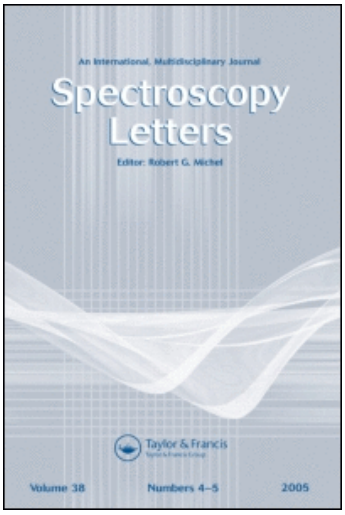

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f-f Transitional Spectral Analysis of $Yb(DPA)_3^{3-}$Complex

Wu Yang[a]; Jinzhang Gao[a]; Miao Chen[a]; Jingwan Kaug[a]; Qingyu Ou[b]
[a] Department of Chemistry, Northwest Normal University, Lanzhou, P. R. China [b] Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, P. R. China

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f-f Transitional Spectral Analysis of $Yb(DPA)_3^{3-}$ Complex

Key Words: DSCPCF model, Spectral analysis, ytterbium complex

Wu Yang Jinzhang Gao* Miao Chen and Jingwan Kang

Department of Chemistry, Northwest Normal University, Lanzhou 730070, P. R. China

Qingyu Ou

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China

Abstract

Absorption spectra of $Yb(DPA)_3^{3-}$ complex (where DPA=dipicolinate) in aqueous solution are studied and all of their spectral peaks are assigned based on Double Sphere Coordination Point Charge Field model(DSCPCF). It is shown that calculated and observed results are agreeable to each other. Meanwhile the coordination structure of the complex reported in aqueous media are also deduced.

* Author to whom correspondence should be addressed.

Introduction

Owing to peculiar optical and magnetic properties of lanthanide elements, a great deal of attention has been given to the spectral study of these elements, both theoretically and experimentally[1-5]. Theoretical studies have been devoted to understanding and clarifying the underlying crystal field splitting mechanisms and experimental studies have focused on characterization of the spectra-structure relationships and spectral peaks assignments of lanthanide complexes.

Chemical and physical properties of the complexes of Ln(III) ions with dipicolinate have been widely investigated [6], but so far the systematic studies on the spectral behaviors of these complexes, especially on crystal field splitting, have not been seen. Dipicolinate is one kind of special ligand which contains two types of donor atoms, i.e. nitrogen atom of pyridyl group and oxygen atom of carboxyl group. In these complexes, lanthanide-ligand interaction are uncylindrically symmetrical, and all atoms from chelate rings and chemical bonds which are very near to lanthanide ions directly influence 4f electrons. And these kinds of complicated interactions could have particular effect on the optical properties of the lanthanide complex system, which is very similar to the interaction between lanthanide ion and biomolecular system. So the studies on the spectral natures of these complexes are very essential.

Because of solvent effect the structure of complexes in aqueous solution differs from that in crystal state, but the exact structure of the complex in solution is usually different to determine.

In the present paper, as a example, we infer the structure of $Yb(DPA)_3^{3-}$ complex according to dependence of spectral characteristic on structural parameters of the coordination polyhedron.

Absorption spectra in UV-VIS-NIR region have been systematically investigated, spectral peaks are assigned and crystal field energy levels are calculated using Double Sphere Coordination Point Charge Field model(DSCPCF)[1,7]. For comparison static point charge field model(PCF) is also exploited to calculate crystal field splittings, and it is shown that DSCPCF energy levels calculated are identical to observed levels, but the deviation of PCF energy levels is very high.

Experimental

Reagents

Stock solution of ytterbium chloride is prepared by dissolving Yb_2O_3(spectral pure) with concentrated hydrochloric acid of guarantee reagent grade, vaporizing near to dry, and then diluting to desired scale with deionized water. Stock solution of cerium chloride is obtained by dissolving CeO_2(99.99% pure) with H_2O_2(analytical pure) and concentrated hydrochloric acid of guarantee reagent grade.

DPA is of analytical reagent grade.

Apparatus

Absorption spectra are recorded on a UV-VIS-NIR spectrophotometer(Hitachi, Japan) and during the detection pH value of the work solution is adjusted using 0.5mol.L^{-1} NaOH and/or 0.5mol.L^{-1} HCl.

Calculation

According to references[6,8-10] coordination polyhedron of the $Ln(DPA)_3^{3-}$ complexes is distorted trigonal prism with a trigonal dihedral symmetry(D_3) as shown in Fig.1.

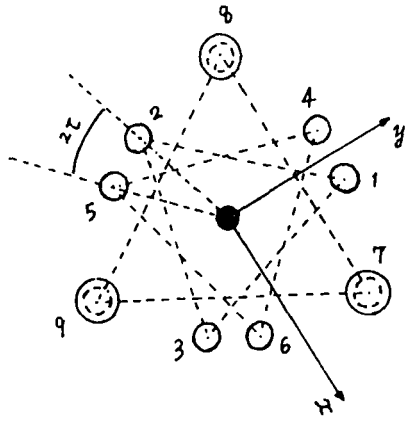

Fig.1 The coordination polyhedron viewed down trigonal axis(Z).
○: nitrogen donor atom; ○: oxygen donor atom; ●: Ln^{3+} ion.

In Fig.1, coordinates of six oxygen donor atoms and three nitrogen donor atoms are respectively listed as follows:

for oxygen atoms:

$(R_1, \pi-\Theta, \pi/2-\tau)_1$, $(R_1, \pi-\Theta, 7\pi/6-\tau)_2$, $(R_1, \pi-\Theta, 11\pi/6-\tau)_3$,

$(R_1, \Theta, \pi/2+\tau)_4$, $(R_1, \Theta, 7\pi/6+\tau)_5$, $(R_1, \Theta, 11\pi/6+\tau)_6$,

and for nitrogen atoms:

$(R_2, \pi/2, \pi/6)_7$, $(R_2, \pi/2, 5\pi/6)_8$, $(R_2, \pi/2, 3\pi/2)_9$.

Coordinates of effective bonding charges are similar to those of the donor atoms but the radial coordinates R_j have been replaced by r_j.

In DSCPCF model crystal field potential is expressed as follows:

$$Hc = A_2^0 r^2 Y_2^0 + A_4^0 r^4 Y_4^0 + A_4^3 r^4 (Y_4^3 - Y_4^{-3}) + A_6^0 r^6 Y_6^0 + A_6^3 r^6 (Y_6^3 - Y_6^{-3}) + A_6^6 r^6 (Y_6^6 + Y_6^{-6}) \quad (1)$$

where $Y_k^m(\Theta, \Phi)$ is spherical harmonic function of 4f electron, $\langle r^k \rangle$ is radial expectation values, and A_k^m is DSCPCF parameter given by:

$$A_2^0 = -6\sqrt{\frac{\pi}{5}}e^2\left[\left(\frac{q_1}{r_1^3} - \frac{Z_1^*}{R_1^3}\right)(3\cos^2\Theta - 1) - \frac{1}{2}\left(\frac{q_2}{r_2^3} - \frac{Z_2^*}{R_2^3}\right)\right] \quad (2a)$$

$$A_4^0 = -\sqrt{\frac{\pi}{2}}e^2\left[\left(\frac{q_1}{r_1^5} - \frac{Z_1^*}{R_1^5}\right)(35\cos^4\Theta - 3\cos^2\Theta + 3) + \frac{3}{2}\left(\frac{q_2}{r_2^5} - \frac{Z_2^*}{R_2^5}\right)\right] \quad (2b)$$

$$A_6^0 = -\frac{3}{4}\sqrt{\frac{\pi}{13}}e^2\left[\left(\frac{q_1}{r_1^7} - \frac{Z_1^*}{R_1^7}\right)(231\cos^6\Theta - 315\cos^4\Theta + 105\cos^2\Theta - 5) - \frac{5}{2}\left(\frac{q_2}{r_2^7} - \frac{Z_2^*}{R_2^7}\right)\right] \quad (2c)$$

$$A_4^3 = \sqrt{35\pi}e^2\left(\frac{q_1}{r_1^5} - \frac{Z_1^*}{R_1^5}\right)\sin^3\Theta\cos\Theta\sin 3\tau \quad (2d)$$

$$A_6^3 = \frac{9}{4}\sqrt{\frac{35\pi}{39}}e^2\left(\frac{q_1}{r_1^7} - \frac{Z_1^*}{R_1^7}\right)\sin^3\Theta(11\cos^3\Theta - 3\cos\Theta)\sin 3\tau \quad (2e)$$

$$A_6^6 = -\frac{9}{8}\sqrt{\frac{77\pi}{39}}e^2\left[-\left(\frac{q_1}{r_1^7} - \frac{Z_1^*}{R_1^7}\right)\sin^6\Theta\cos 3\tau - \frac{1}{2}\left(\frac{q_2}{r_2^7} - \frac{Z_2^*}{R_2^7}\right)\right] \quad (2f)$$

In eq(2), r_1 and r_2 are distances from Ln^{3+} ion to the bond charges q_1 and q_2, and Z1* and Z_2* are respectively effective nuclear charges of oxygen and nitrogen donor atoms. These parameters are calculated according to the method[11]. Spherical polar coordinate Θ, twist angle 2τ and bond angle 2β obey following relationship:

$$\sin\Theta\cos\tau = \cos\beta \quad (3)$$

The reduction of the matrix elements of Hc operator can be performed by making use of equation such as:

$$
\begin{aligned}
&< f^N SLJM \left| \hat{H}_c \right| f^N S'L'J'M' > \\
&= \sum_k \sum_m A_k^m < r^k >< f^N SLJM \left| Y_k^m \right| f^N SLJM' > \\
&= \sum_k \sum_m A_k^m < r^k > (\frac{2k+1}{4\pi})^{\frac{1}{2}} < f^N SLJM \left| C_k^m \right| f^N SLJM' > \\
&= \sum_k \sum_m A_k^m < r^k > (\frac{2k+1}{4\pi})^{\frac{1}{2}} (-1)^{J-M} \begin{pmatrix} J & k & J \\ -M & m & M' \end{pmatrix} (SLJ \| C^k \| SLJ) \\
&= \sum_k \sum_m A_k^m < r^k > (\frac{2k+1}{4\pi})^{\frac{1}{2}} (-1)^{J-M} \begin{pmatrix} J & k & J \\ -M & m & M' \end{pmatrix} (-1)^{S+L+J+k} (2J+1) \\
&\quad \cdot \begin{Bmatrix} S & L & J \\ k & J & L \end{Bmatrix} (l \| C^k \| l) \\
&= \sum_k \sum_m A_k^m < r^k > (\frac{2k+1}{4\pi})^{\frac{1}{2}} (-1)^{J-M} \begin{pmatrix} J & k & J \\ -M & m & M' \end{pmatrix} (-1)^{S+L+J+k} (2J+1) \\
&\quad \cdot \begin{Bmatrix} S & L & J \\ k & J & L \end{Bmatrix} (-1)^l (2l+1) \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}
\end{aligned}
$$

To obtain crystal field wave functions and DSCPCF energy levels, the Hc operator was diagonalized in a JM intermediate coupling basis. Ligand parameter set used in our calculation is given in TABLE 1.

Results and Discussion

Formation of the complexes in aqueous solution

For H_2DPA, $pk_{a1} = 2.16$ and $pk_{a2} = 4.76$[11], so distribution coefficient of DPA^{2-} under selection condition pH = 8.5 is :

$$\delta_{DPA^{2-}} = k_{a1} k_{a2} / ([H^+]^2 + k_{a1}[H^+] + k_{a1}k_{a2}) = 0.9998 \approx 1$$

TABLE 1

Ligand parameter set for $Ln(DPA)_3^{3-}$ complexes*

$Yb(DPA)_3^{3-}$	
$\langle r^2 \rangle = 0.753a_0^2$	$R_1 = 2.38Å$
$\langle r^4 \rangle = 1.49a_0^4$	$R_2 = 2.43Å$
$\langle r^6 \rangle = 7.0a_0^6$	Q_O=-1.18(-0.82)
$Z^*_{Yb(III)} = 24.2$	$Q_N = 0$
$Z^*_O = 1.78$	
$Z^*_N = 3.1$	

* All data are in au except R_1 and R_2 which are in units of Å

Therefore the protonation of DPA^{2-} can be neglected and when $C_{DPA^{2-}}$ = 0.01mol.L^{-1} in the system of Yb(III)- DPA :

$$\delta_{Yb(DPA)_3^{3-}} = \beta_3[DPA]^3/(1 + \beta_1[DPA]^2 + \beta_2[DPA]^2 + \beta_3[DPA]^3) = 0.9999 \approx 1$$

showing that $Yb(DPA)_3^{3-}$ is extremely dominant species in corresponding complex solution, and $Ln(DPA)^+$ and $Ln(DPA)_2^-$ complex species are negligible where β_n are overall stability constants[12].

Identification of Spectral Peaks of the Complexes

Absorption spectra of $Yb(DPA)_3^{3-}$ complex are measured. Beyond 33000cm^{-1} appears strong $\pi-\pi^*$ transition peak. Characteristic f-f transition peaks are in the 6500~ 11000 cm^{-1} wavenumber region.

In absorption spectra of $Yb(DPA)_3^{3-}$ complex three of the strong peaks rise from the ground state level of $^2F_{7/2}$ to three components of the excited state $^2F_{5/2}$. According to the reference[13] we consider the strongest peak (10227.0 cm^{-1})

corresponds to the lowest level of $^2F_{5/2}$. By comparing with calculated DSCPCF energy levels(2β=129.17 ° and 2τ =15 °) (Fig. 2) assignment of the three strongest peaks is completed.

According to transitional selection rule, the transitions from all of the multiplets of $^2F_{7/2}$ to the lowest energy level of $^2F_{5/2}$ can be observed, so from the spectral peaks less than 10227.0cm^{-1} such as 10040.7cm^{-1}, 9682.4 cm^{-1} and 9596.9 cm^{-1} the crystal field components of $^2F_{7/2}$ term can be obtained. And then we refer to the reference[13] and conclude that the peak at 10172.4 cm^{-1} originates from the third crystal field component of $^2F_{7/2}$ to the second energy level of $^2F_{5/2}$, and the peak at 10582.6 cm^{-1} rises from the second component of $^2F_{7/2}$ to the third component of $^2F_{5/2}$. The results are shown in TABLE 2 and Fig. 2.

DSCPCF energy levels of $Ce(DPA)_3^{3-}$ complex are also calculated in above procedure. The transition peak with the highest frequency 3658cm^{-1} has gone beyond near IR region. That is why we have not found the characteristic spectral lines of the Ce(III) complex.

Coordination configuration of $Ln(DPA)_3^{3-}$ complex ion

To explore the coordination configuration of the complexes the DSCPCF energy levels of $Yb(DPA)_3^{3-}$ complex at different bond angle 2β and twist angle 2τ have been calculated and the results have shown in Fig. 3, 4.

When the bond angle 2β is mixed as 129.17 ° , the DSCPCF energy splittings decrease with 2τ increasing. For the trigonal dihedral $Ln(DPA)_3^{3-}$ complexes 2τ varies from 0 ° - 16 ° [14]. When twist angle 2τ is kept as 15 ° , as 2β increases the DSPCF energy splitting decrease at first, and then increase. When 2β = 129.17 ° 2τ = 15 ° the calculated and observed energy field energy levels are in agreement with each other. That structural mode is consistent with that of solid $Ln(DPA)_3^{3-}$ complexes.

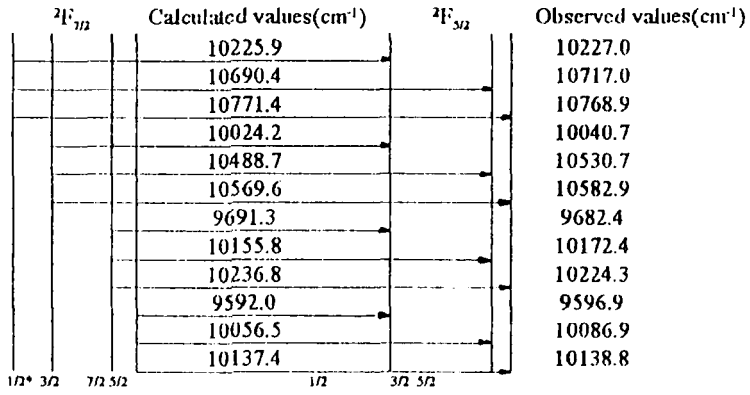

Fig.2 Comparison of theoretical and experimental energy levels of $Yb(DPA)_3^{3-}$ complex(in unit of cm^{-1}), standard deviation σ = 20cm^{-1}.(* $|M|$).

TABLE 2

Calculated and observed crystal field energy levels of $Yb(DPA)_3^{3-}$ complex (cm^{-1}) (2β=129.17° , 2τ=15°).

Terms	DSCPCF values($\|M\rangle$,Γ^*)	Observed values	PCF values($\|M\rangle$) Q_O= -1.18e	Q_O=-0.82e
$^2F_{7/2}$	-342.58($\|1/2\rangle$,E')	0	-1052.3$\|7/2\rangle$	-731.2$\|7/2\rangle$
0	-140.87($\|3/2\rangle$,E")	186.3	-203.5$\|5/2\rangle$	-141.4$\|5/2\rangle$
	192.07($\|7/2\rangle$,E')	544.6	457.5$\|3/2\rangle$	317.9$\|3/2\rangle$
	291.38($\|5/2\rangle$,E')	630.1	798.3$\|1/2\rangle$	554.7$\|1/2\rangle$
$^2F_{5/2}$	-336.66($\|1/2\rangle$,E')	10227.0	-910.8$\|5/2\rangle$	-632.9$\|5/2\rangle$
	127.84($\|3/2\rangle$,E")	10717.0	145.9$\|3/2\rangle$	101.4$\|3/2\rangle$
10220	208.82($\|5/2\rangle$,E')	10768.9	764.9$\|1/2\rangle$	531.6$\|1/2\rangle$

*Irreducible representations.

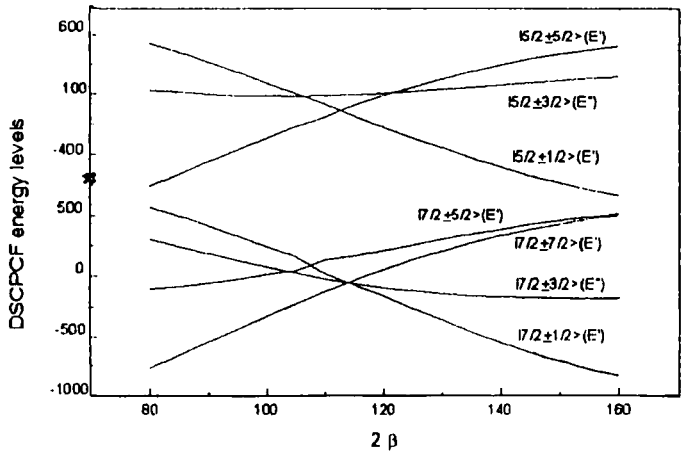

Fig.3 The relationship between DSCPCF energy levels of $Yb(DPA)_3^{3-}$ complex (cm^{-1}) and the bond angle 2β.

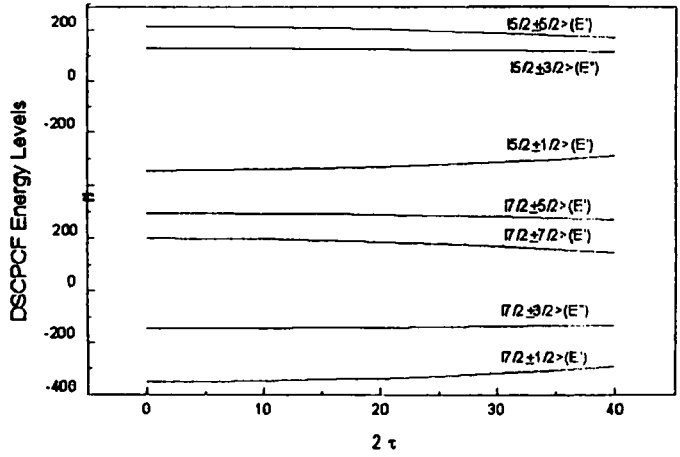

Fig.4 The relationship between DSCPCF energy levels of $Yb(DPA)_3^{3-}$ complex (cm^{-1}) and the twist angle 2τ

In this work, static point charge model(PCF) is also employed to calculate the crystal field energy levels of $Yb(DPA)_3^{3-}$ complex (the charge at oxygen atom from carboxyl is $-1.18e$[14] or $-0.82e$[10], at nitrogen atom from pyridyl $0e$[10]). But the variation of theoretical results from the corresponding observed values is about one magnitude order. Even if shielding effect of $5s^25p^6$ shell is involved, the PCF results are also unsatisfactory.

Conclusion

DSCPCF model is successful in calculating the crystal field energy splittings of Ln(III) complexes. This model is founded on basis of Hellman-Feynman force equilibrium, in which the static interaction and covalent interaction are both involved, so long as the effective nuclear charge of metal ion and donor atoms are reasonably selected good results are able to be obtained.

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