

## Spectroscopic Properties of Ho<sup>3+</sup> Complexes with Dipicolinic Acid in Solution and Single Crystals

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### Abstract

The absorption spectra of hexagonal Na<sub>3</sub>[Ho(dpa)<sub>3</sub>]·NaClO<sub>4</sub>·10H<sub>2</sub>O single crystals were measured in the region 300–2100 nm along the *z* axis at temperature range 293–118 K. Probabilities of f–f transitions were analysed on the basis of the Judd–Ofelt theory. The single crystal results were compared to those of the Ho<sup>3+</sup>–dpa system in aqueous solutions for different molar ratios of Ho<sup>3+</sup>:dpa. The good correspondence between the spectra of [Ho(dpa)<sub>3</sub>]<sup>3–</sup> compounds in solution and in the single crystal suggests analogy between both coordination polyhedra. These results also suggest that the mechanism of the hypersensitive transition is vibronic as well.

### Introduction

In our recent papers [1, 2] we have studied the influence of Ln–N bond formation on the spectral properties of lanthanide polyaminoacid complexes. In these compounds, however, only a weak Ln–N bond exists. For the present studies the system of lanthanide pyridine-2,6-dicarboxylate (dipicolinate or dpa) was chosen because of the existence of a stronger Ln–N bond. Detailed absorption properties of holmium dipicolinates were studied both in solution and in single crystals. Recently, Richardson *et al.* [3, 4] and Davis [5] have studied the spectral properties of the Ho<sup>3+</sup>–dpa system in solution with a molar ratio of Ho<sup>3+</sup>:dpa equal to 1:3.

The special aim in this work was to investigate the monomeric character of species existing in aqueous solution [6–12], as well as the particular stability of 1:3 (Ln<sup>3+</sup>:dpa) species [13]. This coordination mode is also preserved in the solid phase and from X-ray measurements of single crystals it was found that lanthanide complexes from Ce–Dy are triclinic [14]. However, some differences between space groups of crystals are found. For heavy lanthanide complexes from Ho–Lu different crystal lattices (orthorhombic, monoclinic and hexagonal) are observed [15–17]. These changes in lattice

structures give significant changes in Ln–N bond distances (with the same coordination number 9 preserved). In all cases, however, the Ln<sup>3+</sup> ions are well isolated from each to other.

Lanthanide dipicolinates exhibit also optical activity which gives an additional opportunity for studying their structural and optical properties [18–20].

### Experimental

#### Reagents

Stock solutions of Ho<sup>3+</sup> and La<sup>3+</sup> perchlorates were prepared from 99.9% lanthanide oxides (Merck). Concentrations of the lanthanide ions were determined complexometrically. The stock solution of dpa was prepared using NaOH with ratio dpa:NaOH = 1:2. A carbonate free NaOH solution was used to adjust the pH of the ligand solutions to appropriate values.

Crystals of Na<sub>3</sub>[Ho(dpa)<sub>3</sub>]·NaClO<sub>4</sub>·10H<sub>2</sub>O were prepared from aqueous solution of the holmium perchlorate and disodium dipicolinate in the molar ratio 1:3. The pH of the resulting solution was about 5. Single crystals with the habit of hexagonal prisms, were grown by slow evaporation at room temperature.

The concentration of Ho<sup>3+</sup> ion in the crystals was determined complexometrically (1.88569 M).

Crystal density was measured by flotation method in a mixture of chloroform and bromoform (*d*<sup>20</sup> = 1.96 g/cm<sup>3</sup>).

The refractive index (*n*<sub>D</sub>) of investigated single crystals was 1.496 and of the solution medium 1.33.

#### Measurements and Calculations

Solution spectral measurements were made on a Cary 14 spectrophotometer within the region 300–1300 nm. The concentration of Ho<sup>3+</sup> ion was 1.001 × 10<sup>–2</sup> M and the concentration of ligand (dpa) varied from 1.077 × 10<sup>–2</sup> to 3.959 × 10<sup>–2</sup> M. As reference solutions appropriate La<sup>3+</sup> solutions with the same metal and ligand concentration as in the measured sample were used. It was necessary because

of the high absorption of the ligand particularly in the near UV region. All the measured solutions were prepared with the same ionic strength (0.5 M NaClO<sub>4</sub>). The pH of solutions were measured on a Radelkis pH-meter (with an accuracy of ±0.05 pH unit).

Absorption spectra of single crystals were recorded at the spectral range 300–2100 nm on a Cary 14 spectrophotometer at room temperature and on a Beckman UV 5240 spectrophotometer at 293, 223, 193 and 118 K. All spectra were measured along the *z* axis because of the well developed (001) face. Experimental oscillator strength values of 4*f*–4*f* transitions for solutions and single crystals were obtained by a graphic integration of the area under the absorption curves after appropriate correction of the base line (program ICH 30).

According to the Judd–Ofelt theory [21, 22], the oscillator strengths of 4*f*–4*f* transitions can be expressed as

$$P = \frac{8\pi^2 m c \sigma}{3h(2J+1)} \chi \sum_{\lambda=2,4,6} \Omega_{\lambda} (f_{\psi J}^N \parallel U^{(\lambda)} \parallel f_{\psi' J'}^N)^2 \quad (1)$$

where  $\sigma$  is the wave number of  $f_{\psi J}^N \rightarrow f_{\psi' J'}^N$  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.* [23],  $f_{\psi J}^N$ ,  $f_{\psi' J'}^N$  are the initial and final states of the particular electronic transition,  $\Omega_{\lambda}$  are three parameters esti-

mated from the experimental data. These parameters involve the radial parts of the  $f^N$  wave functions, the wave functions of perturbing configurations and the interaction between the central ion and the immediate environment.

Equation (1) is applicable only to unpolarized spectra obtained for optically isotropic samples. Furthermore, it assumes that all the crystal sublevels of the initial ( $f_{\psi J}^N$ ) state are equally populated and it neglects crystal field induced mixing between different multiplets.

## Results and Discussion

It has been reported from NMR studies [10–12] that in aqueous solution lanthanide ions form [Ln(dpa)(H<sub>2</sub>O)<sub>6</sub>]<sup>+</sup>, [Ln(dpa)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>−</sup> and [Ln(dpa)<sub>3</sub>]<sup>3−</sup> species. Lanthanide complexes with one or two molecules of dpa are stable in an acidic pH range only. The strong and stable complexes in solution are formed with a Ln<sup>3+</sup>:dpa ratio equal to 1:3.

The spectra of the Ho<sup>3+</sup>–dpa system were examined for different M:L ratios (1:1, 1:2 and 1:3). The latter were investigated within a broad pH region. The most sensitive transition for the changes of the holmium ion immediate environment is the hypersensitive transition <sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>6</sub> (Fig. 1). Above pH 5.60 the constant oscillator strength values of this transition for the [Ho(dpa)<sub>3</sub>]<sup>3−</sup> complex are registered ( $c_{\text{Ho}^{3+}} = 1.001 \times 10^{-2}$  M,  $c_{\text{dpa}} = 3.006 \times 10^{-2}$  M:

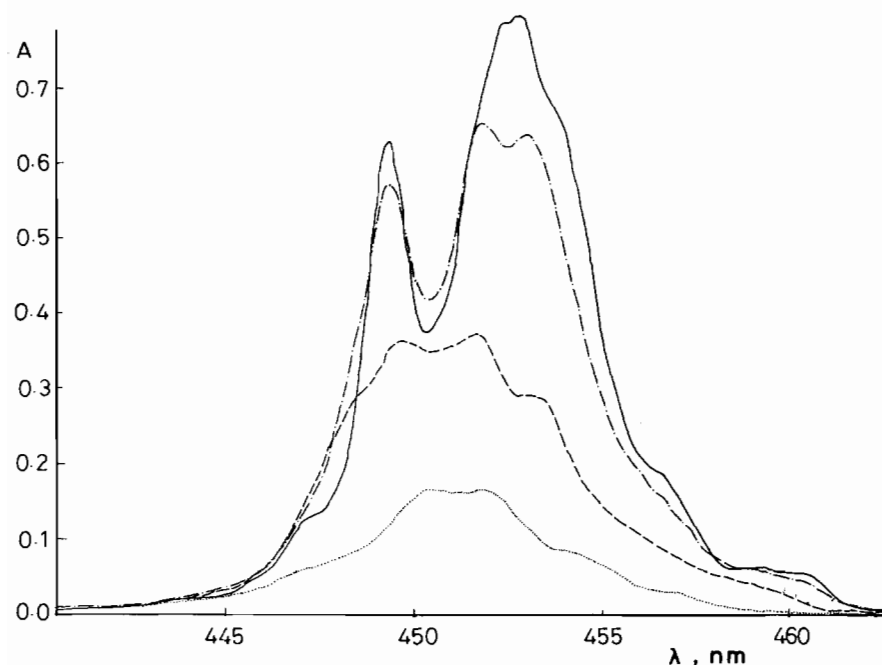


Fig. 1. Effect of dpa concentration on hypersensitive transition <sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>6</sub> in absorption spectrum of Ho<sup>3+</sup> ion for Ho<sup>3+</sup>: dpa ratios of 1:*n* ( $c_{\text{Ho}^{3+}} = 1.001 \times 10^{-2}$  M,  $l = 4$  cm): 1:0, ..... (pH = 3.39); 1:1, - - - (pH = 2.93); 1:2, - · - (pH = 3.17); 1:3, — (pH = 5.89).

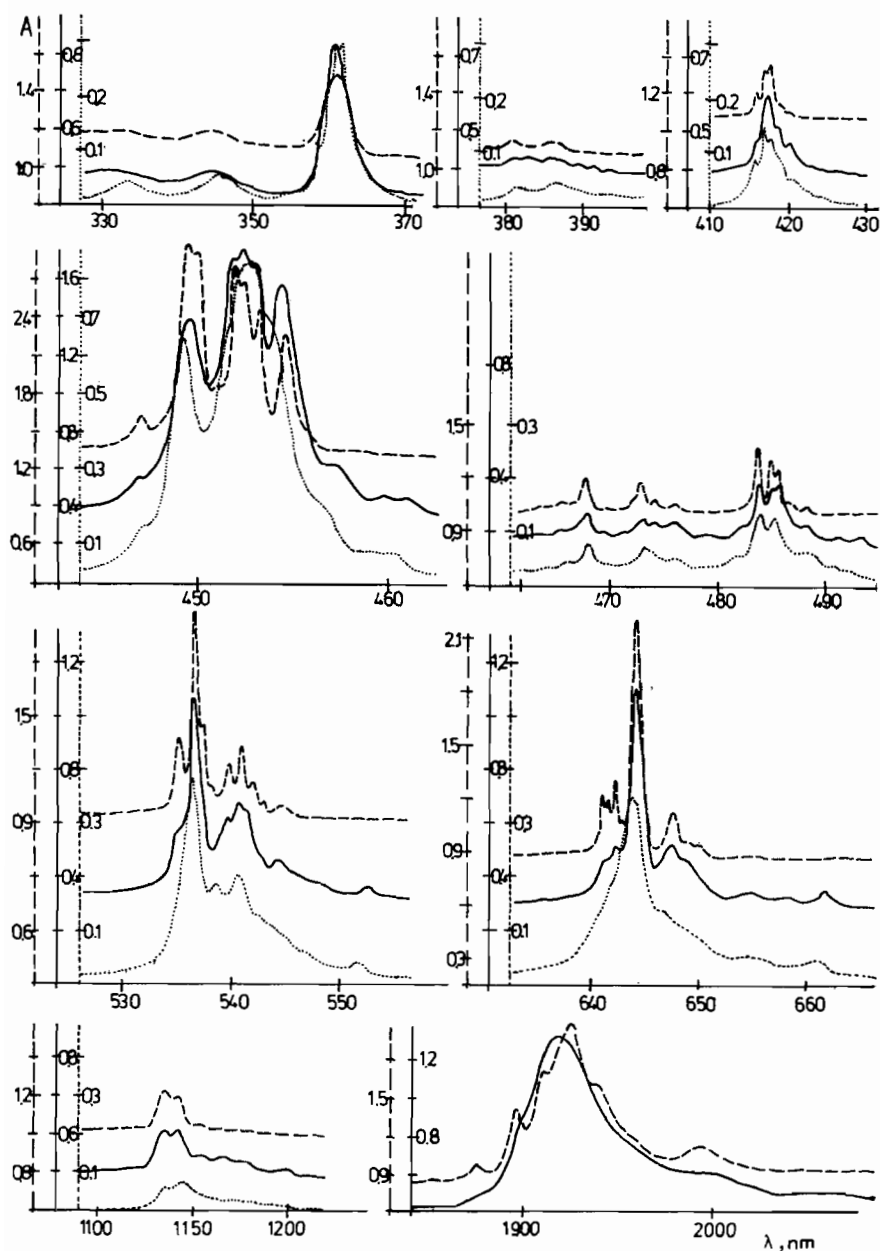


Fig. 2. Absorption spectra of the  $[\text{Ho}(\text{dpa})_3]^{3-}$  complex in solution (.....) and of a  $\text{Na}_3[\text{Ho}(\text{dpa})_3] \cdot \text{NaClO}_4 \cdot 10\text{H}_2\text{O}$  single crystal at 293 (—) and 118 (---) K. (For the solution  $c_{\text{Ho}^{3+}} = 1.001 \times 10^{-2}$  M,  $l = 4$  cm and for the single crystal  $c_{\text{Ho}^{3+}} = 1.88569$  M,  $l = 0.031$  cm.)

pH = 4.64,  $P = 2510.19 \times 10^{-8}$ ; pH = 5.24,  $P = 2504.78 \times 10^{-8}$ ; pH = 5.60,  $P = 2577.75 \times 10^{-8}$ ; pH = 5.89,  $P = 2565.66 \times 10^{-8}$ ). We can assume therefore that for this stable 1:3 species the environment of the  $\text{Ln}^{3+}$  ion in solution is similar to that in the solid state. The absorption spectra of the  $[\text{Ho}(\text{dpa})_3]^{3-}$  complex in aqueous solution and in the single crystal at 293 and 118 K are shown in Fig. 2. Judd–Ofelt intensity parameters ( $\Omega_\lambda$ ) examined

both for solutions and single crystals were evaluated from the set of all available 4f–4f transitions measured with a Cary 14 spectrophotometer. Results are collected in Table 1.

Detailed characteristics of transitions are included in Table 2 where oscillator strength values of 4f–4f transitions for the single crystal at different temperatures (293, 223, 173 and 118 K) measured with a Beckman UV 5240 spectrophotometer are also collected.

TABLE 1. Oscillator strength values ( $P_{\text{exp}}$ ,  $P_{\text{calc}}$ ) and  $\Omega_\lambda$  parameter values for holmium dipicolinates in solution and single crystals

| $c_{\text{dpa}} \times 10^2$ [M]             | $c_{\text{Ho}^{3+}} = 1.001 \times 10^{-2}$ M |                               |                              |                               |                              |                               |  |
|--|---|-------------------------------|------------------------------|-------------------------------|------------------------------|-------------------------------|--|
|  | 0<br>aquoion                                  |                               |                              |                               |                              |                               |  |
| pH   | 3.39  |                               |                              |                               |                              |                               |  |
| No. of absorption band                       | $P_{\text{exp}} \times 10^8$                  | $P_{\text{calc}} \times 10^8$ | $P_{\text{exp}} \times 10^8$ | $P_{\text{calc}} \times 10^8$ | $P_{\text{exp}} \times 10^8$ | $P_{\text{calc}} \times 10^8$ |  |
| 1  | 88.56   | 99.98                         | 86.27                        | 108.78                        | 83.16                        | 119.46                        |  |
| 2  | 97.77   | 127.63                        | 94.91                        | 153.85                        | 110.38                       | 161.63                        |  |
| 3  | 317.43  | 265.07                        | 509.32                       | 417.42                        | 736.50                       | 517.91                        |  |
| 4  | 86.37   | 69.60                         | 112.33                       | 79.75                         | 108.80                       | 83.60                         |  |
| 5  | 317.57  | 319.12                        | 343.76                       | 341.90                        | 376.27                       | 373.27                        |  |
| 6  | 615.63  | 623.71                        | 1374.64                      | 1389.40                       | 1896.59                      | 1933.97                       |  |
| 7  | 46.58   | 104.52                        | 71.64                        | 125.32                        | 84.22                        | 132.89                        |  |
| 8  | 103.16  | 103.19                        | 109.02                       | 115.21                        | 94.97                        | 114.09                        |  |
| 9  | 210.57  | 181.09                        | 211.94                       | 202.39                        | 243.95                       | 201.01                        |  |
| 10   | 548.56  | 553.36                        | 629.99                       | 612.79                        | 600.44                       | 619.82                        |  |
| 11   | 387.41  | 390.44                        | 393.44                       | 427.60                        | 396.19                       | 440.44                        |  |
| 12   | 254.77  |                               |                              |                               |                              |                               |  |
| 13   |   |                               |                              |                               |                              |                               |  |
| rms $\times 10^7$                            | 3.24  |                               | 4.77                         |                               | 8.71                         |                               |  |
| $\Omega_2 \times 10^{20}$ (cm <sup>2</sup> ) | 0.36 $\pm$ 0.20                               |                               | 3.14 $\pm$ 0.30              |                               | 5.14 $\pm$ 0.55              |                               |  |
| $\Omega_4 \times 10^{20}$ (cm <sup>2</sup> ) | 2.28 $\pm$ 0.30                               |                               | 3.52 $\pm$ 0.44              |                               | 3.84 $\pm$ 0.81              |                               |  |
| $\Omega_6 \times 10^{20}$ (cm <sup>2</sup> ) | 3.35 $\pm$ 0.21                               |                               | 3.74 $\pm$ 0.31              |                               | 3.71 $\pm$ 0.57              |                               |  |

<sup>a</sup> $l$  = crystal length.

### Solutions

Absorption spectra of solutions with  $\text{Ho}^{3+}:\text{dpa}$  ratios of 1:1 and 1:2 demonstrate both intensity and shape changes of the hypersensitive  $^5\text{I}_8 \rightarrow ^5\text{G}_6$  transition (Table 1, Fig. 1). It should be pointed out, however, that the energies of the absorption maxima for these systems are constant and the same as for aquoion. In comparison with aquoion significant changes of the  $\Omega_2$  parameter values are observed for these complex species, but  $\Omega_4$  and  $\Omega_6$  remain constant at the limit of estimation error. This can be explained by the existence in these solutions of some equilibria between the aquoion and the relatively unstable complex species. These equilibria are typical for the lower pH range where the real concentration of the deprotonated ligand is even lower than can be estimated from the M:L ratios.

Systems with an excess of dpa ligand with the ratio of  $\text{Ho}^{3+}:\text{dpa} \geq 1:3$  and  $\text{pH} \geq 5.6$  are characterised by the constant oscillator strength values of the hypersensitive transition. These values are significantly higher than for 1:1 and 1:2 systems. Both, shape and intensity distribution in the band of the hypersensitive transition are changed. The results collected in Table 1 indicate that even in this case,  $\Omega_2$  parameter values are distinctly higher both in comparison with the aquoion and with the species considered previously. In this case, however, higher

$\Omega_6$  parameter values are also observed. Among 4f–4f transitions of the  $\text{Ho}^{3+}$  ion, the highest values of the  $\text{U}^{(6)}$  matrix element are for transitions to the states:  $^5\text{F}_4$ ,  $^5\text{S}_2$  and  $^5\text{F}_5$  [23].

Generally, for systems containing ligands with a N donor atom [1–3, 24] relatively high oscillator strength values for these transitions are observed. Some authors assume that polarizability of the ligand can also influence the  $\Omega_6$  parameter value [25].

### Single Crystals

Results of single crystal measurements are presented in Tables 1 and 2. Unfortunately these measurements were taken on two different instruments (Cary 14 and Beckman UV 5240) so we cannot expect full correspondence between the results. As seen from Table 1 and Fig. 2 the most significant difference for the complex  $[\text{Ho}(\text{dpa})_3]^{3-}$  in solution and in the single crystal is observed for the hypersensitive transition. The increase of this transition intensity by about 20% and a small shift of the absorption maximum to the UV region in the crystal in comparison with solution can be caused by lattice effects. Such effects should be averaged in solution.

Studies of the lanthanide spectra intensities at different temperatures are complicated because, except for the  $\text{Eu}^{3+}$  ion, the ground J states are split by the crystal field into a number of levels

|                              |                               |                              |                               |                              |                               | $c_{\text{Ho}^{3+}} = 1.88569 \text{ M}$ |                              |                               |
|------------------------------|-------------------------------|------------------------------|-------------------------------|------------------------------|-------------------------------|--|------------------------------|-------------------------------|
| 3.959                        |                               | 3.959                        |                               | 3.959                        |                               | single crystals                          |                              |                               |
| 3.33                         |                               | 7.10                         |                               | 11.17                        |                               |  |                              |                               |
| $P_{\text{exp}} \times 10^8$ | $P_{\text{calc}} \times 10^8$ | $P_{\text{exp}} \times 10^8$ | $P_{\text{calc}} \times 10^8$ | $P_{\text{exp}} \times 10^8$ | $P_{\text{calc}} \times 10^8$ | $l^a$<br>(cm)                            | $P_{\text{exp}} \times 10^8$ | $P_{\text{calc}} \times 10^8$ |
| 89.97                        | 124.20                        | 92.74                        | 122.12                        | 81.83                        | 124.39                        | 0.0835                                   | 85.68                        | 126.30                        |
| 113.04                       | 183.62                        | 151.06                       | 230.94                        | 168.33                       | 227.15                        | 0.0835                                   | 172.92                       | 232.19                        |
| 721.27                       | 556.13                        | 917.40                       | 687.88                        | 905.20                       | 680.24                        | 0.0410                                   | 917.67                       | 804.96                        |
| 104.67                       | 92.94                         | 137.02                       | 108.24                        | 130.35                       | 107.64                        | 0.0835                                   | 135.61                       | 109.78                        |
| 381.51                       | 386.13                        | 360.55                       | 368.27                        | 384.03                       | 377.35                        | 0.0835                                   | 391.50                       | 378.90                        |
| 2000.26                      | 2027.52                       | 2586.39                      | 2624.81                       | 2552.42                      | 2590.31                       | 0.0150                                   | 3287.68                      | 3305.18                       |
| 73.95                        | 149.22                        | 99.63                        | 182.46                        | 102.11                       | 180.61                        | 0.0410                                   | 63.76                        | 186.22                        |
| 108.97                       | 131.41                        | 123.62                       | 163.58                        | 128.04                       | 161.38                        | 0.0410                                   | 104.86                       | 156.62                        |
| 268.19                       | 231.58                        | 324.65                       | 288.14                        | 349.55                       | 284.25                        | 0.0410                                   | 308.44                       | 275.75                        |
| 696.66                       | 700.90                        | 828.11                       | 829.94                        | 809.65                       | 825.17                        | 0.0150                                   | 844.41                       | 802.22                        |
| 466.23                       | 486.73                        | 504.30                       | 545.76                        | 495.67                       | 545.85                        | 0.0410                                   | 473.23                       | 535.85                        |
|                              |                               |                              |                               | 339.60                       |                               | 0.0835                                   | 246.11                       |                               |
|                              |                               |                              |                               |                              |                               | 0.0190                                   | 897.31                       |                               |
|                              | 7.27                          |                              | 9.61                          |                              | 9.50                          |  |                              | 7.36                          |
|                              | 5.35 ± 0.46                   |                              | 7.72 ± 0.60                   |                              | 7.54 ± 0.60                   |  |                              | 9.27 ± 0.42                   |
|                              | 3.97 ± 0.67                   |                              | 3.80 ± 0.89                   |                              | 3.91 ± 0.88                   |  |                              | 3.49 ± 0.61                   |
|                              | 4.28 ± 0.47                   |                              | 5.32 ± 0.63                   |                              | 5.25 ± 0.62                   |  |                              | 4.55 ± 0.43                   |

(Stark components) whose populations are also changing with temperature. The ground state of hexagonal Ho<sup>3+</sup> crystals splits into 11 components [26]. So, it is difficult to say anything about the temperature dependence of intensities from the ground state <sup>5</sup>I<sub>8</sub> to the excited states, particularly for these transitions which are also a combination of several terms. The most significant change of the intensity of 4f–4f ‘simple’ transitions occurs for the hypersensitive transition <sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>6</sub>. The intensity of this transition decreases by about 20% from 293 to 118 K. For d-metal complexes where the intensity is gained by a vibronic mechanism, a reduction of spectral intensities by some 30–40% should be expected [27]. On the other hand, Peacock [28] calculated that relative intensities of <sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>6</sub> and <sup>5</sup>I<sub>8</sub> → <sup>5</sup>F<sub>4</sub> transitions of hexagonal Ho<sup>3+</sup> crystals in LaCl<sub>3</sub> (*D*<sub>3h</sub> symmetry) [29] should increase at a similar temperature range by 12 and 16%, respectively. The oscillator strength values for the transitions to the remaining excited states of <sup>5</sup>F<sub>3</sub>, <sup>5</sup>F<sub>5</sub>, <sup>5</sup>I<sub>6</sub> and <sup>5</sup>I<sub>7</sub> are changed by about ±10% with the temperature variation. As a result some intensity changes of allowed transitions between them can be expected.

The study on spectroscopic properties of the same compound [Ho(dpa)<sub>3</sub>]<sup>3-</sup> in solution and in the single crystal indicates that the mechanism of the only hypersensitive transition is vibronic.

The existence of the very stable [Ho(dpa)<sub>3</sub>]<sup>3-</sup> complex in solution is clearly seen from its spectroscopic properties. For this complex, in comparison with the aquoion, a very significant change of hypersensitive transition intensity is observed. Some intensity changes are also observed for other f–f transitions (particularly at IR range) which are also reflected in the change of the Ω<sub>6</sub> parameter value. Some small but systematic nephelauxetic effect for all transitions can also be observed in comparison with the aquoion. The good correspondence between spectra of the [Ho(dpa)<sub>3</sub>]<sup>3-</sup> complex in solution and in the single crystal suggests a similarity between both coordination polyhedra. It can be assumed, therefore, that also in solution the intensity of the hypersensitive transition is partially of vibronic origin.

We can also conclude on the symmetry and bonding of less stable species than the 1:3 of holmium complexes with dpa. The shift of <sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>6</sub> absorption maxima of the complexes 1:1 and 1:2 towards the UV region with regard to the complex 1:3 assuming the same coordination number 9 (NMR results [10–12]) would be given by longer bonding distances. This conclusion is in agreement with X-ray results of Na<sub>3</sub>[Yb(dpa)<sub>3</sub>]·NaClO<sub>4</sub>·10H<sub>2</sub>O [17] where the bonding lengths of Yb–O (2.38 Å) and Yb–N (2.43 Å) are shorter in comparison with

TABLE 2. Oscillator strength values ( $P_{\text{exp}}$ ) of  $\text{Na}_3[\text{Ho}(\text{dpa})_3] \cdot \text{NaClO}_4 \cdot 10\text{H}_2\text{O}$  single crystals at different temperatures<sup>a</sup>

| No. of the absorption band                   | Spectral region (nm) | Excited states   | T = 293 K                    |                               | T = 223 K                    |                              | T = 193 K                    |                              | T = 118 K |  |
|--|----------------------|--|------------------------------|-------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|-----------|--|
|  |                      |  | $P_{\text{exp}} \times 10^8$ | $P_{\text{calc}} \times 10^8$ | $P_{\text{exp}} \times 10^8$ | $P_{\text{exp}} \times 10^8$ | $P_{\text{exp}} \times 10^8$ | $P_{\text{exp}} \times 10^8$ |           |  |
| 1  | 328–339              | $^3\text{K}_6, (^3\text{F}_1, ^3\text{H}_1, ^3\text{G})_4$                             | 60.38                        | 119.58                        | 58.77                        | 46.43                        | 40.84                        |                              |           |  |
| 2  | 339–355              | $^3\text{L}_9, ^5\text{G}_3$   | 122.28                       | 248.16                        | 125.43                       | 123.65                       | 139.62                       |                              |           |  |
| 3  | 355–376              | $(^5\text{F}_1, ^3\text{F}_1, ^5\text{G})_2, ^3\text{H}_6, (^5\text{G}, ^3\text{H})_5$ | 988.82                       | 775.32                        | 1026.79                      | 995.58                       | 892.89                       |                              |           |  |
| 4  | 379–400              | $^3\text{K}_7, ^5\text{G}_4$   | 118.82                       | 113.58                        | 135.90                       | 106.04                       | 109.29                       |                              |           |  |
| 5  | 410–430              | $(^5\text{G}, ^3\text{G})_5$   | 330.84                       | 352.20                        | 365.01                       | 332.06                       | 258.48                       |                              |           |  |
| 6  | 440–463              | $^5\text{G}_6$   | 3083.04                      | 3078.61                       | 3093.36                      | 2793.00                      | 2442.87                      |                              |           |  |
| 7  | 463–471              | $^3\text{K}_8$   | 80.91                        | 194.49                        | 83.98                        | 88.26                        | 104.87                       |                              |           |  |
| 8  | 471–481              | $^5\text{F}_2$   | 140.71                       | 171.78                        | 132.43                       | 129.76                       | 99.52                        |                              |           |  |
| 9  | 481–496              | $^5\text{F}_3$   | 308.54                       | 302.56                        | 323.92                       | 307.03                       | 271.16                       |                              |           |  |
| 10   | 529–555              | $^5\text{F}_4, ^5\text{S}_2$   | 850.56                       | 859.54                        | 866.57                       | 872.06                       | 702.62                       |                              |           |  |
| 11   | 634–667              | $^5\text{F}_5$   | 571.49                       | 555.38                        | 585.22                       | 618.24                       | 626.90                       |                              |           |  |
| 12   | 1106–1223            | $^5\text{I}_6$   | 201.23                       |                               | 218.14                       | 228.23                       | 207.57                       |                              |           |  |
| 13   | 1840–2090            | $^5\text{I}_7$   | 1101.20                      |                               | 1160.11                      | 1217.99                      | 1176.24                      |                              |           |  |
| rms $\times 10^7$                            |                      |  | 9.88                         |                               |                              |                              |                              |                              |           |  |
| $\Omega_2 \times 10^{20}$ (cm <sup>2</sup> ) |                      |  | 8.66 ± 0.55                  |                               |                              |                              |                              |                              |           |  |
| $\Omega_4 \times 10^{20}$ (cm <sup>2</sup> ) |                      |  | 3.28 ± 0.82                  |                               |                              |                              |                              |                              |           |  |
| $\Omega_6 \times 10^{20}$ (cm <sup>2</sup> ) |                      |  | 4.91 ± 0.58                  |                               |                              |                              |                              |                              |           |  |

<sup>a</sup> $c_{\text{Ho}^{3+}} = 1.88569 \text{ M}$ , crystal length  $l = 0.031 \text{ cm}$

distances of La–O(H<sub>2</sub>O) (2.51 Å), La–O(dpa) (2.55 Å) and La–N (2.67 Å) of the nine-coordinated complex [La(dpa)(Hdpa)(H<sub>2</sub>O)<sub>2</sub>]·4H<sub>2</sub>O [30].

From these results it can be seen that spectroscopy of single crystals of stoichiometric compounds with a known crystallographic structure can be helpful in the explanation of the symmetry and bonding character of a complex species in solution.

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