Journal of Solid State Chemistry **148,** 347–352 (1999)
Article ID jssc.1999.8459, available online at http://www.idealibrary.com on IDEAL®

Luminescence Spectroscopy and Crystal Field Simulations of Europium Propylenediphosphonate $EuH[O_3P(CH_2)_3PO_3]$ and Europium Glutarate $[Eu(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$

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Received March 3, 1999, in revised form June 11, 1999; accepted July 22, 1999

The results of investigations on the photoluminescence of two europium hybrid compounds, $EuH[O_3P(CH_2)_3PO_3]$ (Eu[diph]) and $[Eu(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$ (Eu[glut]), are presented. In both compounds one local environment is found for the rare earth (*Re*) ion and the symmetry of the *Re* polyhedron is low (C_s) as evidenced by the Eu^{3+} luminescence studies. The electrostatic crystal field (cf) parameters of the ^7F multiplet are obtained by the application of the phenomenological cf theory. The simulations using C_{2v} symmetry for the rare earth ion give good agreement between the calculated and the experimental $^7F_{0–4}$ energy level schemes. The observed optical data are discussed in relation to the crystal structure of the compounds. © 1999 Academic Press

***Key Words*: europium; propylenediphosphonate; glutarate; luminescence; crystal field.**

INTRODUCTION

In an attempt to synthesize new microporous compounds, we began investigations on the rare earth family considering the fact that the rare earth elements, due to their high coordination numbers when compared to Al, Si, Ga, or Fe, could give rise to new template-synthesized fluorinated phosphates with an open framework structure. Unfortunately, the strong affinity of fluoride and phosphate groups for the rare earth (*Re*) elements systematically led to the formation of monazite-type phosphate [*Re*PO_4] and fluoride [*Re*F_3] phases. To prevent the formation of these dense phases, we have replaced the small PO_4 ligand by a larger one. In hydrothermal conditions, we obtained two new families of mixed compounds, rare earth propylenediphosphonates $EuH[O_3P(CH_2)_3PO_3]$, (Eu[diph]) (1) and rare earth glutarates $[Eu(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$, (Eu[glut] (2).

In this paper we describe the luminescence of the Eu^{3+} ion in Eu[diph] and Eu[glut]. The similarities and the differences observed for Eu^{3+} luminescence in these two compounds have been highlighted and discussed based on their crystals structure.

EXPERIMENTAL DETAILES

Synthesis, Structural Determination, and Crystal Structure

The compounds, Eu[diph] and Eu[glut], were synthesized hydrothermally at low temperatures by reaction between propylenediphosphonic acid, or glutaric acid, and europium chloride. For more details see Refs. (1, 2).

X-ray purity crystalline powder of europium diphosphonate was obtained and *ab initio* structure determination was carried out, using the software programs DICVOL91, FULLPROF, and SHELXS (3, 4).

Self-made single crystals of the europium glutarate were selected by optical examination and intensity data were collected on a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector. The structure was solved using the software program SHELXTL (5).

$EuH[O_3P(CH_2)_3PO_3]$

The crystal structure of Eu[diph] has been determined *ab initio* from X-ray powder diffraction data and refined by the

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Rietveld method (1). The compound crystallizes in the monoclinic space group $C2/m$ (No. 12, (6)) with $a = 8.232(1)$ Å, $b = 18.982(1)$ Å, $c = 5.270(1)$ Å, $\beta = 111.95(1)$, and $Z = 4$. The europium cation is coordinated by eight oxygen atoms from the phosphonate groups. The framework consists of edge-sharing rare earth polyhedra-chains. The chains are connected by the PO_3 groups which lead to inorganic Eu–P–O sheets. The P–C bonds point out of the sheets and allow the cross-linking of the inorganic sheets into a pillared layer structure via the organic groups $-(CH_2)_3-$. As already shown by Wang *et al.*, the proton is either randomly distributed between two oxygen atoms of two phosphonic groups or equidistant between them (7).

$[Eu(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$

The crystal structure of Eu[glut] has been determined by single-crystal X-ray diffraction (2). The material crystallizes in the monoclinic space group $C2/c$ (No. 15, (16)) with $a = 8.016(1)$ Å, $b = 15.074(1)$ Å, $c = 19.724(1)$ Å, $\beta = 93.98(1)$, and $Z = 4$ (final agreement factors $R_1 = 3.11$, $wR_2 = 7.13$). The organic–inorganic network is three-dimensional and consists of chains of edge-sharing rare earth polyhedra along the [100] direction, linked together by the carbon chains along the [010] and [001] directions. This arrangement involves the formation of channels parallel to the rare earth chains in which weakly bonded water molecules are situated.

Both the structures have the edge-sharing rare earth polyhedra-chains in common. The formation of this chain is ensured by a double action chelating/bridging of the acidic functions of the organic ligand. This characteristic allows us to find a common orientation for the rare earth polyhedra. A comparison of the polyhedra in Eu[diph] with the polyhedra in Eu[glut] shows a slight change in the direct environment of the cation (Fig. 1). In both the structures, the nearest neighbors of the Eu^{3+} ion are oxygen atoms. In addition, the spatial arrangement and the connection of the acidic functions are similar in both. The salient structural features are: (i) two chelating phosphonate groups in Eu[diph] are replaced by two chelating carboxylate groups in Eu[glut], (ii) two 8-coordinated phosphonate groups in Eu[diph] are replaced by two 9-coordinated carboxylate groups in Eu[glut], and (iii) two 8-coordinated phosphonate groups are replaced by one water molecule and one chelating carboxylate group in Eu[glut]. This is highlighted by comparing the intermolecular distances and angles in each rare earth polyhedron. The main change is the passage from eight to nine for the coordination of the rare earth ion.

Luminescence

The emission spectra of the europium compounds were recorded for the powder samples under 457.9 nm excitation emitted from a 5 W power Spectra Physics 2016–05S Ar–ion laser. A Spectra Physics 375/376 continuous wave dye laser (with rhodamine 6G as the dye) pumped by an argon–ion laser was also used to excite selectively the lowest ^5D_J level ($^5D_0$) situated at 579.7 nm in (Eu[diph]) and at 580 nm in (Eu[glut]), respectively.

To improve the resolution of the line transitions, the luminescence experiments were carried out at low temperatures. The required low temperature is obtained by immersing the sample in liquid nitrogen, contained in a quartz sample holder. The emission was dispersed by a 1-m Jarrell–Ash monochromator and detected by a Hamamatsu

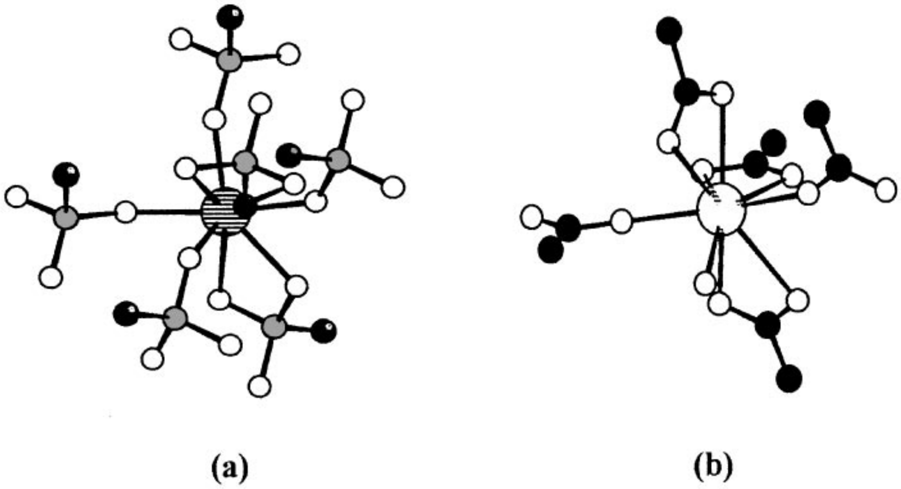

FIG. 1. Rare earth polyhedra in propylenediphosphonates $Re[O_3P(CH_2)_3PO_3]$ (a) and glutarates $[Re(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$ (b). The carbon atoms are represented in black (small circles), the phosphorous atoms in pale grey, the oxygen atoms in white and the europium atoms are the big circles.

R 374 photomultiplier. The luminescence emission spectra were recorded in the visible wavelength region between 400 and 750 nm.

RESULTS AND DISCUSSION

Analysis of the Luminescence Spectra

The emission spectra of Eu[diph] and Eu[glut] are presented in Figs. 2 and 3. The spectra show similar features for both the compounds. They consist of numerous sharp lines attributed to $^5D_0 \rightarrow {}^7F_{0-4}$ electronic transitions (Fig. 2 and Table 1). The $^5D_0 \rightarrow {}^7F_3$ electronic transition is of negligible intensity in Eu[diph] when compared with the intensity of other $^5D_0 \rightarrow {}^7F_J$ transitions and could not be seen in Eu[glut].

From the observed spectra, the following conclusions are drawn:

(1) The sharp single peak observed in both the cases at 579.7 and 580 nm for the $^5D_0 \rightarrow {}^7F_0$ transition confirms (i) one single crystallographic site for the rare earth ion with C_{nv}, C_n, or C_s point group symmetry (8) and (ii) the purity of each phase. Moreover, the presence of numerous electronic lines indicates a low point symmetry for the rare earth ion, which is in agreement with the structural data.

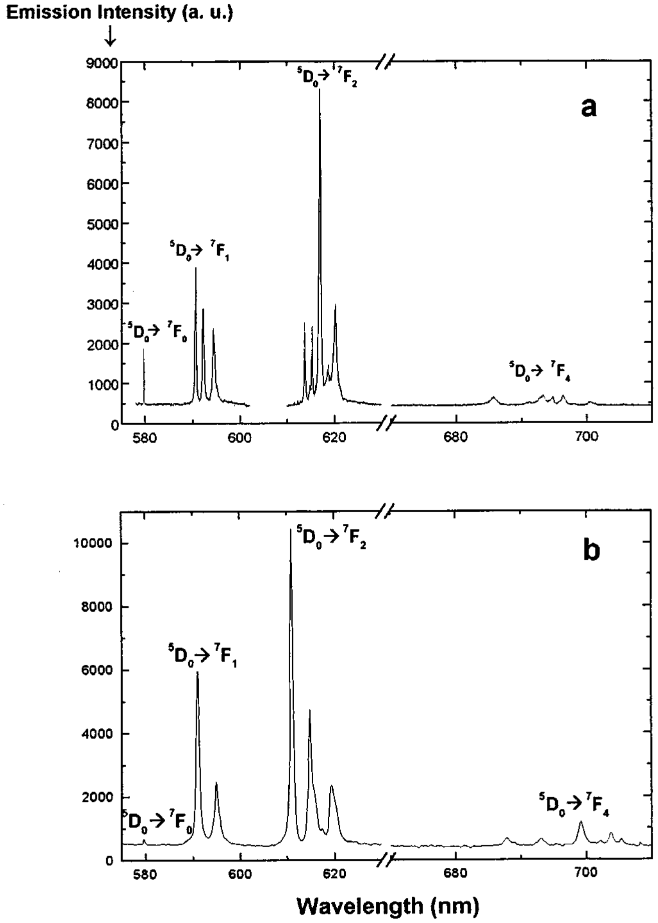

FIG. 2. Emission spectra of glutarate $[Eu(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$ (a) and of propylendeiphosphonate $EuH[O_3P(CH_2)_3PO_3]$ (b) (at 77K, under 457.9 nm argon ion laser excitation).

(2) The C_s symmetry generates no selection rules between different Stark levels (9). Therefore, the degeneracy of the ^7F_J levels is completely lifted and the number of observed lines for each $^5D_0 \rightarrow {}^7F_J$ is equal to $2J+1$ components. Three narrow lines are effectively detected for $^5D_0 \rightarrow {}^7F_1$ transition ($J=1$) in the wavelength range 590–595 nm and five for the transition $^5D_0 \rightarrow {}^7F_2$ ($J=2$) between 610 and 622 nm (Fig. 3). Nine lines are observed for the $^5D_0 \rightarrow {}^7F_4$ electronic transition in Eu[glut] and only seven in Eu[diph] and for the $^5D_0 \rightarrow {}^7F_3$ transition five weak lines from seven expected are present in Eu[diph].

The $^5D_0 \rightarrow {}^7F_0$ transition is observed due to the admixture of high-lying odd parity states into the $^5D_0$ and $^7F_0$ states through the crystal field potential (10, 11). The admixture of $4f^6$ states into the $^5D_0$ and $^7F_0$ states by the even parity crystal field perturbation is also proposed (12–15). Due to this J-mixing effect, the $^5D_0 \rightarrow {}^7F_0$ transition borrows intensity from the $^5D_0 \rightarrow {}^7F_J$ ($J = 2, 4$, and 6) and $^5D_J \leftarrow {}^7F_0$ ($J = 2$ and 4) transitions. According to this, the intensity of the $^5D_0 \rightarrow {}^7F_0$ transition in Eu[glut] may be explained by the stronger J-mixing effect, especially of $^7F_{20}$ and $^7F_{40}$ in $|{}^7F_{00}\rangle$ wave function (16).

In the case of Eu[diph], two of the three observed lines for $^5D_0 \rightarrow {}^7F_1$ transition are very close. It perhaps may suggest a higher symmetry than C_s for the local site around the europium ion (17). The optical data confirm the structural analysis in both the compounds with some reserve on the point group symmetry in Eu[diph].

Crystal Field Simulation

The ground state configuration of the trivalent europium ion (Eu^{3+}) is $4f^6$ which possesses a total of 3003 $|SLMJ\rangle$ Stark sublevels. The treatment of the $4f^6$ configuration as a whole is a very hard task. Usually, the phenomenological crystal field simulation of the Eu^{3+} energy level scheme can be performed, taking into account only the 49 components of the ^7F_J ground multiplet. The cf calculation is then realized by using the matrix diagonalization program GROMINET (18) considering the J mixing between wavefunctions with different J and M_J values.

According to Wybourne's formalism (12), the crystal field Hamiltonian can be expressed as a combination of spherical harmonics C^k_q:

$$H_{\mathrm{cf}} = \sum_{kq}[B^k_q(C^k_q + C^k_{-q}) + iS^k_q(C^k_q - C^k_{-q})],$$

where B^k_q and S^k_q are the real and imaginary cf parameters.

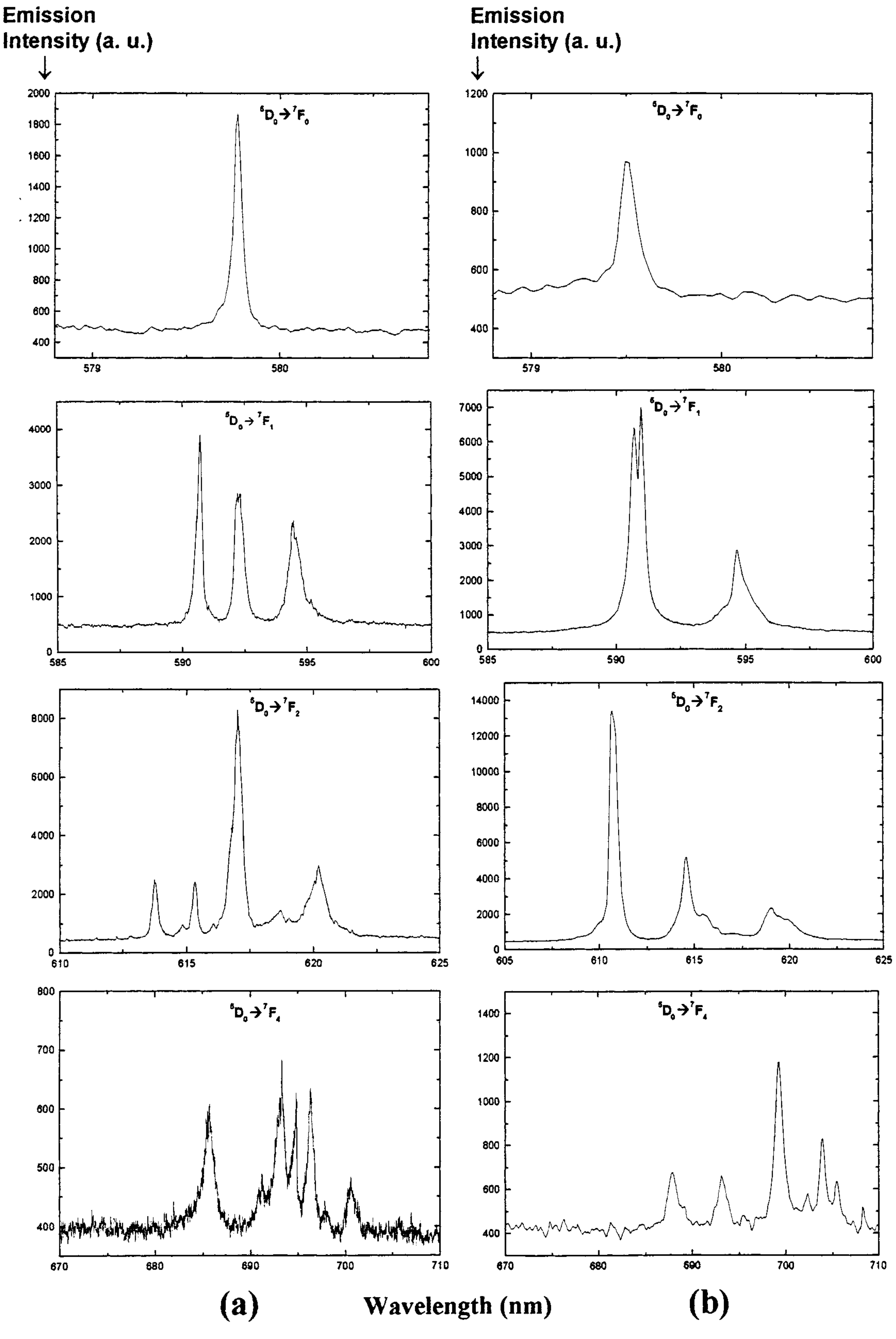

FIG. 3. Emission spectra of glutarate $[Eu(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$ (a) and of propylenediphosphonate $EuH[O_3P(CH_2)_3PO_3]$ (b) in the $^5D_0 \rightarrow {^7F_J}$ ($J = 0$–4) transitions domain (at 77K, under 457.9 nm argon ion laser excitation).

TABLE 1

Experimental and Calculated (Using the Software Program GROMINET (17)), Energy Level Schemes for the Eu^{3+} Ion in (Eu[diph]) and (Eu[glut]) at 77°K (λ_{exc} 457.9 nm)

	Eu[diph]		Eu[glut]	
$^{2S+1}L_J$ level	$E_{exp.}$	$E_{calc.}$	$E_{exp.}$	$E_{calc.}$
$^7F_0$	0	0	0	0
$^7F_1$	327	323	318	318
	334	338	363	361
	439	438	427	428
$^7F_2$	880	875	953	952
	984	982	995	995
	1007	1017	1039	1043
	1101	1100	1084	1083
	1122	1118	1122	1120
$^7F_3$	1824	1831	—	1825
	—	1851	—	1865
	1865	1862	—	1870
	1892	1886	—	1892
	1953	1956	—	1897
	—	1966	—	1933
	1981	1980	—	1961
$^7F_4$	2705	2709	2660	2658
	—	2779	2773	2766
	—	2802	2816	2819
	2819	2816	2850	2850
	2870	2870	2881	2886
	2943	2938	2916	2917
	3002	3000	2968	2972
	3038	3041	3010	3009
	3070	3075	3071	3065
$^5D_0$	17251		17242	
$^5D_1$	19005			
	19008			
	19038			

Note. All values are in em^{-1}.

In Eu[diph] and Eu[glut], the europium cation occupies the C_s point symmetry. The cf Hamiltonian corresponding to the C_s point group symmetry possesses 15 crystal field parameters, 9 real and 6 imaginary. For simplification, we started with the Hamiltonian corresponding to a higher symmetry C_{2v}, which has the advantage of taking into account only the real parameters thereby reducing the number of the phenomenological cf parameters to nine:

$$\begin{aligned} H_{cc}(C_{2v}) = {} & B^2_0 + B^4_0 + B^6_0 + B^2_2(C^2_2 + C^2_{-2}) + B^4_2(C^4_2 + C^4_{-2}) \\ & + B^6_2(C^6_2 + C^6_{-2}) + B^4_4(C^4_4 + C^4_{-4}) \\ & + B^6_4(C^6_4 + C^6_{-4}) + B^6_6(C^6_6 + C^6_{-6}). \end{aligned}$$

The cf simulation procedure is already given (19, 20). The first step is a determination of the second rank crystal field parameters considering only three Stark components of the $^7F_1$ level. For more details see Refs. (19, 20).

The least-squares fitted cf parameter set obtained for the point group symmetry C_{2v} reproduces the experimental energy level scheme (Table 2 and Fig. 4).

Considering the calculated crystal field strength parameters N_v in Eu[diph] and in Eu[glut] (Table 2), it is clear that the crystal field is relatively weak in both the compounds when compared with the value obtained for garnets (N_v being about 4000 cm^{-1}) (21, 22).

Examination of the rare earth polyhedron in Eu[diph] and in Eu[glut] shows slight changes in the first coordination sphere of the cation. The first neighbors of the cation are all oxygen atoms which occupy similar positions in both the compounds. However, the crystal field parameters' set from one structure to the other is different: if each B^k_q (for k equals 2 or 4) has the same sign in both Eu[diph] and in Eu[glut], its absolute value differs; moreover, for k equals 6, the B^6_q values are different in sign as well as in absolute value. This variation is due to the difference in the number of oxygen atoms in the first coordination sphere of the europium cation in both the compounds as well as to the difference in the lanthanide–ligand distances. The mean Eu–O distance is 2.43 Å in Eu[diph] and 2.48 Å in Eu[glut], respectively. The crystal field is notably affected by the modification of the polyhedra; their coordination numbers change from eight to nine, even though a remarkable similar spatial arrangement of the oxygen atoms around the cation

TABLE 2

Phenomenological Crystal Field Parameters and Their Values Obtained Using the Software Program GROMINET (17) for the Eu^{3+} Ion in Propylenediphosphonate $EuH[O_3P(CH_2)_3PO_3]$ (Eu[diph]) and in Glutarate $[Eu(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \cdot 4H_2O$ (Eu[glut])

Parameter	Eu[diph] Value (cm^{-1})	Eu[glut] Value (cm^{-1})
B^2_0	357	303
B^2_2	− 17	− 69
B^4_0	− 406	− 246
B^4_2	− 285	− 643
B^4_4	907	307
B^6_0	− 1045	846
B^6_2	− 84	494
B^6_4	133	− 385
B^6_6	− 120	336
No. levels	21	18
Residue	392	180
σ	5.7	4.5
$N_{vk=2}$	567	504
$N_{vk=4}$	1659	1226
$N_{vk=6}$	1064	1292
$N_{v\text{total}}$	2051	1851

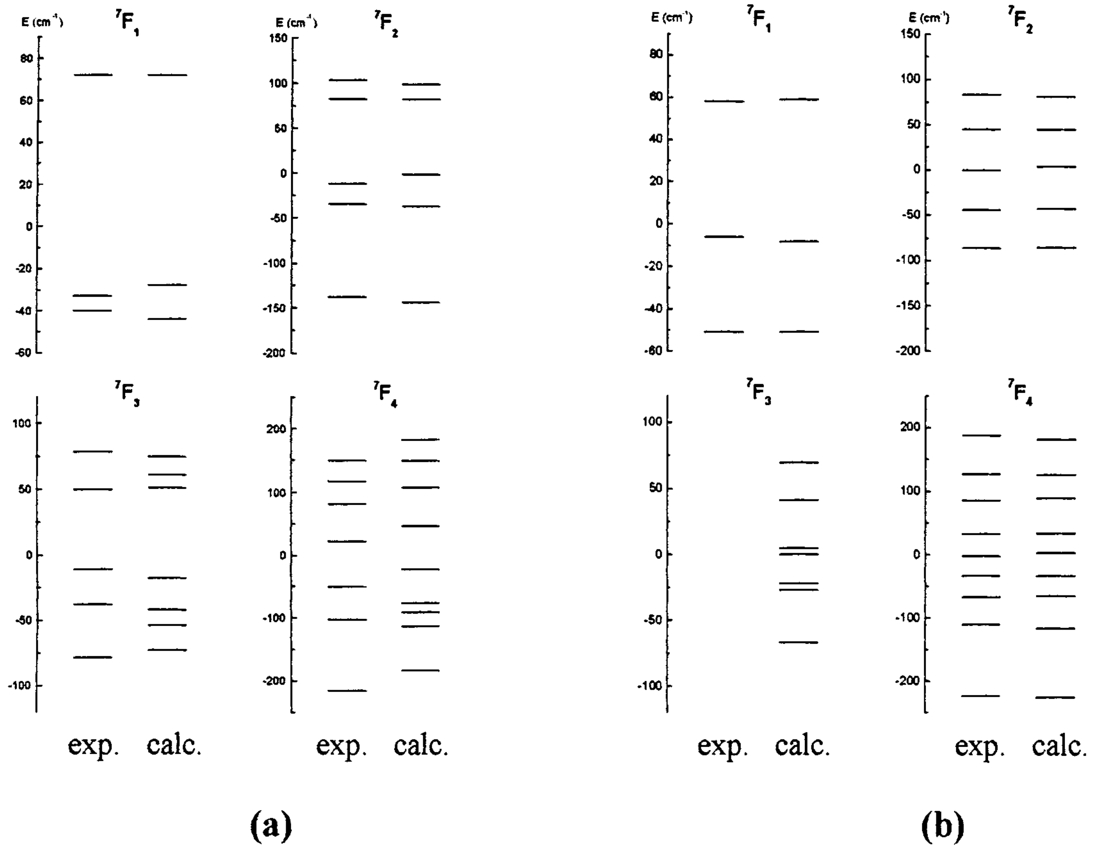

FIG. 4. Experimental and calculated $^{7}F_{1-4}$ energy level schemes for europium propylenediphosphonate, (Eu[diph]) (a) and europium glutarate, (Eu[glut]) (b).

is noticed for both the compounds. We have, however, proved that the 6 rank cf parameters are the most difficult to determine. It is especially true in the case of Eu[glut], due to the lack of the $^{5}D_{0} \rightarrow {}^{7}F_{3}$ electronic transition.

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