Spectral intensities of holmium acetate single crystals

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Abstract

The absorption spectra of the triclinic ($P\bar{1}$) dimeric $Ho_2(CH_3COO)_6 \cdot 4H_2O$ compound were measured in single crystals along the *b* and *c* axes at 293, 118 and 4.5 K. Results of intensity analysis show that in comparison with other lanthanide carboxylate compounds Ω_2 Judd–Ofelt parameter values are distinctly higher, whereas Ω_4 and Ω_6 parameters are close to the values observed for other lanthanide carboxylates. These results are interpreted in terms of the polarization effect caused by the distinctly shorter Ln–O(H_2O) bond in this system in comparison with Ln–O(carboxylic) bond.

Introduction

The most common inner sphere lanthanide complexes are the compounds with carboxylic ligands. Several systems of this kind have been investigated spectroscopically both in crystals and solutions [1–6]. However, the spectral data for complexes with the simplest carboxylic ligands — acetates — are far from complete. The aim of this work was to determine the spectral properties of the heavy lanthanide acetate single crystals. These results should be very helpful in understanding better the spectral intensity correlations with structure and bonding of lanthanide carboxylic complexes.

The crystal structures of the light and heavy lanthanide acetates are different [7, 8]. The crystal structure of $Er_2(CH_3COO)_6 \cdot 4H_2O$ was determined by Porai-Koshits and co-workers [8] as $P\bar{1}$. This structure was refined by Favas *et al.* [9] for the Gd compound. These authors found that the Gd and Er acetates were isomorphic. Even for $Ho_2(CH_3COO)_6 \cdot 4H_2O$ same site symmetry was found (point group C_1). They discussed also the coordination polyhedra of these compounds. The heavy lanthanide acetates are dimeric species with two lanthanide metal atoms bridged by acetate oxygen atoms. The coordination number of each lanthanide atom is nine, through the three bidentate acetate groups, two water molecules and a bridging oxygen from one of the adjacent acetates.

Experimental

Ho_2O_3 (99.9% Merck) was dissolved in concentrated acetic acid and alkalized to pH = 4. The well shaped crystals of $Ho_2(CH_3COO)_6 \cdot 4H_2O$ were formed during very slow evaporation. They were X-ray checked and found to be isomorphic with erbium acetate. The concentration of Ho^{3+} ion in the crystals was determined complexometrically (5.081 M). Crystal density was measured by the flotation method in a chloroform/bromoform mixture ($d^{20} = 2.081$ g/cm^3). The refractive index (n_D) of investigated single crystals was 1.506.

Absorption spectra of the polished single crystals were measured along the *b* and *c* axes on a Cary 2300 (at 293 and 4.5 K) and a Beckman UV 5240 (at 293 and 118 K). The investigated spectral range was 230–1260 nm. It has to be pointed out that the measured crystals were well transparent and the base line was not much different from that displayed by the Ho^{3+} solution spectra with a large acetate ligand excess.

According to the Judd–Ofelt theory [10, 11], the oscillator strengths of 4f–4f transitions can be expressed as

$$P = \frac{8\pi'^2 mc\sigma}{3h(2J+1)} \chi \sum_{\lambda=2,4,6} \Omega_\lambda (\mathrm{f}^N \Psi_J \| U^{(\lambda)} \| \mathrm{f}^N \Psi'_{J'})^2 \qquad (1)$$

where σ is the wave number of the $\mathrm{f}^N \Psi_J \rightarrow \mathrm{f}^N \Psi'_{J'}$ transition, J is the total quantum number related to the ground state; $\chi = (n^2+2)^2/9n$, n is the refractive index; $U^{(\lambda)}$ are matrix elements of the unit tensor operator calculated by Carnall *et al.* [12]; $\mathrm{f}^N \Psi_J$, $\mathrm{f}^N \Psi'_{J'}$ are the initial and final states of the particular electronic transition; Ω_λ are three parameters estimated from the experimental data.

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Results and discussion

The absorption spectra of $Ho_2(CH_3COO)_6 \cdot 4H_2O$ at liquid He temperatures were measured in the single crystal. The spectra of this single crystal were also measured at the 293 and 118 K. We were only able to measure the more intense bands because the crystal was not thick enough. The good agreement between the number of crystal field components found in this spectrum and that given by the group theory for Ho^{3+} crystals with such a low symmetry, ensured us that the Ho^{3+} ion occupied only one position in this crystal lattice.

Detailed results of the spectral intensities of the holmium acetate spectra are presented in Table 1. The oscillator strength values for holmium acetate solution (1:20) and for single crystal spectra along the *c* and *b* axes at 293, 118 and 4.5 K are also collected. For comparison purposes spectral data for Ho^{3+} aquoion spectra in solution are included.

The Judd–Ofelt Ω_λ parameter values evaluated from these data for the solution and single crystal spectra at 293 K are also listed in Table 1. These parameters were computed from the same set of band intensities for single crystal and solution spectra. Some intensities of the crystal and solution spectra at temperatures over 4.5 K undoubtedly derive from the transitions between higher crystal field components of ground electronic level and appropriate components of excited electronic level (hot transitions). It is particularly evident for the ${}^5I_8 \rightarrow {}^5F_3$ transition where the low *J* number 3 facilitates this observation and at room temperature more than half the intensities for that transition derives from the higher Stark components of the ground state (Table 1).

Application of the Judd–Ofelt method to single crystals such as biaxial holmium acetate requires a definite procedure. According to Lomheim and Shazer [13] the best way is to consider the averaged intensities measures separately along the *a*, *b* and *c* axes. However, the shape and dimensions of our single crystals limited our measurements to those along the *b* and *c* axes. We have found that absorption band intensities vary no more than 10% along these two crystallographic directions.

As was reported in our previous papers [5, 6], the intensities of holmium acetate solution spectrum did not change above some defined Ln:L ratio. So it could be assumed that in solutions with a large ligand excess (1:20) the thermodynamically stable species are predominant. Thus, when in solution, one species with a similar structure as in the solid state is present; the hypersensitive transition (${}^5I_8 \rightarrow {}^5G_6$, ${}^5F_1$ for Ho^{3+} ion) should be similar as well. This was supported by the Ω_λ parameter values (Table 1), where for the solution in comparison with the solid state, only a slight increase of Judd–Ofelt parameter values was observed.

The transition intensities of the single crystal spectra decrease in a significant way when the temperature is decreased. However this decrease ranges for the individual transitions from 60% for the hypersensitive ${}^5I_8 \rightarrow {}^5G_6$, ${}^5F_1$ transition to 8% for the magnetically allowed ${}^5I_8 \rightarrow {}^3K_8$ transition. These results could be useful for estimation of the vibronic mechanism contribution to intensities of 4f–4f transitions. We cannot tell, however, which part of intensity changes is related to the vibronic mechanism, because of the high Ho^{3+} *J* manifold at both ground and excited electronic states. Unfortunately, we failed to find a particular band which could be applied for such an estimation. Holmium acetate is characterized by a high Ω_2 parameter value, in comparison with other holmium carboxylate complexes [2, 4]. In this group of compounds drastic differences between the mode of the carboxylic group coordination are observed [4, 8, 9] so we should be very careful in making comparisons. The compound whose structure could be helpful in understanding the spectral properties of holmium acetate is the holmium glycinate complex studied by Legendziewicz *et al.* [1–3]. The crystal structure of monoclinic (C_c) Ho and Dy glycinates has been determined precisely [3]. Triclinic $P\bar{1}$ holmium glycinate was found to be isomorphic with the appropriate Nd compound [1].

All carboxylic groups in holmium acetate and holmium glycinate complexes are coordinated with the holmium ion in the same way as described above for holmium acetate. In both cases two water molecules complete the coordination sphere of each holmium cation. The Ω_2 parameter value for Ho acetate differs significantly from that of the holmium glycinato perchlorates, whereas the Ω_4 and Ω_6 values are close to each other (Table 2). (For comparison with ref. 2 the Ω_λ values for the acetates were recalculated to τ_λ.)

These spectral intensity differences cannot be explained by the different polarizability of Ln–O-(carboxyl) bonding because the symmetry and bond length in both compounds are similar (Table 3).

If we look carefully at the coordination polyhedra of both compounds one main difference between them can be stated. In the holmium acetate crystal the Ho–O(H_2O) bonds are distinctly shorter than the Ho–O(carboxyl) bonds. The opposite situation is observed for the holmium glycinato perchlorates, where the Ln–O(H_2O) bonds are slightly longer than the Ln–O(carboxyl) bonds.

It means that these distinctly shorter Ln–O(H_2O) bonds could be responsible for the particularly high

TABLE 1. Oscillator strength values (P_{exp}, P_{calc}) and Ω_λ parameter values of holmium aquoion, holmium acetate complex in solution and of $Ho_2(CH_3COO)_6 \cdot 4H_2O$ single crystal

S′L′J′	Spectral region (nm)	Solutions $c_{Ho^{3+}} = 0.02014$ M				Single crystals $c_{Ho^{3+}} = 5.0281$ M					
		Aquoion		$c_{Ac^-} = 0.4001$ *M*		A			B		
						$T = 293$ K		$T = 118$ K	$T = 293$ K		$T = 4.5$ K
		$P_{exp} \times 10^8$	$P_{calc} \times 10^8$	$P_{exp} \times 10^8$	$P_{calc} \times 10^8$	$P_{exp} \times 10^8$	$P_{calc} \times 10^8$	$P_{exp} \times 10^8$	$P_{exp} \times 10^8$	$P_{calc} \times 10^8$	$P_{exp} \times 10^8$
$^5D_2$, $(^3F, ^5D)_4$	237–246					220.32			168.17^a		
$^5D_3$, $(^3D, ^5D, ^3P)_1$, $^3I_6$, $^3M_9$, $^3I_5$	247–257					107.15			81.07^a		
$^3F_4$, $^3I_7$, $^3L_7$, $(^3P, ^1D)_2$	257–266					94.69			86.16^a		
$(^3H, ^3G)_5$, $^1L_8$, $^3F_2$, $(^3H, ^5D, ^1G)_4$, $^3P_0$	269–282	255.57	237.56	206.86	221.09	200.99	200.43		179.78^a	178.67	
$(^3F, ^5G)_3$, $(^5G, ^5D, ^3G)_4$	282–291	399.39	424.55	330.24	391.03	324.35	354.61		200.72^a	215.33	
$^3L_8$, $^3M_{10}$	291–300								80.35^a	95.69	
$^3K_6$, $(^3F, ^3H, ^3G)_4$	328–339	88.91	93.92	56.32	90.98	56.40	82.18	54.79	63.14^a	73.44	
$^3L_9$, $^5G_3$	340–352	83.65	130.69	80.79	139.72	81.32	119.54	97.78	78.73^b	106.31	
$(^5F, ^3F, ^5G)_2$, $^3H_6$, $(^5G, ^3H)_5$	354–370	300.56	263.94	648.58	527.35	586.64	492.27	528.80	567.79^b	450.79	337.04^b
$^3K_7$, $^5G_4$	376–403	82.48	69.21	76.84	68.79	66.53	59.43	74.79	91.52^a	52.82	
$(^5G, ^3G)_5$	411–428	320.64	297.76	321.38	277.60	266.59	251.42	267.42	217.63^b	224.34	104.67^b
$^3G_6$, $^5F_1$	440–464	623.16	628.34	2147.63	2216.31	2099.20	2114.48	1643.48	1935.27^a	1955.02	782.46^b
$^3K_8$	464–471	64.58	105.62	55.67	114.37	45.13	98.80	61.42	42.08^a		38.90^b
									104.13	153.91	
$^5F_2$	471–479	99.22	105.29	67.89	91.37	59.19	76.20	61.45	62.05^a		33.69^b
$^5F_3$	479–498	192.03	185.06	173.88	160.59	140.28	132.64	142.68	128.43^a		41.09^b
$^5F_4$, $^5S_2$	530–555	603.86	555.25	485.84	488.49	411.00	410.71	438.23	353.22^b	116.17	257.24^b
$^5F_5$	630–663	321.09	384.61	381.42	343.69	308.12	293.13	335.98	271.15^b	362.93	141.89^b
										258.82	
$^5I_5$	878–910					15.06		11.60			
$^5I_6$	1106–1260					103.70		83.10	109.62^a		
$\Omega_2 \times 10^{20}$ (cm^2)		0.45 ± 0.19		6.81 ± 0.29		5.85 ± 0.18			5.45 ± 0.21		
$\Omega_4 \times 10^{20}$ (cm^2)		3.06 ± 0.23		2.85 ± 0.21		2.30 ± 0.23			2.05 ± 0.26		
$\Omega_6 \times 10^{20}$ (cm^2)		3.42 ± 0.23		2.97 ± 0.21		2.17 ± 0.23			1.91 ± 0.24		
r.m.s. $\times 10^7$			3.66		5.59		3.99			4.45	

A: spectra measured on a Beckman UV 5240 spectrophotometer along the *c* axis; crystal length $l = 0.0225$ cm. B: spectra measured on a Cary 2300 spectrophotometer along the *b* axis; $^a l = 0.105$ cm, $^b l = 0.018$ cm.

TABLE 2. Structures and intensity parameters of Ho acetate and glycinate

Compound	Space group	Coordination number	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
$Ho_2(CH_3COO)_6 \cdot 4H_2o$	$P\bar{1}$	9	8.51 ± 0.26	3.34 ± 0.33	3.16 ± 0.33
$Ho(Gly)_3(ClO_4)_3 \cdot 5H_2O$	$P\bar{1}$	9	2.69 ± 0.46	4.08 ± 0.52	4.18 ± 0.59

TABLE 3. Bond lengths of Er acetate and Ho glycinate

Compound	Ln–O(carboxyl) (Å) averaged	Ln–O(H_2O)	Reference
$Er_2(CH_3COO)_6 \cdot 4H_2O$	2.44	2.35	8
(isomorphous with Ho)			3
$Ho(Gly)_3(ClO_4)_3 \cdot 3H_2O$	2.44	2.49	

Ω_2 (τ_2) parameter values for the holmium acetate single crystal in comparison with holmium glycinato perchlorates. This fact is a good confirmation of the role of the dynamic coupling mechanism [14] in spectral intensities of the f–f transition in lanthanide complexes. It should be pointed out, that it is a rather rare example of a lanthanide low symmetry compound, where the polarization effect could be related to the determined Ln–O(H_2O) bonds.

References

1 J. Legendziewicz, E. Huskowska, A. Waśkowska and Gy. Argay, *Inorg. Chim. Acta, 92* (1984) 151.

2 J. Legendziewicz, E. Huskowska, Gy. Argay and A. Waśkowska, *Inorg. Chim. Acta, 95* (1984) 57.

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

4 J. Legendziewicz and E. Huskowska, *Excited States of Transition Elements,* World Scientific Publ., Singapore, 1989, p. 228 and refs. therein.

5 K. Bukietyńska and A. Mondry, *Bull. Acad. Pol. Sci. Chim., 28* (1980) 215.

6 K. Bukietyńska and A. Mondry, *Inorg. Chim. Acta, 72* (1983) 109.

7 G. G. Sadikov, G. A. Kukina and M. A. Porai-Koshits, *Zh. Strukt. Khim., 8* (1967) 551.

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

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

10 B. R. Judd, *Phys. Rev., 127* (1962) 750.

11 G. S. Ofelt, *J. Chem. Phys., 37* (1962) 511.

12 W. T. Carnall, P. R. Fields and K. Rajnak, *J. Chem. Phys., 49* (1968) 4424.

13 T. S. Lomheim and L. G. De Shazer, *Phys. Rev. B, 20* (1979) 4343.

14 S. F. Mason, R. D. Peacock and B. Stewart, *Mol. Phys., 30* (1975) 1829.