accompanying the reduced spin[21] of a 1D or 2D antiferromagnet. The average value of H_{int} at 1.6 K is ~500 kG. This is a reasonable value for the usual single ion covalency reduction effects, assuming a Fermi contact contribution of 11 T/unpaired electron and negligible dipolar and orbital contributions to H_{int}.

In the present context, it is useful for us to summarize the major conclusions of Figgis et al.'s refinement of polarized neutron diffraction data[22] for the *Pccn* polymorph of $[\mathrm{Fe(bpy)_2Cl_2}][\mathrm{FeCl_4}]$:

(1) There is ~15% spin delocalization from the iron(III) of the cation, and most of it is to the chlorine ligands.

(2) For the anion the spin delocalization is slightly[24] larger (~17%) and nonspheric.

(3) The site magnetizations for the cation and anion are not equal and have different temperature dependencies.

(4) There is no evidence of extended cooperative magnetic order from the neutron study to 4.2 K.

We believe that metal ion to chlorine ligand spin-delocalization patterns very similar to that in points 1 and 2 and the magnetization behavior (point 3) are undoubtedly operative for the present $P2_12_12_1$ polymorph and are integral to its exchange and ultimate ordering. The nonobservation of clear-cut magnetic ordering in the polarized neutron study[22] of the *Pccn* polymorph is likely related to the fact that only four reflections were studied in detail at the presumed lowest temperature (2.07 K) of the neutron investigation. On the other hand, differences in packing between the two polymorphs might somehow contribute to a somewhat lower critical temperature for the *Pccn* analogue. The susceptibility study[23] of the *Pccn* polymorph leads us to favor the former explanation. Specifically, there is a sharp downward bend of the reciprocal susceptibility (χ_M^{-1}) at ~2.9 K, paralleling that observed by us at ~3.0 K and suggesting the onset of some type of complex magnetic ordering behavior for both polymorphs.

In passing, we also mention that we have performed Mössbauer spectroscopy and susceptibility studies of the phenanthroline analogue, $[\mathrm{Fe(phen)_2Cl_2}][\mathrm{FeCl_4}]$, which crystallizes in space group $P\bar{1}$ and whose structure has recently been determined[13] and a sample furnished to us. Our helium-4 experiments show that this material exhibits incipient magnetic hyperfine splitting–relaxation broadening effects in its zero-field Mössbauer spectrum at 1.5 K. Preliminary helium-3 studies show that the material is fully hyperfine split at 0.35 K. Complete details for this system will be published subsequently.

Acknowledgment. This work was supported by the NSF DMR Solid State Chemistry Program, Grant Nos. DMR 8016441 and 8313710 (Northeastern University), and by the Office of Naval Research (Brandeis University). W.M.R. thanks Professor H. J. Goodwin of the University of New South Wales for his donation of a sample of the $P\bar{1}$ polymorph of $[\mathrm{Fe(phen)_2Cl_2}][\mathrm{FeCl_4}]$.

Supplementary Material Available: Tables of least-squares planes, nonessential bond lengths and angles, anisotropic temperature factors, H-atom coordinates, intramolecular nonbonded contacts, and observed and calculated structure amplitudes (12 pages). Ordering information is given on any current masthead page.

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(24) A more recent detailed X-ray study (120 K) (Figgis, B. N.; Reynolds, P. A.; White, A. H. *Inorg. Chem.* **1985**, *24*, 3762) of the *Pccn* polymorph has appeared since the acceptance of the present work. This work suggests *somewhat* larger total spin delocalization to the anion ligands as opposed to the cation ligands. Specifically, there is a total of 0.88 spin delocalized to the anion chlorine atoms vs. 0.60 spin for the cation (0.23 spin/$\mathrm{Cl^-}$), and for the latter, little spin density appears beyond the nitrogen atoms of the bipyridyl ligand rings. These observations are consistent with noninvolvement of the cation in the ordered state, a possibility alluded to earlier in the Discussion.

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Laser Spectroscopic and X-ray Structural Investigation of Europium(III)-Oxydiacetate Complexes in Solution and in the Solid State

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Dye-laser-induced luminescence excitation spectra and excited-state-lifetime measurements on solutions of europium(III) chloride and sodium oxydiacetate (ODA) reveal the presence of three complexes: $\mathrm{Eu(ODA)(H_2O)_7^+}$, $\mathrm{Eu(ODA)_2(H_2O)_3^-}$, and $\mathrm{Eu(ODA)_3^{3-}}$. The X-ray structure of monoclinic $\mathrm{Na_3[Eu(ODA)_3]\cdot 6H_2O}$ has been determined (space group *Cc*, a = 17.542 (4) Å, b = 8.474 (2) Å, c = 19.181 (3) Å, β = 111.46 (2)°, Z = 4) and is compared with the known structure for $\mathrm{Na_3[Eu(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O}$ (space group *R*32, a = 9.7391 (18) Å, b = 28.2012 (74) Å). The spectroscopic results are consistent with the crystallographic metal ion site symmetries (C_1 and D_3, respectively). The $\mathrm{Eu(ODA)_3^{3-}}$ solution species resembles the higher symmetry crystalline form.

Physical techniques applicable to both solid-state and solution phases are important in that they permit a comparison between the structures of molecules in the two states. Such methods allow one to extrapolate to the solution state the structural information obtainable from X-ray crystallography on crystalline materials, provided that the experiment in question is sufficiently sensitive to structural details. Considerable effort has been devoted in this laboratory to the development of laser-excited lanthanide ion luminescence as a probe of structure and dynamics in chemistry and biology.[1,2] In particular we have concentrated on the excitation spectroscopy of the highly luminescent and environmentally sensitive Eu(III) ion.[3] The experiment involves exciting the Eu(III) ion from its nondegenerate $^7\mathrm{F}_0$ ground state to one of the excited states of the $4\mathrm{f}^6$ electronic configuration, $^5\mathrm{D}_0$, $^5\mathrm{D}_1$, or $^5\mathrm{D}_2$, the first of which is also nondegenerate. This excitation is accomplished by using a tunable pulsed dye laser while the emission corresponding to the $^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_2$ transition is monitored. A variety of types of information are obtainable from these experiments, some of which are indicated in Table I.

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Table I. Spectroscopy of Eu(III)

quant measd	information obtained	ref
$^7F_0 \rightarrow {}^5D_0$, no. of bands	number of environments	1, 4
$^7F_0 \rightarrow {}^5D_0$, transition energy	total charge on ligands coordinated to Eu(III)	5
$^7F_0 \rightarrow {}^5D_0$, intensity as a function of ligand concn	speciation, binding constants	6-8
$^7F_0 \rightarrow {}^5D_J$, $^5D_0 \rightarrow {}^7F_J$ splittings	site symmetry	9, this work
$^5D_0$ excited-state lifetimes in H_2O and D_2O	number of -OH or -NH oscillators in 1st coordn sphere	1, 10
$^5D_0$ lifetimes in the presence of energy acceptor ions	inter metal ion distances	1, 11-15
time course of luminescence emission in intermediate exchange situations	ligand exchange rates	2

Table II. Crystallographic Parameters for $Na_3[Eu(ODA)_3]\cdot 6H_2O$

formula	$Na_3EuC_{12}H_{24}O_{21}$
fw	725.24
space group	*Cc*
Z	4
cryst size, mm	0.43 × 0.50 × 0.48
a, Å	17.542 (4)
b, Å	8.474 (2)
c, Å	19.181 (3)
β, deg	111.46 (2)
V, Å^3	2851 (2)
d_{calcd}, g cm^{-3}	1.815
abs coeff (μ), cm^{-1}	24.96
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite (takeoff angle 2.8°)
scan width, deg	$1.00 + 0.347 \tan \theta$
scan speed, deg/min	1.0-5.0
2θ, deg	$3.2 \leq 2\theta \leq 60.0$
octants colled	$h,k,\pm l$
no. of measd reflcns	4409
no. of unique nonzero reflcns	3854
no. of obsd reflcns ($I > 3\sigma(I)$)	3598
mean discrepancy among multiply measd reflcns	0.031
no. of variables	332
no. of reflcns/param	10.84
R	0.0488 (using unit weighting scheme)
R_w	0.0657
ESD	5.894
max shift/error	0.42
largest peak remaining, e Å^{-3}	2.54 (0.73 Å from Eu)

The present research is concerned with the structures of Eu(III) complexes of oxydiacetate, $O(CH_2COO^-)_2$, ODA^{2-}, in solution and in the solid state as revealed by laser luminescence spectroscopy and X-ray crystallography. We were especially interested to determine the ability of excitation spectroscopy to reveal the subtle structural differences between the high- and low-symmetry forms of the tris chelate complex, $Eu(ODA)_3^{3-}$. The X-ray structure of the latter is presented in this paper.

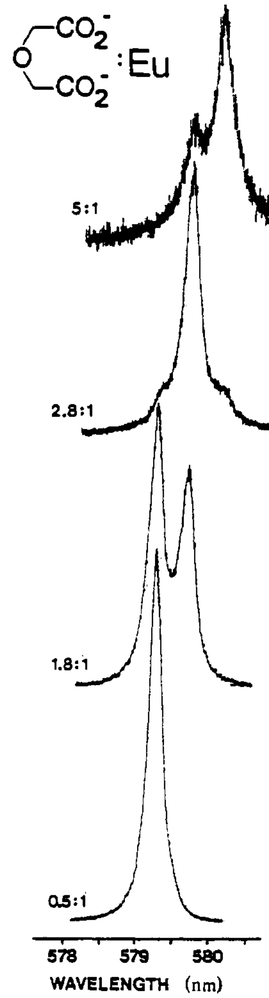

Figure 1. $^7F_0 \rightarrow {}^5D_0$ excitation spectra of solutions containing the indicated mole ratio of ODA:Eu ([Eu] = 1 mM, pH 6.0, λ_{em} = 614 nm).

Experimental Section

Materials. Oxydiacetic acid (practical grade, Fluka), $EuCl_3\cdot 6H_2O$ (99.9%, Aldrich Chemical Co.), and $Eu(ClO_4)_3\cdot 6H_2O$ (>97%, Alfa Ventron) were used as received. Eu(III) concentrations were determined from titrations with EDTA using arsenazo as indicator.[16] Crystals of $Na_3[Eu(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ were grown by slow evaporation at room temperature of a solution containing a 3:1 mole ratio of H_2ODA:$Eu(ClO_4)_3\cdot 6H_2O$ at a pH of ~6 (adjusted with NaOH). The unit cell of the crystal used in the spectroscopic measurements agreed with literature values (*a* = 9.7391 (18), *b* = 28.2012 (74) Å).[17] Crystals of $Na_3[Eu(ODA)_3]\cdot 6H_2O$ were grown in an analogous manner, with $EuCl_3\cdot 6H_2O$ used instead of $Eu(ClO_4)_3\cdot 6H_2O$.

Spectral Measurements. Excitation spectra and lifetime traces were obtained at ambient room temperature (24 ± 2 °C) on a previously described laser system.[1,18-20] Single crystals were mounted on a goniometer head, which was placed on an *x*-*y* translator to allow for positioning of the crystal in the laser beam. Exponential decay traces were digitized by using a Summagraphics Model MM1200 digitizer and analyzed on an IBM 9000 computer by using a nonlinear regression analysis (Marquardt).[21]

X-ray Data Collection and Reduction. A crystal was mounted in a capillary and placed on an Enraf-Nonius four-circle CAD4 diffractom-

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Table III. Spectral Features of Eu(III) Complexes with ODA

complex	$\nu(^7F_0 \rightarrow {}^5D_0)$,[a] cm^{-1}	calcd charge	$\nu(^7F_0 \rightarrow {}^5D_1)$,[a] cm^{-1}	$\nu(^7F_0 \rightarrow {}^5D_2)$,[a] cm^{-1}	$\tau_{H_2O}^{-1}$, ms^{-1}	$\tau_{D_2O}^{-1}$, ms^{-1}	no. of coord H_2O's
$Eu(ODA)^+$	17266	-1.7			7.20[b]	0.30	7.2
$Eu(ODA)_2^-$	17253	-3.8			2.83[b]	0.31	2.6
$Eu(ODA)_3^{3-}$	17238	-5.4			0.78	0.29	0.5
$Na_3[Eu(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$	...	...	18990[d]	21495 21445	0.56	c	
$Na_3[Eu(ODA)_3]\cdot 6H_2O$	17235	-5.8	18993 18987	21496 21445 21436	0.50	c	

[a] An absolute frequency accuracy of ±2 cm^{-1} is estimated on the basis of the dye-laser alignment and calibration procedure using a He–Ne laser. [b] Values from ref 2. [c] The deuterium-substituted crystals were not synthesized. [d] There is an indication of a shoulder on the high-energy side of the spectral feature.

eter. A detailed description of the procedures used is given elsewhere.[22] The structure was solved by standard Patterson and Fourier techniques. The crystallographic parameters are given in Table II. A listing of the final observed and calculated structure factors and the anisotropic thermal parameters is available in the supplementary material.

Results and Discussion

Solution Species. Figure 1 shows excitation spectra of solutions containing different mole ratios of ODA^{2-}:Eu^{3+}. As the ratio increases (from 0 to 5), separate peaks due to $Eu(ODA)^+$, $Eu(ODA)_2^-$, and $Eu(ODA)_3^{3-}$ are observed. Each species has a characteristic $^7F_0 \rightarrow {}^5D_0$ excitation frequency (ν in cm^{-1}), which, along with the reciprocal excited-state lifetimes in H_2O and D_2O solution, is given in Table III. As each successive ODA^{2-} ligand binds to the Eu(III) ion, the $^7F_0 \rightarrow {}^5D_0$ peak shifts to lower energy. This is due to a nephelauxetic effect, which has been quantitated for Eu(III) systems.[5] The use of eq 1 allows one to calculate the

$$\nu\ (cm^{-1}) = -0.76p^2 + 2.29p + 17\,273 \qquad (1)$$

total charge, p, on the ligands bound to Eu(III) (i.e. the number of bound carboxylates of the ODA^{2-} ligands). The results (Table III) indicate that ~2, 4, and 5 or 6 carboxylate groups are bound to the metal in the 1:1, 2:1, and 3:1 ODA^{2-}:Eu^{3+} complexes, respectively.

As pointed out by us[4] and others,[23] highly symmetric species such as the aqua ion and tris chelate complexes of D_3 symmetry produce much less intensity in a $^7F_0 \rightarrow {}^5D_0$ excitation experiment than do their lower symmetry counterparts. This reflects the forbidden nature of the absorptive transition in high symmetry. This effect accounts for the fact that no signal from the Eu(III) aqua ion (578.9 nm) is apparent in the lowermost trace in Figure 1. It is also manifested in the lower signal to noise ratio apparent in the uppermost trace of Figure 1 where the highly symmetric $Eu(ODA)_3^{3-}$ species is predominant.

Reciprocal excited-state-lifetime measurements in H_2O and D_2O[2,10] for each species provide a measure of the number of coordinated water molecules, q (eq 2).[10] The data show that ~7,

$$q = 1.05(\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1}) \qquad (2)$$

~3, and ~0 water molecules are bound to Eu(III) in the 1:1, 2:1, and 3:1 ODA:Eu(III) species, respectively. The data in Table III are consistent with the assignment of the solution species as $Eu(ODA)(H_2O)_7^+$, $Eu(ODA)_2(H_2O)_3^-$, and $Eu(ODA)_3^{3-}$. This implies a total coordination number of nine or ten for Eu(III) in all three cases. Three or four water molecules are expelled from the first coordination sphere of the metal as each ODA^{2-} ligand coordinates. This is consistent with the tridentate nature of the ligand coordinating via its two carboxylate groups and its ether oxygen atom.

Table IV. Final Atomic Positional and Thermal Parameters for $Na_3[Eu(ODA)_3]\cdot 6H_2O$

atom	x	y	z	B, Å^2
Eu	0.000	0.05302 (5)	0.000	1.157 (6)
Na1	-0.2763 (3)	0.5323 (6)	-0.2183 (3)	2.1 (1)
Na2	-0.3746 (4)	-0.1451 (8)	-0.2200 (3)	3.0 (1)
Na3	-0.2178 (3)	-0.0689 (6)	-0.2827 (3)	1.86 (9)
O1	0.0624 (5)	-0.140 (1)	0.0976 (4)	2.0 (2)
O2	0.1728 (6)	-0.245 (1)	0.1771 (5)	2.7 (2)
O4	0.1202 (6)	-0.103 (1)	-0.0066 (5)	2.4 (2)
O6	0.1371 (6)	0.133 (1)	-0.1536 (5)	2.7 (2)
O7	0.0460 (5)	0.124 (1)	-0.0988 (5)	2.3 (2)
O11	-0.1245 (7)	0.164 (1)	-0.0842 (6)	2.8 (2)
O12	-0.2107 (5)	0.365 (1)	-0.1276 (5)	2.5 (2)
O14	-0.0055 (7)	0.3470 (9)	-0.0035 (9)	2.3 (1)
O16	0.1972 (7)	0.410 (1)	0.1209 (7)	3.4 (2)
O17	0.1196 (5)	0.192 (1)	0.0765 (5)	1.8 (2)
O21	-0.0623 (7)	-0.142 (1)	-0.0883 (6)	3.2 (2)
O22	-0.1861 (8)	-0.239 (1)	-0.1771 (6)	3.8 (3)
O24	-0.1212 (5)	-0.090 (1)	0.0119 (5)	2.1 (2)
O26	-0.1326 (8)	0.164 (2)	0.1545 (7)	4.5 (3)
O27	-0.0445 (6)	0.143 (1)	0.0968 (5)	2.4 (2)
O30	-0.2205 (8)	0.393 (1)	-0.3023 (7)	4.1 (3)
O31	-0.3911 (8)	0.337 (2)	-0.2677 (6)	3.4 (3)
O40	-0.395 (1)	-0.018 (1)	-0.1260 (7)	9.3 (5)
O41	-0.5007 (5)	-0.229 (1)	-0.3053 (4)	1.9 (2)
O42	-0.2864 (7)	0.076 (1)	-0.2132 (6)	3.1 (2)
O50	-0.1110 (7)	0.137 (1)	-0.2393 (6)	3.3 (2)
C2	0.1347 (7)	-0.187 (1)	0.1155 (6)	1.5 (2)
C3	0.1725 (6)	-0.179 (1)	0.0615 (5)	1.0 (2)
C5	0.163 (1)	-0.061 (2)	-0.0567 (8)	3.8 (3)
C6	0.1136 (6)	0.081 (2)	-0.1036 (6)	1.7 (2)
C12	-0.1464 (6)	0.319 (2)	-0.0873 (6)	1.9 (2)
C13	-0.0763 (9)	0.427 (1)	-0.0405 (9)	2.9 (3)
C15	0.062 (1)	0.446 (2)	0.044 (1)	3.9 (4)
C16	0.1294 (6)	0.333 (2)	0.0831 (6)	2.0 (2)
C22	-0.138 (1)	-0.181 (2)	-0.1110 (9)	3.3 (3)
C23	-0.180 (1)	-0.165 (2)	-0.0489 (8)	3.6 (3)
C25	-0.1563 (6)	-0.027 (2)	0.0597 (7)	2.2 (2)
C26	-0.1068 (8)	0.098 (2)	0.1109 (7)	2.4 (3)

Solid-State Results. The crystal structure of $Na_3[Eu(ODA)_3]\cdot 6H_2O$ consists of monomeric tris(oxydiacetato) complexes in which the Eu(III) ion is nine-coordinate (one ether and two carboxylate oxygens from each ODA^{2-} ligand). The final atomic positional coordinates are given in Table IV, where the atom-numbering scheme indicated in the stereoview of Figure 2 is used. Oxygen atoms labeled O30, O31, O40, O41, O42, and O50 belong to water molecules in the lattice, none of which are coordinated to the Eu(III) ion. The average Eu–O distances are 2.518 and 2.395 Å for the Eu–ether oxygen and Eu–carboxylate oxygen bonds, respectively. These numbers are in good agreement with the respective values of 2.49 and 2.41 Å quoted[24] for the high-symmetry ($R32$) structure of $Na_3[Eu(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$. Selected bond distances and angles for the present low-symmetry (Cc) structure of $Na_3[Eu(ODA)_3]\cdot 6H_2O$ are given in Table V. In the high-symmetry ($R32$) crystal the Eu(III) ion lies at a position of crystallographic D_3 symmetry, while in the present Cc structure there is no crystallographically imposed symmetry. In the Cc structure the three angles subtended at the central Eu by the Eu–ether oxygen bonds are 117.1, 119.8, and 123.1°, which sum to 360.0°, implying a planar arrangement of the four atoms in the equatorial plane but with small deviations from 120.0° for an idealized D_3 structure.

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Table V. Selected Interatomic Distances (Å) and Angles (deg) for $Na_3[Eu(ODA)_3]\cdot 6H_2O$

Eu-O1	2.427 (6)	Eu-O11	2.385 (8)	Eu-O21	2.331 (7)
Eu-O4	2.531 (8)	Eu-O14	2.493 (4)	Eu-O24	2.530 (7)
Eu-O7	2.392 (7)	Eu-O17	2.386 (7)	Eu-O27	2.387 (8)
O1-Eu-O4	62.4 (2)	O4-Eu-O21	76.8 (3)	O11-Eu-O24	70.0 (3)
O1-Eu-O7	126.4 (2)	O4-Eu-O24	119.8 (1)	O11-Eu-O27	85.5 (3)
O1-Eu-O11	146.3 (3)	O4-Eu-O27	136.2 (3)	O14-Eu-O17	62.6 (3)
O1-Eu-O14	134.2 (3)	O7-Eu-O11	81.7 (3)	O14-Eu-O21	133.2 (3)
O1-Eu-O17	79.2 (2)	O7-Eu-O14	75.5 (3)	O14-Eu-O24	117.1 (3)
O1-Eu-O21	92.4 (2)	O7-Eu-O17	83.5 (3)	O14-Eu-O27	71.4 (3)
O1-Eu-O24	76.3 (2)	O7-Eu-O21	78.8 (3)	O17-Eu-O21	150.4 (3)
O1-Eu-O27	78.4 (3)	O7-Eu-O24	136.9 (3)	O17-Eu-O24	139.5 (2)
O4-Eu-O7	64.1 (2)	O7-Eu-O27	146.9 (2)	O17-Eu-O27	80.1 (3)
O4-Eu-O11	138.3 (3)	O11-Eu-O14	64.5 (3)	O21-Eu-O24	62.6 (3)
O4-Eu-O14	123.1 (3)	O11-Eu-O17	127.1 (2)	O21-Eu-O27	126.3 (3)
O4-Eu-O17	74.2 (2)	O11-Eu-O21	73.6 (3)	O24-Eu-O27	63.7 (3)

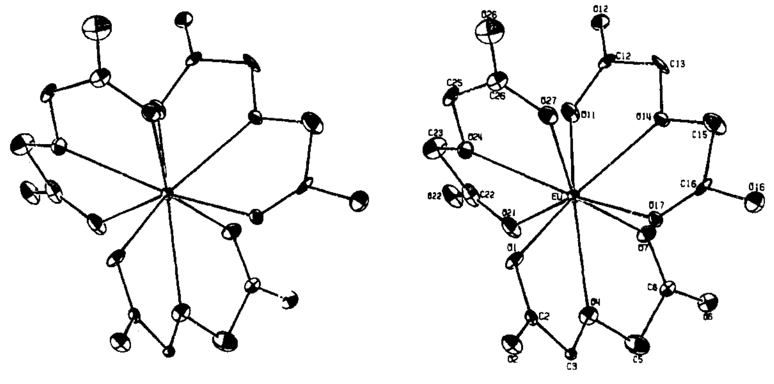

Figure 2. Stereoview of $Na_3[Eu(ODA)_3]\cdot 6H_2O$.

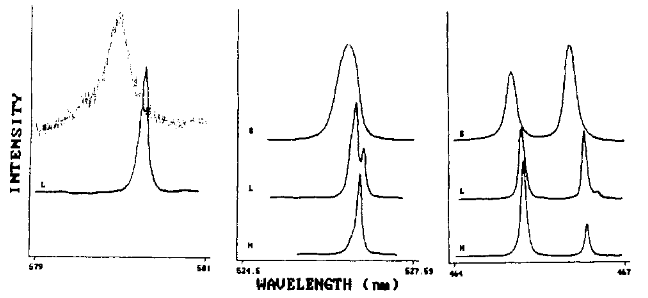

Figure 3. Excitation spectra (λ_{em} = 614 nm) of (H) $Na_3[Eu(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ (single crystal), (L) $Na_3[Eu(ODA)_3]\cdot 6H_2O$ (single crystal), and (S) $Eu(ODA)_3^{3-}$ (solution, [Eu] = 1 mM; mole ratio ODA:Eu = 30:1).

The spectroscopic results obtained on the single crystals are summarized in Table III and shown in Figure 3. The data on $Na_3[Eu(ODA)_3]\cdot 6H_2O$ are consistent with its low-symmetry structure in the following respects: (1) the appearance of a single, sharp peak (half-width 3.4 cm^{-1}) in the $^7F_0 \rightarrow {}^5D_0$ region is indicative of a single Eu(III) environment; (2) the $^7F_0 \rightarrow {}^5D_0$ transition occurs at 17 235 cm^{-1}, which yields (eq 1) a total ligand charge of −5.8, indicating six bound carboxylates; (3) the $^7F_0 \rightarrow {}^5D_1$ and $^7F_0 \rightarrow {}^5D_2$ transition regions each contain three bands, implying less than axial symmetry for the metal complex (in agreement with the lack of any crystallographic symmetry); (4) the τ^{-1} value for the complex is 0.50 ms^{-1}, implying that there are no metal-coordinated water molecules (eq 2).

Consistent with the D_3 site symmetry of Eu(III) in the higher symmetry double salt, $Na_3[Eu(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$,[17] our laser studies revealed no observable emission upon excitation in the region of the $^7F_0 \rightarrow {}^5D_0$ transition, which is forbidden in this symmetry. A single excitation peak with a suggestion of a shoulder on the high-energy side is observed for the $^7F_0 \rightarrow {}^5D_1$ transition and two well-separated bands are observed in the $^7F_0 \rightarrow {}^5D_2$ region, again consistent with the high symmetry at the metal ion site (Figure 3). Our finding of a very low τ^{-1} value (0.56 ms^{-1}) for these water-containing crystals is consistent with the absence of water molecules coordinated to Eu(III).

In both crystalline forms the europium(III) ion is nine-coordinate with the positions of the liganding atoms approximating a tricapped trigonal prism. The distortion from this idealized symmetry to C_1 in $Na_3[Eu(ODA)_3]\cdot 6H_2O$ is a function of crystal packing forces. The presence of $NaClO_4$ in the unit cell apparently limits the distortion of the polyhedron. The extent of the distortion is also small in solution. The spectral results for $Eu(ODA)_3^{3-}$ (Figure 3) indicate that the aqueous complex resembles more closely the higher symmetry salt.

Emission spectra for $Na_3[Eu(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$[25-28] reveal the same splitting pattern as the excitation spectra with the same ΔJ values (i.e. the $^5D_0 \rightarrow {}^7F_1$ emission corresponds to the $^7F_0 \rightarrow {}^5D_1$ excitation, etc). This again is consistent with the crystallographic findings.

Conclusions. Laser-excited Eu(III) luminescence excitation spectroscopy is shown to be able to detect subtle differences between high- and low-symmetry forms of a coordination complex. It provides a direct means of making structural comparisons between the solution and solid states and allows solution-state species to be characterized with regard to the total charge on the ligands and the number of coordinated water molecules.

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Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal parameters (*U*'s) (19 pages). Ordering information is given on any current masthead page.

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