JKAU: Sci., **Vol. 21** No. 1, pp: 71-78 (2009 A.D. / 1430 A.H.)

Synthesis and Spectroscopic Characterization of Some Praseodymium (III) - 1,1-1, 1- Carbonyldiimidazol Chelates

A.H. Qusti

Department of Chemistry, Faculty of Science,
King Abdulaziz University, Jeddah, Saudi Arabia

Abstract. A series of praseodymium (III) chelates containing - 1, 1-diimidazylketone was prepared. The values of Slater-Condon (F_2, F_4, F_6), Racah (E^1, E^2, E^3), Judd- Ofelt (T_2, T_4, T_6), spin-orbit (ξ_{4f}) and intensity parameter of the prepared praseodymium (III) complexes are critically determined. The observed energy levels and spectral intensities were correlated with the theoretically values. The shift in the peak positions due to the host was critically used on the evaluation of the nephelauxetic parameters, covalence and bonding parameters for Pr^{3+} of the prepared two complexes. The nature of the bonding in the praseodymium (III) complexes complex is discussed.

1. Introduction

The optical characteristics of electronically active materials, particularly the rare earth compounds are of great interest because of their use as laser materials, online optical amplifiers and detectors[1-3]. Because of 4f-4f_ transition of the triply ionized (Ln^{3+}-ions), rare earth compounds exhibit very sharp lines in the visible and near infrared regions.

The wavelength of the spectral lines changes slightly from their free ions, positions when they are in complexes form (nephelauxetic effect) and from one lattice to another due to different interactions with the surroundings in the lattice. These small spectral changes sometimes lead to a major difference in the radiation characteristics of the material. Interest in the study of these materials have increased manifolds due to the discovery of strong lasing action involving rare earth ions in some of the compounds such as glass[4].

In continuation to our previous work on the spectral studies on praseodymium (III) complexes[5-7], the present manuscript is focused on the spectroscopic characterization and the absorption spectra of the two prepared praseodymium (III)- 1,1-carbonyldiimidazol complexes. A comparison between the absorption spectra of the prepared complexes and the free ion is included. On the other hand, the shift in the peak positions due to the host was used on the evaluation of the nephelauxetic parameters, covalence and bonding parameters for Pr^{3+} of the prepared complexes.

2. Experimental

2.1. Materials and Chemicals

Praseodymium nitrate pentahydrate, 99.9% purity (Fluka), praseodymium chloride hexahydrate, 99.9% purity (Aldrich), dimethylsulphoxide (DMSO), and acetic acid (BDH), 1, 1-carbonyldiimidazol (Fluka). All glassware's were first washed with chromic acid solution, thoroughly washed with water, rinsed with distilled water, ethanol, acetone, air dried and finally stored on a desiccator's.

2.2. Apparatus

The UV-Visible, and near IR spectra of the complexes in water and in ethanol were recorded on a Cary D-17 model Spectrophotometer and UV-260 spectrophotometer. Optical cells with path lengths 5 and 10 mm were used in the absorption measurements. All absorption spectra were recorded at room temperature (22-24°C). Analysis of C, H and N, content was carried out with Perkin-Elmer mode 240/B elemental analyses.

2.3. Preparation of the Complex $PrL_3(NO_3)_3$, L = 1, 1-carbonyldiimidazol

To the salt praseodymium (III) chloride (0.06 mol) in 120 mL of water an accurate weight of the ligand 1, 1-carbonyldiimidazol (0.20 mole) was slowly added. The reaction mixture was refluxed with constant stirring for 2h. On cooling the solution to the room temperature, a crystalline light green solid was separated out, filtered off and finally dried in an oven to give $PrL_3(NO_3)_3$.

2.4. Preparation of the Complex $PrL(NO_3)_3$

On the other hand, when the reaction was carried in ethanol a light blue crystals was separated out, filtered off and finally dried to give the complex $PrL(NO_3)_3$. Analytical data for both complexes are listed on Table 1. Both complexes are non-volatile, in-soluble in methanol, ethanol and dimethylformamide and decompose in acetic acid.

Table 1. Characterization and physical data for praseodymium (III) complex with 1,1-carbonyldiimidazol.

Compound	Solvent	Calculated% composition			Observed % composition		
		C	N	H	C	N	H
$PrL(NO_3)_3$	Water	17.20	20.70	1.23	17.70	20.30	1.90
$PrL3(NO_3)_3$	Ethanol	30.98	25.80	2.21	31.20	26.10	3.10

3. Results and Discussion

3.1. Absorption Spectra

The electronic spectrum of the reagent 1, 1- carbonyldiimidazol in DMSO at room temperature showed a series of absorption bands on the region 300-200 nm. The spectra of the two complexes are summarized on Table 1. The absorption bands of the ligand don't overlapping with any of Pr^{+3} spectral bands. The observed spectra of the praseodymium (III) - complex in DMSO, praseodymium (III) complex in acetic acid and $Pr(NO_3)_3.5H_2O$ in acetic acid showed four characteristic lines in the region 400-800 nm (Table 2). The observed band maxima positions and their most probable assignments and calculated energy levels are presented in Table 2.

Table 2. Experimental and calculated energy levels for Pr^{+3}-complex in DMSO and acetic acid, Pr^{+3}-complex in acetic acid and DMSO.

Levels $^3H_4$	$Pr(NO_3)_3.5H_2O$ + in MDSO		$Pr(NO_3)_3$ + L in CH_3OOH		$Pr(NO_3)_3.5H_2O$ in CH_3COOH	
	$P_{exp.}$	P_{cal}	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^1D_2$	16830	16830	16892	16890	16903	16900
$^3P_0$	20686	20690	20687	20690	20678	20680
$^3P_1(^1I_6)$	21240	21240	21304	21300	21259	21260
$^3P_2$	22420	22420	22502	22500	22452	22450
	r.m.s. 1.6×10^{-12}		r.m.s.1.82×10^{-12}		r.m.s 1.58×10^{-12}	

The energy E_J of the J^{th} levels may be written in Tyler's series expansion as

$$E_J = E_{0J} + \sum_{k=2,4,6} \frac{dE_J}{dF_k} \Delta F_k + \frac{dE_J}{d\xi_{4f}} \Delta \xi_{4f} \quad (1)$$

where, E_{oJ} is the zero order energy, (dE_J/d_k) and $(dF_J/d\xi_{4f})$ are the partial derivatives. The values of the zero order energies and partial derivative are taken from the data published by Wong.[8]

To evaluate the changes in (F_2, F_4, F_6), and ξ_{4f}, the observed energy values were substituted for E_J in the Taylor–series expansion. A least squares fit (Gauss Method)[6] was also employed to evaluate there parameters. The Slater-Condon (F_2, F_4, F_6), Racah (E^1, E^2 and E^2), Judd-Ofelt, spin-orbit (ξ_{4f}) and intensity (Ω_2, Ω_4 and Ω_6) parameters are given in Table 3.

Table 3. Slater-Condon (F_2, F_4 and F_6), Racah (E^1, E^2 and E^3), Judd- Ofelt (T_2, T_4, T_6), spin-orbit (ξ_{4f}) and intensity (Ω_2, Ω_4 and Ω_6) parameters for praseodymium (III)-complex in solution.

Parameters	$PrL(NO_3)_3.5H_2O$ In DMSO	$Pr(NO_3)_3$ in CH_3COOH	$PrL(NO_3)_3.5H_2O$ in CH_3COOH
F_2	314.0	314.96	314.04
F_4	73.80	64.866	61.423
F_6	6.506	5.958	5.694
E^1	5784	5440	5286
E^2	15.350	18.01	18.848
E^3	473.57	473.92	473.52
$T_2\times10^9$	–29.73	–16.11	–29.4
$T_4\times10^9$	1.998	0.760	0.873
$T_6\times10^9$	4.91	2.86	4.41
ξ_{4f}	763.89	747.68	760.17
$\Omega_2\times10^{20}$	–187.62	–120.69	–220.45
$\Omega_4\times10^{20}$	12.609	5.693	6.45
$\Omega_6\times10^{20}$	30.98	21.43	33.02
F_4/F_2	0.235	0.206	0.196
F_6/F_2	0.021	0.019	0.018
T_4/T_2	– 0.067	–0.047	–0.03
T_6/T_2	– 0.165	–0.178	–0.15

3.2. Spectral Intensities

The measured value of the oscillator strength (P_{exp}), is most likely expressed[9] in terms of the molar function coefficient and the wavenumbes (ν) by:

$$P_{\exp} = 4.318\times10^{-9}\int_{\nu_1}^{\nu_2}\varepsilon(\nu)d\nu \tag{2}$$

Where $\int\varepsilon(\nu)d\nu$ is the area under the corresponding band, ε(ν) is the molar extinction coefficient defined by:

$$\varepsilon = \frac{\ell}{C}\log\frac{I_0}{I} \tag{3}$$

where, C is the molar concentration, ℓ is the light path length in (cm) and log I_0/I is the optical density.

3.3. Judd-Ofelt Parameters

The absorption spectra of the Pr^{3+} ion in the visible region involve parity forbidden 4f–4f transitions from the $^3H_4$ ground state to various excited states. Spectra parameters of $PrL(NO_3)_3.5H_2O$ dissolved in DMSO and CH_3COOH are listed in Table 4.

Table 4. Experimental and calculated oscillator strengths of Pr^{3+} ion in complexes.

Energy levels	$Pr(NO_3)_3.5H_2O$		Ligand in DMSO	$Pr(NO_3)_3.5H_2O$ in CH_3COOH			$PrL(NO_3)_3$ in CH_3COOH		
	Pexp.	Pcal U=^{3}Po	Pcal U=^{3}po+^{1}I6	pexp	Pcal=^{3}P0	Pcal U=^{3}po+I	pexp	Pcal U=^{3}po	Pcal U=^{3}p0+^{1}I6
$^1D_2$	3.36	3.36	4.432	2.63	2-63	3.897	1.914	1.914	2.687
$^3P_0$	5.33	7.14	5.664	1.54	3.12	1.936	1.435	2.714	1.677
$^3P_1$	9.01	7.23	8.739	4.72	3.17	4.40	4.012	2.748	3.816
$^3P_2$	16.5	16.5	16.24	14.11	14.11	13.8	9.3	9.3	9.11
r.m.s	1.2	7×10–6	5.51×10–7	1.	11×10–6	6.51×10	8.99×	10–7	3.98×10–7
Judd-Oflet parameters ×10^9	T_2 = –29.7 T_4 =1.99 T_6 =4.91		T2=-6.31 T4=1.59 T6=4.92	T2=-2929.4 T4=0.873 T6=4.41		T_2 = 2.01 T_4=0.542 T6 = 4.38	T_2 = –16.11 T_4 = 0.760 T_6 = 2.86		T_2=0.70 T_4=0.469 T_6=2.87

The oscillator strengths of the 4f–4f transitions Table 4 were used to calculate (T_λ) parameters Judd-Ofelt equation (in the form given in Ref. [10])

$$P_{ed} = \nu \sum_{\lambda=2,4,6} T_\lambda \langle \Psi_i J \| U^\lambda \| \Psi_f J \rangle^2 \quad (4)$$

where, $\langle \Psi_i J \| U^\lambda \| \Psi_f J \rangle$ are the reduced matrix elements of unit tensor operator U^λ between the initial $\Psi_i J$ and final $\Psi_f J$ levels of the lanthanide ion and ν is the wave number of the $\psi_i J \rightarrow \psi_f J$ transition.

3.4. Nephelauxetic Effect of Pr^{3+} Complex (β)

The nephelauxetic effect is quantitatively by a nephelauxetic parameter $\overline{\beta}$. In the lanthanide complexes, $\overline{\beta}$ can be expressed by the average value of the ratio of frequency in the complex and in the aquo-ion[11]

$$\overline{\beta} = \frac{1}{n} \sum \frac{\overline{\nu}_c}{\overline{\nu}_a} \quad (5)$$

where, $\overline{\nu}_c$ and $\overline{\nu}_a$ are the wavenumber in cm^{-1} of 4f-4f transitions band in complex and aqueous solution, respectively and *n* is the number of observed bands. This ratio was obtained for all observed transitions and the average $\overline{\beta}$ was used to estimate the bonding parameter δ (%). The proposed Sinha parameter was also used to measure the degree of covalency employing the following equation[12]:

$$\delta = \frac{1}{\overline{\beta}} (1 - \overline{\beta}) \times 100\ \% \quad (6)$$

The bonding parameter, $b^{1/2}$, the magnitude of which suggests the comparative involvement of the 4f orbital metal-ligand band is correlated to nephelauxetic ratio $\overline{\beta}$ by the expression

$$b^{1/2} = \left[\frac{1}{2} (1 - \overline{\beta}) \right]^{\frac{1}{2}} \quad (7)$$

The positive values of bonding parameters, suggest the occurrence of some covalent character in the metal-ligand bond. The energies at which the various bands appear for $PrL(NO_3)_3$ complex are lower as compared to the aqua ion. The extent of this red shift is most likely related to the covalence in the metal-ligand bond. The values of $\overline{\beta}$, δ (%) and $b^{1/2}$ parameters are presented in Table 5. The positive values of bonding parameters in Table 5 (0.030) for pr^{+3} in complex and (0.0255) for Pr^{+3} in the metal salt, suggest the occurrence of some covalent character in

metal-ligand band. On the other hand, such complexes are nonvolatile, in soluble in common organic solvents and decompose in acetic acid. Here we offer a speculation to explain that fact, since complex is insoluble in common organic solvents this means δ (%), $b^{1/2}$, and $\overline{\beta}$ (nephelauxetic effect) not enough for covalence in metal-ligand bond, this seems to be credible because the lone pair of donor atom of the ligand are in SP^2-hybridization and decompose by acetic acid, due to ionic character conferred acetate.

Table 5. Calculated values of various covalency parameters of Pr^{3+} complex.

Parameters	$Pr(NO_3)_3.5H_2O$ + L in DMSO	$Pr(NO_3)_3$ + L complex in CH_3COOH	$Pr(NO_3)_3.5H_2O$ in CH_3COOH
$\overline{\beta}$	0.9949	0.9964	0.9974
δ (%)	0.5126	0.3613	002607
$b^{1/2}$	0.0357	0.0300	0.0255

References

[1] **Ajroud, M., Haouari, M., Ouada, H.B., Maaref, H.** and **Garapon, C.,** *J. Phys.: Condens. Matter*, **12**: 325 (2000).

[2] **Han, X.M.** and **Wang, G.F.,** *J. Cryst. Growth*, **247**: 551 (2003).

[3] **Ratnakaram, Y.C.** and **Sudharani, N.,** *J. Phys. Chem. Solids*, **59**: 2 (1998).

[4] **Kumar, K.** and **Rai, S.B.,** *Progress in Crystal Growth and Characterization of Materials*, **52**: 27 (2006).

[5] **Qusti, A.H.** and **Chrysochoos, J.,** *J. Less-Common. Metals*, **112**: 291 (1985).

[6] **Qusti, A.H.** and **Chrysochoos, J.,** *J. Less-Common. Metals*, **126**: 169 (1986).

[7] **Qusti, A.H.** and **Al-Sehemi, A.G.,** *J. KAU: Sci*., **7**:57 (1995).

[8] **Wong, E.Y.,** *J. Chem. Phys*., **35**:544 (1961).

[9] **Scarbourough, J.B.,** *Numerical Mathematical Analysis*, Oxford Publishing Co., New Delhi (1966).

[10] **Carnall, W.T. Crosswhite, H.M.** and **Crosswhite, H.,** *Energy Levels Structure and Trausition Probabilities of Trivalent Lanthanides in laf3*, Argonne National Laboratory, Argonne, Illionois, U.S.A. (1978).

[11] **Sinha, S.P.,** *Spectro Chim. Acta*, **22**: 57 (1966).

[12] **Henrie, D.E.** and **Choppin, C.R.,** *J. Chem. Phys.*, **49**: 477(1968).

تحضير وتوصيف عدد من المتراكبات لعنصر البرازيوديميم مع المركب المخلبى ثنائى الأمين ثنائى الأزيل الكيتون

عبدالله حسين قستي

قسم الكيمياء– كلية العلوم – جامعة الملك عبدالعزيز– جدة– المملكة العربية السعودية

المستخلص. تضمنت الدراسة تحضير وتوصيف عدد من المتراكبات لعنصر البرازيوديميم مع المركب المخلبى ثنائي الأمين ثنائي الأزيل الكيتون (1, 1- Carbonyldiimidazol) باستخدام العديد من الطرق الطيفية المختلفة والتحليل العنصري (Elemental analysis). تم أيضًا حساب العديد من الدوال الطيفية (Nephelauxetic parameter $\overline{\beta}$)، وكذلك معاملات رشا (Racah)، ومقارنتها مع قيم أيون البرازيوديميم الحر. تم أيضًا حساب بعض الدوال الأخرى مثل معاملات udd–Ofelt, spin– orbit (ξ4f) المعبرة عن التركيب الإلكتروني والفراغى للمتراكبات المحضرة.