroscopic evidence for a chromium dimer reported by van Gorkom, Henning, and van Stapele.[27] It may be demonstrated by straightforward calculations that an increase in the angle at the bridging oxygen atom increases the overlap of ψ_1 with the combination of oxygen p_y orbitals while a like increase in angle decreases the overlap of ψ_2 with oxygen p_x orbitals. The significance of these observations will be discussed below.

Molecular orbitals involving interactions with the out-of-plane oxygen p_z orbitals are π-type overlaps which have been shown by van Gorkom, Henning, and van Stapele[27] to be about 5 times less than that of the in-plane contribution to J_{AF}.

With J_f being essentially constant and the second two terms in eq 3 being dominated by the first term, then it follows that, in general, J should increase with an increase in ϕ, the angle at the bridge, reach some maximum value, when the difference $|E_2 - E_1|$ is minimized, and then decrease with a further increase in ϕ. The exact behavior that will be observed in a given set of complexes depends on the relative ordering of E_2 and E_1. It is conceivable that these energy levels could be widely different in energy over a range of characterized complexes

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and that only a monotonic change would be seen in the exchange coupling constant. Whether J would increase or decrease with ϕ/r for such a series of complexes would depend largely on the identity of the lowest lying level. However, as Scaringe[1] has shown for the complexes under consideration here, the magnetic data clearly demonstrate that the difference $|E_2 - E_1|$ determines the observed trend in the exchange coupling.

Attempts to understand the exchange coupling mechanism and the magnitude of the singlet–triplet splitting must take into account both the bilinear exchange coupling constant from the term $-2JS_1 \cdot S_2$ and the biquadratic exchange coupling constant from the term $-2j(S_1 \cdot S_2)^2$. This latter term accounts for the departure of the energy levels from the interval rule given by $J[S'(S' + 1)]$ and results in a triplet–singlet splitting $|\Delta E|$ of $2J - 6.5j$. The singlet–triplet splittings, ΔE, from Table I are plotted as a function of ϕ/r in Figure 2. It may be seen in Figure 2 that the expected behavior of the singlet–triplet splitting is observed, that is, ΔE increases with an increase in ϕ/r, reaches a maximum at about 50°/Å and then decreases with a further increase in ϕ/r, although there is some scatter in the data. Presumably these minor variations from the overall trend arise from intermolecular interactions through hydrogen-bonding networks which differ widely in the set of complexes, from electronic effects that arise as a result of orbitals on nonbridging donor atoms, and from structural variations other than ϕ and r. Data on additional members of this series of hydroxo-bridged chromium(III) complex may permit an understanding of these secondary effects, but it is clear from these studies that the major structural factors affecting exchange coupling in these complexes are the angles at the bridging oxygen atom and the chromium(III)–oxygen bridge) bond distance. Furthermore, the experimental results may be described qualitatively by molecular orbital theory and these results provide considerable stimulation for quantitative calculations.

Acknowledgment. This research was supported by the National Science Foundation through research Grant No. CHE80 09685.

Registry No. $Cr_2(EDDA)_2(OH)_2$, 78340-40-6; Cr(EDDA)(acac), 26085-42-7.

Contribution from the Paul M. Gross Chemical Laboratory,
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Hypersensitive Transition Probability in Tris(1,3-diphenyl-1,3-propanedionato)aquolanthanides(III)

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Received January 16, 1981

Experimental oscillator strengths are found for f → f electronic transitions in solid-state tris(1,3-diphenyl-1,3-propanedionato)aquolanthanides(III) and used in the determination of Judd–Ofelt parameters. The dynamic coupling model is employed to predict the electric dipole intensity of certain hypersensitive transitions. Theoretical calculations concerning hypersensitivity are compared with experimental findings.

Introduction

In the last several years, there has been a considerable interest in the potential mechanism responsible for the anomolous intensity observed for certain f → f electronic transitions in lanthanides.[1-5] Recently, we have reported a detailed investigation of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ hypersensitive transition in solid-state tris(1,3-diphenyl-1,3-propanedionato)aquoneodymium(III) ($Nd(DBM)_3H_2O$) where theoretical calculations of oscillator strengh were carried out within the context of the dynamic coupling model proposed by Mason et al.[6] In this study, we wish to report a similar investigation of the hypersensitive transitions of europium ($^7F_0 \rightarrow {}^5D_2$), holmium ($^5I_8 \rightarrow {}^5G_6$), and erbium ($^4I_{15/2} \rightarrow {}^4G_{11/2}$), in which the host is isomorphic with the neodymium analogue (see Table V).

In the dynamic coupling model, mutual perturbation of the metal ion and ligands results in a Coulombic correlation between transient-induced dipoles of the ligands and the quadrupole of the metal ion.[1] The extent of this coupling will be directly determined by the polarizability of the ligands. Specifically, this *theoretical* model predicts that the strength of the transition will be determined by eq 1, where Ω_2(dyn)

$$\Omega_2(\text{dyn}) = \frac{28}{5}\langle 4f|r^2|4f\rangle^2 \sum_{m=0}^{3} (2 - \delta_{m,0})|\Sigma\bar{\alpha}_{(L)}R_{(L)}^{-4}C_{-m}^{(3)}(L)|^2 \quad (1)$$

(dyn = dynamic), a transition strength parameter, is related to a sum of the product of $\bar{\alpha}_{(L)}$, the mean polarizability of the ligand, $R_{(L)}$, the metal–ligand bond distance, and $C_{-m}^{(3)}$, a third rank spherical tensor which is determined by the pertinent structural parameters. The radial expectation value of the f electron must also be calculated, as expressed by the $\langle 4f|r^2|4f\rangle$ radial integral.

On the other hand, a particularly useful means for ordering the *experimentally observed* oscillator strengths of all transitions in a lanthanide spectrum is afforded by the Judd–Ofelt equation.[7,8] The expression is given by eq 2, where P is the

$$P_{ed} = \chi\left[\frac{8\pi^2 mc}{3h}\right]\bar{\nu}\sum_{\lambda=2,4,6}\Omega_\lambda\langle f^n||U^\lambda||f^{n'}\rangle^2(2J + 1)^{-1} \quad (2)$$

electric dipole oscillator strength of an f → f transition as expressed by the sum of the products of the Ω_λ parameters and the appropriate transition matrix elements at $\bar{\nu}$, the frequency of the transition, and corrected by χ, the Lorentz field factor, which is a function of the refractive index of the bulk medium. It is common practice to find a set of Ω_λ parameters by a

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