SPECTROSCOPY STUDIES OF ERBIUM AND DYSPROSIUM ACETATE SINGLE CRYSTALS

A. Mondry and K. Bukietyńska

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

Electronic absorption spectra of erbium and dysprosium acetate single crystals were measured. The intensities of $4f$–$4f$ transitions were calculated and the Judd–Ofelt Ω_λ parameters evaluated. Heavy lanthanide acetates differ from other lanthanide carboxylate compounds by relatively high "hypersensitive" transition intensities and the Ω_2 parameters. These results are discussed in terms of a stronger polarization effect which can be explained by the distinctly shorter Ln–OH$_2$ bond in comparison with the Ln–OOC bond in the investigated system.

PACS numbers: 78.20.Wc, 81.40.Tv

1. Introduction

Recently we examined the spectral intensities of $4f$–$4f$ transitions in holmium acetate single crystal spectra [1]. The relatively high intensity of the "hypersensitive" transition of that compound in comparison with other carboxylate complexes was explained by the dynamic coupling mechanism [2] resulting from the properties of acetate crystals, in which water molecules are bonded closer to the lanthanide ion than oxygen atoms from carboxyl groups.

X-ray data for heavy lanthanide acetates [3–5] indicate the existence of dimeric species with the both lanthanide atoms bridged by acetate oxygen atoms. The coordination number of each metal ion is nine through the three bidentate acetate groups, two water molecules and a bridging oxygen from one of the adjoining acetates.

In this paper we report single crystal spectral investigations of some other heavy lanthanide crystal acetates.

2. Experimental

Lanthanide oxide Ln_2O_3 (where Ln = Dy, Er) was dissolved in concentrated acetic acid and alkalized to pH = 4. The well shaped crystals of $Ln_2(CH_3COO)_6 \cdot 4H_2O$ were formed during very slow evaporation. The crystals were checked by X-ray diffraction and found to be isomorphic with those known

from literature [3]. The crystallographic axes referred to hereinafter are those de-
fined in [3].

The concentration of Ln(III) ions in the crystals was determined by EDTA
titration using xylenol orange as the indicator. The Dy(III) and Er(III) concen-
trations were: 4.9867 M and 5.0567 M, respectively. The densities, measured by
the flotation method in a mixture of chloroform and bromoform, were found to be
2.052 g·cm^{-3} for Dy(III) and 2.105 g · cm^{-3} for Er(III). The refractivity indices n
for the crystals were 1.50.

Absorption spectra of the investigated crystals were recorded on a Cary 2300
spectrophotometer at room temperature (for Dy and Er) and at 5 K (for Er). The
investigated spectral range was 250–1900 nm for Dy(III) and 250–1600 nm for the
Er(III) crystals.

The natural dimensions of the $Dy_2(CH_3COO)_6 \cdot 4H_2O$ crystals restricted
the absorption measurements to only one crystal plate orientation perpendicular
to the (010) direction. Absorption spectra of the $Er_2(CH_3COO)_6 \cdot 4H_2O$ crystals
were measured for crystals polished parallel to the planes (001) and ($\bar{1}50$) as well
as for a polycrystalline sample.

The intensities of the $4f$–$4f$ transition (P) and values of the Ω_λ parameters
were calculated from the following Judd–Ofelt [6,7] relation:

$$P = \chi \frac{8\pi^2 mc\sigma}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_\lambda \langle f^n \psi J \| U^{(\lambda)} \| f^n \psi' J' \rangle^2, \tag{1}$$

where P denotes the oscillator strength, $\chi = (n^2+2)^2/9n$, n is the refractive index,
J is the total quantum number of the ground state, $\langle f^n \psi J \| U^{(\lambda)} \| f^n \psi' J' \rangle$ is the
reduced matrix element of the unit tensor operator $U^{(\lambda)}$ tabulated by Carnall et
al. [8] and Ω_λ are the empirical least squares fitted parameters.

3. Results and discussion

The oscillator strength values (P) for $4f$–$4f$ transitions observed for erbium
acetate at 293 K and 5 K are presented in Table I. It can be seen that the oscillator
strength values measured for two orientations of the crystals – along the crystal-
lographic c^* axis and in the direction ($\bar{1}50$) — differ slightly within the limit of
experimental error. The direction ($\bar{1}50$) of the polished crystal is nearly parallel to
the b^* axis (deviation is about 14°).

Our primary results on intensity measurements for erbium acetate crys-
tal (a polycrystalline sample) are also included in Table I. The polycrystallinity
can be a reason that oscillator strength values are much lower, especially for the
$^4I_{15/2} \rightarrow {}^4G_{11/2}$ and $^4I_{15/2} \rightarrow {}^2H_{11/2}$ "hypersensitive" transitions in comparison
with intensities measured along the c^* and b^* axes.

As can be seen from Table I, an intensity decrease in almost all transitions in
the single crystal with the change of temperature from 293 K to 5 K is observed.
This decrease ranges for the individual transitions from 74% to 14%. Such effect
was also observed for holmium acetate crystals [1] as well as for other light and
heavy lanthanide acetates [9]. None of the known carboxylate compounds [10–12]
loses the intensities so efficiently as the acetates.

TABLE I

Oscillator strength values (P_{exp}, P_{calc}) and Ω_λ parameter values of $Er_2(CH_3COO)_6 \cdot 4H_2O$ crystals for different orientations of crystals.

| Direction l [cm]*	Polycrystalline sample 0.048 $T = 293$ K		(001) 0.0295 $T = 293$ K		$(\bar{1}50)$ 0.023 $T = 293$ K		$(\bar{1}50)$ 0.023 $T = 5$ K
Transition(s) $^4I_{15/2} \Rightarrow$	P_{exp} ×10⁸	P_{calc} ×10⁸	P_{exp} ×10⁸	P_{calc} ×10⁸	P_{exp} ×10⁸	P_{calc} ×10⁸	P_{exp} ×10⁸
$^4I_{13/2}$	201.15	130.54	274.47	170.58	233.18	142.45	121.56
$^4I_{11/2}$	56.82	60.21	89.23	84.76	50.70	70.48	17.67
$^4I_{9/2}$	33.43	26.06	26.26	25.46			1.34
$^4F_{9/2}$	157.15	181.49	184.94	204.80	159.29	175.88	66.34
$^4S_{3/2}$	41.98	50.93	64.52	66.75	50.87	55.55	13.86
$^2H_{11/2}$	640.85	560.34	920.98	978.30	808.23	816.61	308.97
$^4F_{7/2}$	157.90	194.70	179.12	243.02	168.80	204.25	52.57
$^4F_{5/2}, {}^4F_{3/2}$	85.71	97.99	119.41	128.44	91.58	106.89	70.68
$(^2G, {}^4F, {}^2H)_{9/2}$	57.50	74.24	68.58	95.44	59.41	79.73	45.88
$^4G_{11/2}$	946.84	992.95	1766.63	1735.18	1452.99	1448.30	581.36
$^4G_{9/2}$	154.12	117.66	172.28	127.48	138.94	110.49	36.53
$^2K_{15/2}, {}^2G_{7/2}$	111.95	94.34	142.17	133.65	103.01	111.50	88.88
$^2D_{5/2}, {}^4D_{7/2}$	668.93		1119.11		937.22		528.42
$\Omega_2 \times 10^{20}$ [cm²]	3.58 ± 0.33		6.91 ± 0.37		5.72 ± 0.29		
$\Omega_4 \times 10^{20}$ [cm²]	1.24 ± 0.51		1.19 ± 0.57		1.06 ± 0.45		
$\Omega_6 \times 10^{20}$ [cm²]	1.36 ± 0.27		1.78 ± 0.30		1.48 ± 0.23		
rms×10⁷	4.44		4.99		3.84		

*l = crystal thickness.
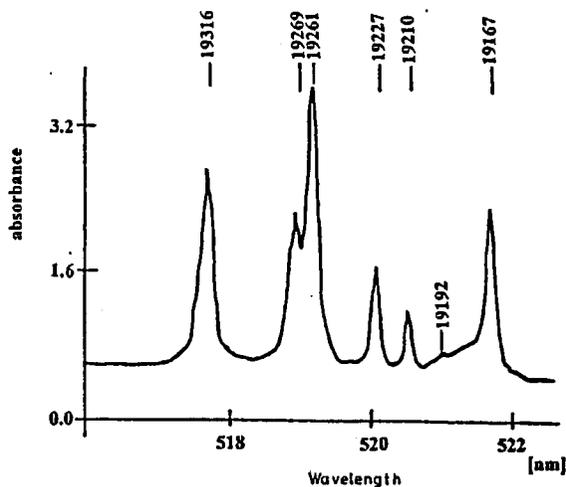
Fig. 1. The $^4I_{15/2} \rightarrow {}^2H_{11/2}$ "hypersensitive" transition of the $Er_2(CH_3COO)_6 \cdot 4H_2O$ crystal at 5 K (crystal thickness $l = 0.023$ cm).

In Table I the Ω_λ parameter values for erbium acetate are also included. Similarly as for holmium acetate, a relatively high Ω_2 parameter value is observed. It is distinctly higher than for the two other known simple Er(III) carboxylate compounds i.e. formamide solvates [13] and trichloroacetate hydrates [11].

The Stark splitting of electronic bands in the 5 K spectra of Er(III) acetate is in agreement with the $J + 1/2$ manifold resulting from the group theory for a single Er(III) ion site. It means that each Er(III) ion in the dimeric species has the same environment. It can be well exemplified in Fig. 1 where the Stark splitting of the $^4I_{15/2} \rightarrow ^2H_{11/2}$ transition is presented. In this figure, besides the electronic lines, also a side band of vibronic origin can be observed. It is 25 cm^{-1} apart from the electronic sublevel of lowest energy. For the whole erbium acetate spectrum, a rich side band structure is observed. Among them the lowest energy side bands which appear in some of the electronic Er(III) transitions are the bands situated at 25 cm^{-1} from adjacent electronic levels. These side bands (about 25 cm^{-1}) are also observed in the spectra of other lanthanide acetates as those of neodymium and europium [9].

The next investigated heavy lanthanide acetate single crystal was dysprosium acetate. The spectral intensity results of this compound are presented in Table II.

It is interesting to compare the received results for the acetate crystals with those reported for other lanthanide monocarboxylates i.e. with ligands similar to acetates such as glycinates and trichloroacetates. Single crystals of Dy(III) glycinates and trichloroacetates were studied recently [14, 15].

Dysprosium glycinate as well as acetate have the same coordination number (C.N. = 9). The most important difference between the crystal structures of both compounds is the distinctly shorter Dy–OH$_2$ bond in comparison with the Dy–OOC bond in the acetate crystal. For dysprosium glycinate the values of the oscillator strength for the $^6H_{15/2} \rightarrow ^6H_{9/2}$, $^6F_{11/2}$ "hypersensitive" transition as well as the Ω_2 parameter are distinctly lower than for dysprosium acetate. These results are very similar to those obtained by us for holmium acetate [1] and thus confirm also the role of the dynamic-coupling mechanism in lanthanide compounds [2].

Since the lanthanide trichloroacetates have dimeric structures in which the two Ln(III) ions have different coordination numbers 7 and 8, no such comparison with the lanthanide acetate crystals could be done. Furthermore, the number of water molecules in the inner sphere of heavy lanthanide ions is different for trichloroacetates (3 molecules) and for acetates (4 molecules). However, even in the case of a lowering of the coordination number in trichloroacetates one does not state a shortening of the Ln–OH$_2$ bonds, similar to that in the acetates. On the other hand, because of the lower coordination numbers, the average Ln–O distances for trichloroacetates are shorter than for acetates mainly, due to the contraction of Ln–OOC bonds. Nevertheless, both the oscillator strength of "hypersensitive" transitions and the Ω_2 parameters for Dy(III) and Er(III) trichloroacetates are lower than those for dysprosium and erbium acetates.

TABLE II
Oscillator strength values (P_{exp}, P_{calc}) and Ω_λ parameter values for $Dy_2(CH_3COO)_6 \cdot 4H_2O$ crystal (crystal thickness $l = 0.092$ cm).

Transition(s) $^6H_{15/2} \Rightarrow$	$P_{exp} \times 10^8$	$P_{calc} \times 10^8$
$^6H_{11/2}$	203.47	162.48
$^6H_{9/2}$, $^6F_{11/2}$	660.83	663.99
$^6F_{9/2}$, $^6H_{7/2}$	259.52	315.46
$^6H_{5/2}$, $^6F_{7/2}$	261.05	284.77
$^6F_{5/2}$	155.19	141.14
$^6F_{3/2}$	27.86	26.61
$^4F_{9/2}$	22.72	22.19
$^4I_{15/2}$	50.18	57.79
$^4G_{11/2}$	16.58	6.56
$^4F_{7/2}$, $^4I_{13/2}$, $^4M_{21/2}$, $^4K_{17/2}$	211.60	256.99
$^4M_{19/2}$, $(^4P, {}^4D)_{3/2}$, $^6P_{5/2}$	249.12	204.42
$^4I_{11/2}$, $^6P_{7/2}$	294.40	271.19
$(^4M, {}^4I)_{15/2}$, $(^4F, {}^4D)_{5/2}$, $^4I_{9/2}$	37.66	29.92
$^4G_{9/2}$, $^6P_{3/2}$, $^4M_{17/2}$, $(^4G, {}^2F)_{7/2}$, $^4K_{15/2}$, $^4D_{1/2}$, $(^4D, {}^4G)_{5/2}$, $^4L_{19/2}$	246.46	154.88
$^4H_{13/2}$, $^4F_{3/2}$, $(^4K, {}^4L)_{13/2}$, $^4D_{7/2}$, $^4H_{11/2}$, $^4G_{9/2}$, $^4F_{5/2}$, $^4G_{11/2}$, $^4L_{17/2}$	163.74	
$(^4G, {}^4H)_{7/2}$, $^4K_{11/2}$, $(^4G, {}^4P)_{5/2}$, $^4G_{9/2}$	35.09	
$^4H_{7/2}$, $^4F_{3/2}$	9.66	
$(^2K, {}^2L)_{15/2}$, $(^4G, {}^4P)_{5/2}$, $(^4P, {}^4F)_{3/2}$	86.21	
$\Omega_2 \times 10^{20}$ [cm^2]		6.69 ± 0.70
$\Omega_4 \times 10^{20}$ [cm^2]		1.89 ± 0.30
$\Omega_6 \times 10^{20}$ [cm^2]		3.67 ± 0.32
rms $\times 10^7$		4.13

It means that the polarization effect [2] caused by the more tightly bonded water molecules in the acetate structure plays an important role in the enhancement of intensity.

Acknowledgement

References

[1] A. Mondry, K. Bukietyńska, *Inorg. Chim. Acta* **186**, 135 (1991).

[2] S.F. Mason, R.D. Peacock, B. Stewart, *Mol. Phys.* **30**, 1829 (1975).

[3] Ł.A. Asłanov, J.K. Abdulminev, M.A. Porai-Koshits, V.I. Ivanov, *Dokl. Akad. Nauk SSSR* **205**, 343 (1972).

[4] M.C. Favas, D.L. Kepert, B.W. Skelton, A.H. White, *J. Chem. Soc., Dalton Trans.*, 454 (1980).

[5] S. Ganapathy, V.P. Chacko, R.G. Bryant, M.C. Etter, *J. Am. Chem. Soc.* **108**, 3159 (1986).

[6] B.R. Judd, *Phys. Rev.* **127**, 750 (1962).

[7] G.S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962).

[8] W.T. Carnall, P.R. Fields, K. Rajnak, *J. Chem. Phys.* **49**, 4424 (1968).

[9] A. Mondry, K. Bukietyńska, in preparation.

[10] A. Mondry, P. Starynowicz, *J. Alloys Comp.* **225**, 367 (1995).

[11] J. Legendziewicz, G. Oczko, *Polyhedron* **10**, 1921 (1991).

[12] G. Oczko, J. Legendziewicz, *Mater. Chem. Phys.* **31**, 111 (1992).

[13] J. Legendziewicz, T. Głowiak, G. Oczko, Dao Cong Ngoan, *J. Less-Common Met.* **125**, 45 (1986).

[14] J. Legendziewicz, E. Huskowska, Gy. Argay, A. Waśkowska, *J. Less-Common Met.* **146**, 33 (1989).

[15] J. Legendziewicz, C. Szafrański, G. Oczko, B. Jeżowska-Trzebiatowska, *Bull. Acad. Pol. Sci., Chim.* **36**, 190 (1988).