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Single-Crystal Electronic Absorption of Tris(1,3-diphenyl-1,3-propanedionato)aquoneodymium(III): Oscillator Strength of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ Hypersensitive Transition

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The ligand polarization model is examined for the calculation of f → f electronic intensity in the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ hypersensitive transition of tris(1,3-diphenyl-1,3-propanedionato)aquoneodymium(III). The electronic oscillator strengths of the single crystal are found experimentally and used in the determination of the phenomenological Ω_λ parameters of the Judd–Ofelt equation. Theoretical hypersensitive intensity calculations are based on X-ray structural data and average ligand polarizabilities and are compared to experimental values.

Introduction

Those who see electronic spectra of neodymium(III) compounds for the first time are often captivated by a very peculiar transition near the middle of the visible region. The relatively high intensity of this f → f transition and its unusual sensitivity to the chemical environment about the metal ion have led to its classification as "hypersensitive"; its behavior is in sharp contrast to the many other typically weak and consistently unvaried, normal f → f transitions.[1] Such anomalous transitions are also observable in several other lanthanides, most notably holmium(III) and erbium(III).

In the last two decades, a general interest has developed in the oscillator strengths of all f → f transitions within the basic framework of the Judd–Ofelt theory.[2,3] In short, this model predicts an intensity arising principally from a "forced electric dipole" mechanism given by eq 1, where P is the electric dipole

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

oscillator strength 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.

In theory, Ω_2, Ω_4, and Ω_6 are directly related to the crystal field, yet attempts to calculate them on the basis of an electrostatic point charge model have failed.[4,5] Hence, the Ω_λ parameters are generally left as "phenomenological", in that they are derived systematically by a linear least-squares fitting of the experimental data. In practice, these three parameters have proven to be a very useful tool in the discussion of transition intensities with a single lanthanide spectrum.[6,7]

However, particularly in complexes of sufficiently low symmetry, the oscillator strengths of hypersensitive transitions are of such a magnitude that their description in terms of a forced electric dipole mechanism becomes meaningless.[8] Because true hypersensitive transitions invariably obey quadrupole selection rules for the quantum numbers L and J, the Judd–Ofelt intensities are dominated primarily by the products of matrix elements in which the connecting tensor, $U^{(\lambda)}$, is of rank 2. Futhermore, $U^{(2)}$ elements seldom contribute much in the calculation of the intensity of nonhypersensitive transitions, thus freeing Ω_2 of its dependence on Ω_4 and Ω_6 and the experimental observations used to determine them.

Several imaginative models have been proposed to account for the large and independent magnitude observed for Ω_2 in different compounds, but each has met with only a limited degree of success.[8] The main emphasis has been on a mechanism which is operative for only noncentrosymmetric symmetries and one related to the quadrupole selection rules invariably obeyed. In various theories hypersentivity has been linked to ligand covalency, the nephelauxetic efect, inhomogeneity of the medium, and crystal field symmetry, as well as several other causes.[8]

However, Mason, Peacock, and Stewart[9–12] have proposed a particularly remarkable model which independently relates the magnitude of a hypersensitive transition to the polarizability and disposition of the bonding ligands. In this "dynamic coupling" model mutual perturbation of the metal ion and ligands results in a coulombic correlation between transient induced dipoles on the ligands and the quadrupole of the metal ion. The major contribution to the intensity of the hypersensitive transition is then

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

where Ω_2(dyn) (dyn = dynamic) is related to a sum of the products of $\bar{\alpha}_{(\mathrm{L})}$, the mean polarizability of the ligands, $R_{(\mathrm{L})}$, the metal–ligand distance, and $C_m{}^{(3)}$, a third rank spherical tensor which contains the structural parameters. It is also related to the expection value of the f electron as expressed by the radial integral.[10]

As derived, this mechanism is operative in every symmetry point group where hypersensitivity of an electric dipole nature has been observed. It also reaffirms the dipole nature of the frequency dependence, which is exhibited experimentally.[8] Furthermore, owing to the specific nature of the structural factors involved in the spherical tensor, the dynamic coupling model can potentially be used to derive structural information concerning the coordination environment, by virtue of hypersensitive intensity, which is a truly distinquishing feature of this model.[12]

Experimental Section

Preparation and Structure Determination. Tris(1,3-diphenyl-1,3-propanedionato)aquoneodymium(III) (or $Nd(DBM)_3H_2O$) was prepared by the methods of Melby et al.[13] Single crystals of suitable

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(1) Moeller, T.; Ulrich, W. F. *J. Inorg. Nucl. Chem.* **1956**, *2*, 164.
(2) Judd, B. R. *Phys. Rev.* **1962**, *127*, 750.
(3) Ofelt, G. S. *J. Chem. Phys.* **1962**, *37*, 511.
(4) Krupke, W. F. *Phys. Rev.* **1966**, *145*, 325.
(5) Newman, D. J. *Adv. Phys.* **1971**, *20*, 197.
(6) Carnall, W. T.; Fields, P. R.; Wybourne, B. G. *J. Chem. Phys.* **1965**, *42*, 3797.
(7) Carnall, W. T.; Fields, P. R.; Rajnak, K. *J. Chem. Phys.* **1968**, *49*, 4412.
(8) Peacock, R. D. *Struct. Bonding (Berlin)* **1975**, *22*, 83.
(9) Mason, S. F.; Peacock, R. D.; Stewart, B. *Chem. Phys. Lett.* **1974**, *29*, 149.
(10) Mason, S. F.; Peacock, R. D.; Stewart, B. *Mol. Phys.* **1975**, *30*, 1829.
(11) Peacock, R. D. *J. Mol. Struct.* **1978**, *46*, 203.
(12) Mason, S. F. *Struct. Bonding (Berlin)* **1980**, *39*, 43.
(13) Melby, L. R.; Rose, N. J.; Abramson, E.; Caris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117.

0020-1669/81/1320-1030$01.25/0

size were grown by cooling from acetone/KOH. Preliminary Weissenberg photographs indicated the lattice was rhomobohedral and potentially isomorphic with the holmium analogue of known structure.[14] Cell dimensions were determined, and intensity measurements were made with use of a GE XRD-5 quarter-circle manual diffractomer and a Cu anode at a takeoff angle of 1°. The data set included 729 independent reflections of which 70 were Friedl pairs, i.e., *hk*0 and *h* + *k*,*h*,0 sets. While corrections were made for Lorentz and polarization effects, no absorption correction was made. Standard scattering factors for neutral neodymum, carbon, oxygen, and hydrogen were used. Structure refinement was completed with the programs SHEL-X 76.

Instrumentation. Single crystals of suitable size were selected for electronic absorption measurement with a Cary 14 spectrometer, using the visible mode. Orthoaxial measurments were made with light polarized by a quartz Glan-Thompson prism placed in the entrance window of the same compartment. The purity of polarization was greater than 99.99%. An iris diaphram and/or neutral density filters were used to attenuate the reference beam. Crystal spectra were measured at ~295, 77, and ~5 K. Solution spectra were determined in 1-cm cells by standard techniques. Crystals were mounted by methods well described elsewhere.[15]

Treatment of Spectral Data. Spectra were collected for several different crystal thicknesses, both pure and diluted in the lanthanum analogue host. Corrections were made by substracting base lines taken at identical instrumental settings and polarizer orientations. Absolute and relative strenghts of the transitions giving rise to spectral bands were determined in terms of integrated band intensities, *I*, given by eq 3, where ϵ is the molar absorptivity at energy $\bar{\nu}$.

$$I = \int (\epsilon/\bar{\nu})\, d\bar{\nu} \simeq \frac{1}{\bar{\nu}_{\max}} \int \epsilon\, d\bar{\nu} \tag{3}$$

Crystal thicknesses were determined with a micrometer to ±0.01 mm, and concentration was, in turn, obtained from the calculated X-ray density.

Integrated intensities were corrected to isotropic (or random) orientation by the statistical approximation (4), where $I_\perp$ and $I_\parallel$ are

$$\langle I_{\text{iso}} \rangle = \frac{2}{3} I_\perp + \frac{1}{3} I_\parallel \tag{4}$$

the perpendicular and parallel intensities of the orthoaxial spectra.[15] Experimental oscillator strengths were then computed by eq 5.

$$P_{\text{exptl}} = 4.318 \times 10^{-9} \int (\epsilon/\bar{\nu})\, d\bar{\nu} \tag{5}$$

Theoretical Oscillator Strengths. Oscillator strengths for the transitions of Nd(DBM)$_3$H$_2$O were computed by eq 1 after determining the Ω_λ parameters by a least-squares approximation. The error function used was

$$\text{rms dev} = \left(\frac{\sum \Delta_i^2}{N} \right)^{1/2} \tag{6}$$

where Δ is the difference between P_{exptl} and P_{calcd} and N is the number of levels.[16] The Lorentz correction was based on the refractive index as a function of the simple Cauchy relation[4] where

$$\chi = \frac{(n^2 + 2)^2}{9n} \tag{7}$$

n being the refractive index at (λ) where

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \cdots \tag{8}$$

The constants *A* and *B* were determined by simultaneous equations based on the measurement of the refractive index at several wavelengths.[4]

Average Molecular Polarizabilities. Polarizabilities were determined by the recently introduced method of Miller and Savchik, where the average molecular polarizability, α, is related to a sum of the appropriate "atomic hybrid components" by eq 9, where N is the total

$$\alpha(\text{ahc}) = \frac{4}{N} \left(\sum_A \tau_A \right)^2 \text{Å}^3 \tag{9}$$

number of electrons in the molecule summed over *A* atoms of component τ_A.[17]

Table I. Positional Parameters for Atoms Other Than Hydrogen for Nd(DBM)$_3$H$_2$O

atom	*x*	*y*	*z*
Nd[a]	0	0	0
H$_2$O[a]	0	0	0.3825 (46)
O(1)	0.0706 (9)	−0.0150 (10)	−0.2407 (30)
O(2)	0.1165 (9)	0.0764 (13)	0.0944 (36)
C(1)	0.1137 (21)	0.0076 (14)	−0.2726 (60)
C(2)	0.1868 (18)	0.0588 (10)	−0.1474 (50)
C(3)	0.1773 (11)	0.0908 (14)	0.0232 (46)
C(4)	0.1543 (13)	−0.0192 (15)	−0.4491 (61)
C(5)	0.2192 (22)	0.0045 (23)	−0.5241 (89)
C(6)	0.2378 (32)	−0.0121 (44)	−0.7161 (85)
C(7)	0.1826 (18)	−0.0791 (20)	−0.7901 (81)
C(8)	0.1145 (44)	−0.0986 (30)	−0.7653 (86)
C(9)	0.1060 (20)	−0.0617 (22)	−0.5883 (78)
C(10)	0.2300 (16)	0.1414 (16)	0.1379 (51)
C(11)	0.2240 (16)	0.1640 (14)	0.3292 (56)
C(12)	0.2765 (30)	0.2197 (24)	0.4273 (82)
C(13)	0.3448 (26)	0.2545 (21)	0.3339 (95)
C(14)	0.3550 (26)	0.2349 (24)	0.1486 (85)
C(15)	0.3302 (20)	0.1824 (18)	0.0481 (87)

[a] Special positions fixed by symmetry; Nd at origin.

Table II. Structural Parameters[a] for Nd(DBM)$_3$H$_2$O

atoms	*R*, Å	θ, deg	ϕ, deg
Nd-OH$_2$	2.46	0.0[b]	0.0[b]
Nd-O(1)	2.37	131.0	9.4
Nd-O(2)	2.39	75.3	40.2
Nd-C(1)	3.42	120.9	2.9
Nd-C(2)	3.85	104.3	17.9
Nd-C(3)	3.47	87.5	30.8
Nd-Ph(1)[c]	6.11	75.0	42.4
Nd-Ph(2)	6.06	132.6	12.5

[a] Spherical polar coordinates are for the asymmetric unit; the angle ϕ has an arbitrary reference near the projection of C(1). [b] Position fixed by symmetry. [c] Distances and angles represent a geometric average for the phenyl substituents.

Results

Crystal Structure and Morphology. Tris(1,3-diphenyl-1,3-propanedionato)aquoneodymium(III) crystallizes in the enantiomorphic space group *R*3 with one molecular unit per rhomobohedral cell or three units per hexagonal cell. The structure is isomorphic with that of the previously reported holmium analogue.[14] Unit cell dimensions are a_h = 22.58 ± 0.01 and c_h = 6.45 ± 0.01 Å, giving a calculated X-ray density of 1.454 g/cm^3 and a crystal molarity of 1.749 mol/L. The final positional parameters for atoms other than hydrogen are given in Table I. Structure factors, thermal parameters, and other details of the refinement are available from the authors.

The coordination structure is best described as octahedral but capped by a single water molecule on the 3-fold axis. The hydrogens on the water molecule are evidently disordered, yielding an overall metal ion site symmetry of C_3. Structural parameters in the form of spherical polar coordinates centered on the metal atom (which are the parameters pertinent to the theoretical calculations to be discussed) are given in Table II.

The Ln(DBM)$_3$H$_2$O crystals grow as hexagonal prismatic needles. The lanthanide series is isomorphic from lanthanum through holmium (Ce, Er, Tm, and Lu were not investigated),

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(14) Zalkin, A.; Templeton, D. H.; Karraker, D. G. *Inorg. Chem.* **1969**, *8*, 2680.

(15) Palmer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864.

(16) Mehta, P. C.; Tandon, S. P. *J. Chem. Phys.* **1970**, *53*, 414.

(17) Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206.

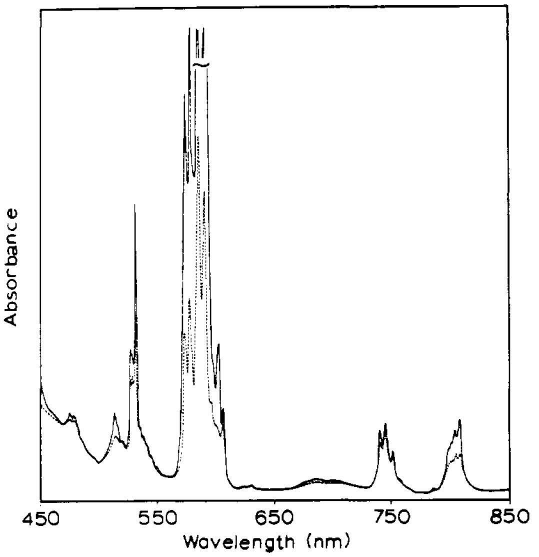

Figure 1. Orthoaxial single-crystal electronic absorption spectrum of $Nd(DBM)_3H_2O$ at ambient temperature: ---, π polarization; —, σ polarization.

Table III. Measured and Calculated Oscillator Strengths for $Nd(DBM)_3H_2O$

$[S',L']J'$	energy, cm^{-1}	$P_{exptl} \times 10^{-6}$	$P_{1,calcd} \times 10^{-6}$ [a]	$P_{2,calcd} \times 10^{-6}$ [b]
$^4F_{5/2}$, $^2H_{9/2}$	12 300	4.0	5.3	6.9
$^4F_{7/2}$, $^4S_{3/2}$	13 300	4.1	3.7	3.1
$^4F_{9/2}$	14 500	weak	0.52	0.50
$^2H_{11/2}$	16 000	weak	0.11	0.13
$^4G_{5/2}$, $^2G_{7/2}$	17 500	150	204	150[c]
$^2K_{13/2}$, $^4G_{7/2}$	18 800	18	18[c]	16
$^4G_{9/2}$, $^2G_{9/2}$	19 500	5.4	3.1	3.6
$^2K_{15/2}$, $^2D_{3/2}$, $^4G_{11/2}$	20 800	2.8	1.8	2.3
$^2P_{1/2}$, $^2D_{5/2}$	23 000	obscured		

[a] Rms = 1.29×10^{-6}. [b] Rms = 1.70×10^{-6}. [c] Weighted more heavily.

but ytterbium shows a departure from the rhomobhedral lattice.

Spectra. The single-crystal electronic absorption spectrum of tris(1,3-diphenyl-1,3-propanedionato)aquoneodymium(III) was measured at room temperature, 77 K, and ~5 K. Measurements were made perpendicular to the {100} face polarized both parallel and perpendicular to the unique *c* axis. Only the visible transitions of the room-temperature spectrum, with excited-state terms as assigned in Figure 1, were used in the determination of the phenomenological Judd–Ofelt parameters. Absolute experimental oscillator strengths were obtained by taking two-thirds of the integration of the σ-polarized spectrum plus one-third of the π-polarized spectrum.[15] These final "isotropic" oscillator strengths are listed in Table III, as well as the oscillator strengths calculated by the Judd–Ofelt parameters as expressed in eq 1. The connecting matrix elements used in the determinations of Ω_2, Ω_4, and Ω_6 were those of Carnall et al.[6,7]

In order to obtain the Judd–Ofelt parameters Ω_λ(J–O) for crystalline $Nd(DBM)_3H_2O$, we performed two separate simplex-type calculations. The first set of calculated oscillator strengths in Table III were determined with the integrations from six separate transitions or groups of transitions in the visible, including the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ hypersensitive transition, but the second column of calculated oscillator strenghts excluded this transition in the determination of Ω_λ. The rms error was improved when the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ hypersensitive transition was excluded. The final error for both sets of calculated oscillator strengths is relatively high, but this can be attributed to the great range of intensities between normal and hypersensitive transitions.

Table IV

Ω_λ Parameters for $Nd(DBM)_3H_2O$ ($\Omega_\lambda/10^{-20}$ cm^2 from Eq 1)

$P(^4I_{9/2} \rightarrow {}^4G_{5/2}) \times 10^6$	Ω_2	Ω_4	Ω_6	medium[a]	ref
101	47.7	5.27	12.4	MeOH	16
73	34.7	2.56	9.2	MeOH/EtOH	16
122	55.3	2.46	21.1	DMF	16
80	35.7	3.58	17.3	DMFA	16
44				benzene[b]	20
151	44.7	12.0	1.25	crystal	P_2, Table III

Ω_2(dyn) from Ligand Polarization Model (Eq 2)

$\langle 4f|r^2|rf\rangle = 1.001$ au[21]
$\Omega_2(\text{dyn}) = 56.6 \times 10^{-20}$ cm^2

[a] MeOH/EtOH (1:3), dimethylformamide (DMF), DMF plus solvent (1:4) (DMFA). [b] Anhydrous $Nd(DBM)_3$ in benzene.

Judd–Ofelt Ω_λ parameters for the solid state complex have not previously been determined. The relatively large value of the index of refraction for $Nd(DBM)_3H_2O$ and its large dispersion over the spectral region studied makes the Lorentz field correction in eq 1 very important. The Ω indices of refraction (perpendicular to the *c* axis), determined by a dispersion staining technique at wavelengths of 486, 589, and 656 nm, were found to be 1.787, 1.728, and 1.705, respectively. The ϵ index of refraction (parallel to the *c* axis) was determined at 589 nm to be approximately 2.04. The dispersion of the index is farily well accounted for by the Cauchy relation (eq 9) where the constants *A* and *B* were found to be 1.606 and 0.0426, respectively. Table IV lists the value of Ω_2, Ω_4, and Ω_6 for solid-state $Nd(DBM)_3H_2O$, as well as Ω_λ parameters for the complex in several different aqueous and nonaqueous media.

For the theoretical calculations of Ω_2(dyn) by the ligand polarization model, the structral parameters used were those listed in Table II. Experimental isotropic polarizabilities[17] were used for each phenyl substituent and for the water molecule, and each of these were placed at their average geometric position in the coordination sphere. Polarizabilities, angular coordinates, and distances were determined separately for each atom of the chelate ring, due to the $1/R^8$ sensitivity of the calculation with respect to ligand distance as expressed in eq 2.

The $^4I_{9/2} \rightarrow {}^4G_{5/2}$ hypersensitive transition of Figure 1 has a single-crystal ϵ_{max} at ca. 17 000 cm^{-1}. This is in good agreement with previous difuse reflectance spectral measurements.[18] The calculated oscillator strengths for the hypersensitive transition in solution and as a single crystal are listed in Table IV. The Ω_2's used in these claculations can be compared to the independent Ω_2(dyn) of the dynamic coupling model.

Discussion

The difference between the Ω_2 values when determined with and without the hypersensitive transition at ca. 17 000 cm^{-1} is some 25%. This is a consequence of the fact that the $^4I_{9/2} \rightarrow {}^4G_{7/2}$ transition at 18 800 cm^{-1} also has some hypersensitive character, due to a significant U^2 matrix element contribution to its intensity. This contribution tends to have a dominating influence on the calculated magnitude of Ω_2 in the absence of data from the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition. However, this discrepancy is not unusual, as the oscillator strengths of hy-

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(18) Tandon, S. P.; Govil, R. C. *Spectrosc. Lett.* **1971**, *4*, 73.

persensitive transitions are known to show unusual deviations within a spectrum when calculated by the same Ω_λ parameters.[22] This problem illustrates some of the difficulty encountered when attempts are made to rationalize the intensity of hypersensitive transitions within the context of the Judd–Ofelt theory.

From the data presented in Table IV, it can be seen that the magnitude of Ω_2 is quite variable; depending on the medium, it ranges from a high of 55.3×10^{-20} cm^2 to perhaps less than 25×10^{-20} cm^2 for benzene (noting that $\Omega_2 \times 10^{20}$ cm^2 is always less than half of $P \times 10^6$). This raises doubt concerning the nature of the chemical environment at the chromophore in each solvent presented in Table IV. Problems arise in attempting to speculate that solvent polarizability is contributing to an enhanced oscillator strength because evidence of at least some degree of solvent coordination is needed to establish this.[8]

The calculation of Ω_2(dyn) by the ligand polarizability model gives an Ω_2 of 56.6×10^{-20} cm^2 for crystalline $Nd(DBM)_3H_2O$. This is not in close agreement with the value of Peacock[11] (30.6×10^{-20} cm^2). However, exact structural data was not available in that work, and approximations may have been involved with perhaps different experimental polarizabilities. The method of tensor solution was, however, identical.[19]

When Ω_2(dyn) is calculated for the hypothetical six-coordinate D_3 complex of $Nd(DBM)_3$, its magnitude is considerably reduced. The addition of the single water molecule on the C_3 axis at 2.46 Å increases Ω_2(dyn) by some 26%. In benzene, $Nd(DBM)_3$ exists as a discrete six-coordinate complex,[20] and the band shape of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition is nearly identical with the band shape in MeOH/EtOH. The variability of Ω_2(Judd–Ofelt) in solution may be evidence that the structure is not necessarily seven-coordinate in some media, and in fact, the enhanced or reduced hypersensitive intensity is intimately related to that fact. It is conceivable that various degrees of coordination of the water molecule play a significant role in the promotion of hypersensitive oscillator strength for $Nd(DBM)_3H_2O$ in solution.

In this analysis, it must be noted that the magnitude of Ω_2(J–O), when obtained from the Judd–Ofelt equation, depends almost entirely on the measured intensity of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition. Therefore, Ω_2(J–O) of Table IV for the single crystal is little more than a reflection of a single oscillator strength. On the other hand, the value of Ω_2(J–O), ignoring the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition, is 66×10^{-20} cm^2, giving a range of $(45–66) \times 10^{-20}$ cm^2, in which the magnitude of Ω_2 will depend on how much weight is accorded the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition. Under these circumstances, the *theoretically calculated value* (Ω_2(dyn)) of 56.6×10^{-20} cm^2 is quite reasonable in that it falls squarely within the *experimentally determined* range predicted by the Judd–Ofelt theory.

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[19] Mason, S. F., personal communication.

[20] Karraker, D. G. *Inorg. Chem.* **1967**, *6*, 1863.

[21] Freeman, A. J.; Watson, R. E. *Phys. Rev.* **1962**, *127*, 2058.

[22] Peacock, R. D. *Chem. Phys. Lett.* **1972**, *16*, 590.

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Exchange Coupling in the Alternating-Chain Compounds *catena*-Di-μ-chloro-bis(4-methylpyridine)copper(II), *catena*-Di-μ-bromo-bis(*N*-methylimidazole)copper(II), *catena*-[Hexanedione bis(thiosemicarbazonato)]copper(II), and *catena*-[Octanedione bis(thiosemicarbazonato)]copper(II)

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Magnetic susceptibility data have been collected for *catena*-[octanedione bis(thiosemicarbazonato)]copper(II), Cu-OTS, and *catena*-[hexanedione bis(thiosemicarbazonato)]copper(II), Cu-HTS, in the temperature range 1.8–120 K and the data analyzed in terms of an alternating-chain Heisenberg-exchange model to yield $J = -10.1 \pm 0.2$ cm^{-1}, $\alpha = 0.91 \pm 0.02$, and $g = 2.06 \pm 0.02$ for Cu-HTS and $J = -12.9 \pm 0.2$ cm^{-1}, $\alpha = 0.90 \pm 0.02$, and $g = 2.11 \pm 0.02$ for Cu-OTS. Anomalies in the temperature-dependent capacitance data for *catena*-di-μ-chloro-bis(4-methylpyridine)copper(II) and *catena*-di-μ-bromo-bis(*N*-methylimidazole)copper(II) provide evidence for structural phase transitions presumably from uniform-chain structures at room temperature to alternating-chain structures at low temperatures. Magnetic parameters for $Cu(4\text{-methylpyridine})_2Cl_2$ are $J = -9.6 \pm 0.2$ cm^{-1}, $g = 2.17 \pm 0.02$, and $\alpha = 0.67 \pm 0.02$. An expression for the magnetic susceptibility of a Heisenberg alternating chain of $S = {}^1/_2$ ions has been developed in terms of the alternation parameter, the exchange coupling constant, and the g factor.

Introduction

Paramagnetic organic compounds with alternatingly spaced linear-chain structures have been known and studied extensively for a number of years,[1] since such compounds frequently have unusual magnetic properties and are often alternating Heisenberg antiferromagnets. Exchange-coupled transition metal compounds with alternating structures have received much less attention. The most thoroughly studied transition metal example of an alternating Heisenberg antiferromagnet is $Cu(NO_3)_2{\cdot}2.5H_2O$,[2] a compound which has a ladderlike

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[1] Nordio, P. L.; Soos, Z. G.; McConnell, H. M. *Annu. Rev. Phys. Chem.* **1966**, *17*, 237.

[2] Diederix, K. M.; Blöte, H. W. J.; Groen, J. P.; Klaassen, T. O.; Poulis, N. J. *Phys. Rev. B: Condens. Matter* **1979**, *19*, 420.

0020-1669/81/1320-1033$01.25/0