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Electronic energy-level structure of $4f^6$ configuration in europium(III) triacetate tetrahydrate

Mirosław Karbowiak *, Anna Mondry

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50–383 Wrocław, Poland

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ABSTRACT

Analysis of high-resolution absorption and emission spectra of europium(III) triacetate tetrahydrate (EuAC) crystal enabled assignment of 130 experimental crystal-field levels of the $4f^6$ configuration between 0 and 35,050 cm^{-1}. These experimentally determined levels were simulated using a semi-empirical 35 parameters Hamiltonian representing the combined free-ion and crystal-field interactions for Eu^{3+} ion in the C_1 symmetry site, with the final relatively low r.m.s. deviation of 9.0 cm^{-1}. The reliable starting values of B_q^k parameters were obtained from the superposition model analysis. The crystal-field strength (S_{cf}) for EuAC is slightly smaller than for europium(III) trioxydiacetate complex (EuODA). It is probably brought about by the presence of two water molecules in the first coordination sphere of the metal ion in the acetate crystal.

1. Introduction

Previously, the f–f transition intensities of europium(III) triacetate tetrahydrate were analyzed by means of the Judd–Ofelt theory [1]. Absorption lines observed in 250–650 nm range were assigned, but no further attempts to analyze energy levels were endeavored. In the present paper, the analysis is extended onto the crystal-field energy level calculations, which allow for the unequivocal assignment of the bands observed in the spectra and simulation of the electronic energy-level structure.

As it was established by the X-ray analysis, the $[Eu(CH_3COO)_3(H_2O)_2] \cdot 2H_2O$ (EuAC) crystals are isomorphic with those of the dimeric, centrosymmetric gadolinium [2], holmium [3] and erbium [4] acetates. The nine-coordinated metal atom is surrounded by the oxygen atoms of three bidentate acetate ligands, two water molecules and a bridging oxygen atom from an acetate ligand of the adjacent moiety [2–4]. In this way one of three acetate ligands surrounding the metal atom is tridentate and forms the shortest and longest M–O bonds of a carboxyl group with Ln^{3+} ion. A small size of the acetate ligand favours such a steric arrangement of a COO^- group around a metal atom and is a reason that water molecules can come very closely to the Ln^{3+} coordination sphere. The M–O bonds to water molecules in lanthanide acetates are slightly shorter than those to the carboxyl groups what is rarely found in a majority of lanthanide carboxylates. Although the actual symmetry of the metal atom environment is C_1, it was pointed out that it may be approximated by C_3 [2]. Nevertheless, using Hamiltonian with the latter symmetry is not suitable, since the $2J + 1$ degeneracy of $4f^6$ Stark levels for this symmetry is not completely lifted, contrary to the experimental data. There are also no hints for relating uniquely the C_1 experimental spectra to the C_3 symmetry irreducible representation labels, which disables the application of symmetry descending method. Moreover, the assumption of C_3 symmetry requires the same contribution of acetate and water oxygen ligands to the crystal-field, what is obviously not correct. The orientation of the coordination system presented in Fig. 1 reveals the existence of an approximate C_2 axis, but as it will be shown in further part of this paper, also the C_2 symmetry is too a crude approximation. Therefore, our CF calculations were carried out in terms of a parametric Hamiltonian for the actual C_1 symmetry at the Eu^{3+} ion site. Such calculations are usually not possible for Eu^{3+} complexes with organic ligands due to the limited experimental data set as compared to a large number of CF parameters. However, EuAC is a unique system in this respect. The absorption transitions could be analyzed in relatively broad energy range. Combining these data with those found from emission spectra, as many as 130 energy levels could be obtained. This permitted inclusion of 27 crystal-field parameters (CFPs), required for the C_1 symmetry Hamiltonian, in the fitting procedure.

2. Experimental

The details of the crystal synthesis and electronic absorption measurements are given in Ref. [1], whereas a typical IR spectrum of lanthanide(III) triacetate tetrahydrate compounds together with the vibrational frequency assignments is presented in Ref. [5]. The IR spectra of EuAC in a KBr pellet and nujol suspension were

* Corresponding author. Fax: +48 71 328 23 48.
E-mail address: karb@wchuwr.pl (M. Karbowiak).

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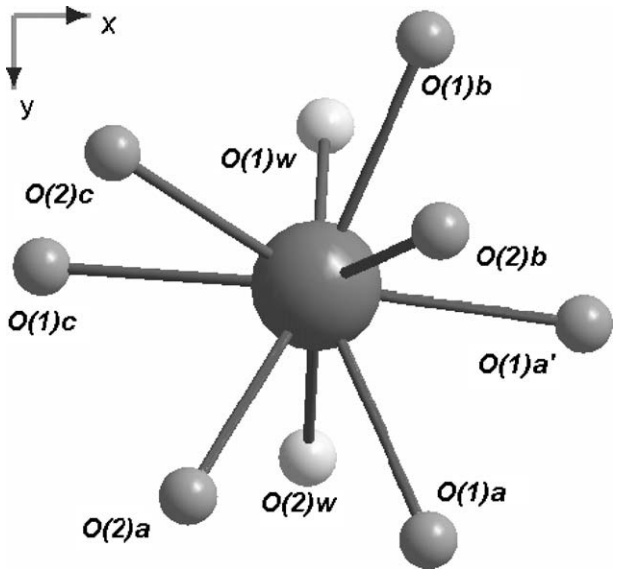

Fig. 1. Coordination polyhedron of EuAC.

recorded in the range 50–4000 cm^{-1} with a Bruker IF S66 spectrometer. The emission and excitation spectra of EuAC crystals were recorded at room and 77 K temperatures on a SLM Aminco SPF 500 spectrofluorometer. The luminescence spectra were also measured at 77 K and 5 K using a nitrogen laser pumped tunable dye laser (coumarin 460). These spectra were analyzed with a Zeiss model GDM 1000 grating monochromator and detected by a cooled photomultiplier. A resulting signal was averaged by a SRS 250 boxcar integrator.

3. Results and discussion

The 4.2 K absorption spectra of the $^7F_0 \rightarrow {}^5D_0$, $^5D_1$ and $^5D_2$ transitions recorded for EuAC crystal are presented in Fig. 2. The number of peaks, of a half-width equal to 3–4 cm^{-1}, observed in the spectra of these transitions indicates that degeneracy of the $^5D_1$ and $^5D_2$ levels is completely removed and confirms the low C_1 symmetry for the Eu^{3+} site as obtained from the crystal structure determination. The spectra of the remaining absorption transitions of Eu^{3+} ion are shown in Fig. 1 of Ref. [1]. Transitions to the $^5D(3)_3$, $^5L_8$, $^5L_9$, $^5L_{10}$, $^5H(1)_3$ and $^5H(1)_7$ levels are observed in the spectra as very weak lines, nevertheless the assignment of some crystal-field components of these multiplets was possible. The very low intensity of these transitions results from the fact that they do not obey the $0 \leftrightarrow J = 2, 4$ or 6 selection rule for electric-dipole transitions. Electronic spectra of EuAC reveal a vibronic structure. It was found that the absorption band located at 29,990 cm^{-1}, which could not be assigned to any of f–f transitions, is of vibronic origin. This peak which is also observed in the room temperature spectra of the crystal as well as of the solution of the Eu^{3+}–acetate complex, was attributed to the ν_{asCOO} vibration coupled with the $^5D_2$ manifolds (Fig. 1 and Table 1 in Ref. [1]). This vibronic transition has been also found in the excitation spectrum of EuAC recorded at 77 K while monitoring the $^7F_0 \rightarrow {}^5D_2$ emission at 617 nm. The excitation spectrum measured in the spectral range of the most suitable transitions to study the electron–phonon coupling is presented in Fig. 3. Whereas only a single broad and intense band is located at 214 cm^{-1} apart from the $^7F_0 \rightarrow {}^5D_0$ transition, several well separated lines appear on the higher energy side of the $^7F_0 \rightarrow {}^5D_2$ transition. While the $^7F_0 \rightarrow {}^5D_J$ spectra demonstrate the electron–phonon coupling of higher IR frequencies with the $^5D_2$ state, the emission spectra reveal that the strongest such interaction is observed for the $^7F_0$ ground level. As it results from spectra presented in Fig. 4, some vibrations of higher energy frequencies are associated with the $^5D_0 \rightarrow {}^7F_0$ transition. While the latter transition consists of one electronic line, the $^5D_0 \rightarrow {}^7F_1$ transition is split into 2 lines at room and 77 K temperatures. Therefore, two of the three lines observed for this transition in the spectrum at 5 K must be very close, what might suggest a higher symmetry than C_1 for the local site around the europium ion. Contrary to the $^5D_0 \rightarrow {}^7F_1$ spectra, the splitting of the $^5D_0 \rightarrow {}^7F_2$ transition discloses evidently six besides expected five lines ($2J + 1 = 5$) for all three temperature measurements. The additional line in the $^5D_0 \rightarrow {}^7F_2$ spectra is 934 cm^{-1} apart from the $^5D_0 \rightarrow {}^7F_0$ transition and indicates a phonon coupling with the $^7F_0$ state. This vibration frequency which is fairly intense in the IR spectrum of EuAC was assigned as ν_{C-C} stretching [6,7] and also appears in the absorption spectrum of the $^7F_2 \rightarrow {}^5D_0$ transition recorded at room temperature for EuAC crystal (Fig. 4). Thus the additional lines observed in the both $^5D_0 \rightarrow {}^7F_2$ and $^7F_2 \rightarrow {}^5D_0$ result from transitions to, or from the coupled $^7F_0 + \nu_{C-C}$ electronic–vibronic state. Presence of this and other vibronics in the spectra of EuAC complicates assignments of the energies within the ^7F_J manifolds.

For the energy level calculations we have applied the effective operator model [8,9]. The observed energy levels were fitted to the phenomenological Hamiltonian $\hat{H} = \hat{H}_{FI} + \hat{H}_{CF}$ by a simultaneous diagonalization of the free-ion ($\hat{H}_{FI}$) and crystal-field Hamiltonian ($\hat{H}_{CF}$). The free-ion Hamiltonian was given by

$$\hat{H}_{FI} = E_{ave} + \sum_{k=2,4,6} F^k(nf,nf)\hat{f}_k + \zeta_{4f}\hat{A}_{SO} + \alpha\hat{L}(\hat{L}+1) + \beta\hat{G}(G_2) + \gamma\hat{G}(R_7) + \sum_{i=2,3,4,6,7,8} T^i\hat{t}_i + \sum_{j=0,2,4} M^j\hat{m}_j + \sum_{k=2,4,6} P^k\hat{p}_k \quad (1)$$

where each of the interaction operators and parameters are defined according to the conventional practice [8,9].

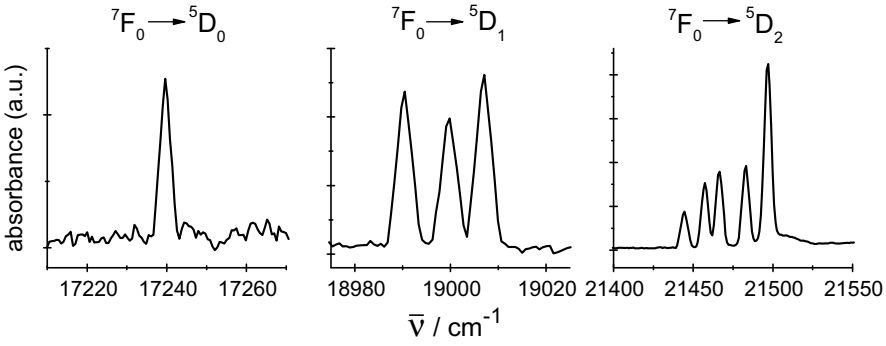

Fig. 2. Absorption spectra of EuAC at 4.2 K.