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Research Article

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Comparative 4f–4f absorption spectral study for the interactions of Pr(III) with selected urea and thiourea: Energy and electric dipole intensity parameters

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ABSTRACT

The complexation of urea and thiourea with Pr(III) has been studied in different organic solvents like methanol (CH_3OH), acetonitrile (CH_3CN), dioxane ($C_4H_8O_2$) and DMF (C_3H_7NO) and their equimolar mixtures by employing absorption difference and comparative absorption spectrophotometry. The complexation of Pr(III) with ureas and thioureas is indicated by the changes in the absorption intensity following the subsequent changes in the oscillator strength of different 4f–4f bands and Judd-Ofelt intensity (T_λ) parameters. The other spectral parameters like energy interaction parameters namely Slater–Condon (F_k), Racah (E^k), Lande (ξ_{4f}), Nephelauxetic ratio (β) and bonding parameters ($b^{1/2}$) are further computed to explain the nature of complexation. The difference in the energy parameters with respect to donor atoms and solvents reveal that the chemical environment around the lanthanide ions has great impact on f–f transition and any change in the environment result in modification of the spectra. Various solvents and their equimolar mixtures are also used to discuss the participation of solvents in the complexation.

Key words: 4f–4f Transition spectra, oscillator strength, pseudohypersensitive, nephelauxetic effect

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INTRODUCTION

The photophysical property of lanthanides has been becoming an active area of research to both chemists and spectroscopists for many years, because of their potential applications in many fields. Most of these applications are based on their luminescent and absorption spectral properties of lanthanides [1-4]. The 4f–4f transition spectra of lanthanide have been found to exhibit significant sensitivity towards even minor change in the immediate coordination environment around lanthanide ion through variation in the absorption spectral pattern, degree of red shift and intensification of 4f–4f bands. The intensities of these hypersensitive transitions [5–9] have also been used extensively between outer and inner sphere coordination, in identifying the coordinating sites of ligands, in determining the immediate coordination environment and in predicting the coordination number of lanthanides. Recently, Khan *et al.* [10] have used the intensity and band shapes for both hypersensitive and non-hypersensitive transitions in studying the effect of changes in the environment upon 4f–4f absorption spectra of Ho(III) and Er(III) complexes with thiocyanate and 2,2-bipyridine. Our interest in the present study lies in investigating the interaction behaviour of hard metal ion, Pr(III) with ally urea/thiourea and phenyl urea/thiourea having different donor atom with different π-electron density.

The present study deals with the interaction of Pr(III) ions with ureas viz. allyl urea (au), phenyl urea(pu) and thioureas viz. allyl thiourea (atu), phenyl thiourea (ptu) using absorption difference and comparative absorption spectrophotometry. The major structural difference between these systems are (i) the possible ligand and metal orbital interaction in ureas and thioureas (ii) different π-electron density and (iii) the varying coordination ability of the different solvents involved in our study. Both ureas and thioureas are ambidentate ligand each possessing two donor sites (N & O in ureas and N & S in thioureas) which possess different affinities towards different metal ions. The interaction are studied by computation of various spectral parameters namely energy interaction (Slator–Condon ($F_{k's}$), nephelauxetic effect (β), bonding ($b^{1/2}$) and percent covalency (δ) parameters) and intensity parameters (oscillator strength and Judd–Ofelt parameters).

EXPERIMENTAL SECTION

2.1 Materials

Ureas (allyl ureas and phenyl urea) and thiourea (allyl thiourea and phenyl thiourea,) from Sisco Chemical Laboratories, Praseodymium(III) nitrate hexahydrate (99.9%) purity from M/S Indian Rare Earths Ltd. are used for synthesis and spectral analysis. The solvents used are CH_3OH, CH_3CN, DMF and Dioxane which are of A/R grade from E. Merk.

The absorption spectra of Pr(III) complex with ureas/thioureas were recorded on Perkin Elmer Lambda-35 UV–Vis Spectrometer in the range 350-910 nm. The concentrations of all the solutions were maintained at 0.01 mol L^{-1}. The temperature of all observations was maintained by using Perkin Elmer PTP1 Peltier-temperature system. For a typical absorption study, a solution of Pr(III) nitrate (0.01 mol L^{-1}) and urea (0.01 mol L^{-1}) in double distilled water were added and the resultant mixture was stirred for sufficient time to form the complex in solution. The solution was scanned for the absorption spectra in the spectral region 350 nm – 1000 nm.

2.2 Methods

Nephelauxetic ratio has long been regarded as a measure of covalency. The Nephelauxetic effect has been interpreted in terms of Slater-Condon and Racah parameters, by the ratio of the free ion and complex ion [11-12].

$$\beta = \frac{F_K^C}{F_K^f} \text{ or } \frac{E_C^K}{E_f^K} \tag{1}$$

Where, F_K (K= 2,4,6) is the Slater-Condon parameters and E^K, the Racah parameters for complex (C) and free ions (f) respectively. The bonding parameter and percent covalency are calculated as

$$b^{1/2} = \left[\frac{1-\beta}{2}\right]^{1/2} \tag{2}$$

$$\delta = \left[\frac{1-\beta}{\beta}\right] \times 100 \tag{3}$$

In the electronic transition of 4f-4f, the energy, E_{so} arises from the most important magnetic interactions, while the spin orbit interactions may be written as,

$$E_{so} = A_{so}\xi_{4f} \tag{4}$$

Where A_{so} is the angular part of spin orbit interaction and ξ_{4f} is the radial integral and is known as Lande's parameter. By first order approximation the energy E_j of the j^{th} level is given by Wong[13] as

$$E_j(F_K, \xi_{4f}) = E_{oj}(F_K^o, \xi_{4f}) + \frac{\partial E_j}{\partial F_K}\Delta F_K + \frac{\partial E_j}{\partial \xi_{4f}}\Delta\xi_{4f} \tag{5}$$

Where E_{oj} is the zero order energy of the j^{th} level.

The value of F_K and ξ_{4f} are given by

$$F_K = F_K^o + \Delta F_K \tag{6}$$

and $\xi_{4f} = \xi_{4f}^o + \Delta\xi_{4f}$

The differences between the observed E_j value and the zero order value ΔE_j is evaluated by

$$\Delta E_j = \sum_{K=2,4,6} \frac{\partial E_j}{\partial F_K} + \frac{\partial E_j}{\partial \xi_{4f}} \Delta\xi_{4f} \qquad (7)$$

By using the zero order energy and partial derivatives of Pr(III) ion given by Wong (7), the above equation can be solved by least squares technique and the value of ΔF_K and $\Delta\xi_{4f}$ can be found out. From these values the value of F_2, F_4, F_6 and ξ_{4f} are found out by using equation (6).

The calculation of the band intensities is based upon the theoretical treatment derived by Judd and Ofelt [14]. They considered the transitions are essentially electric dipole in character and the oscillator strength corresponding to the induced electric dipole transition $\Psi J \rightarrow \Psi^{/}J^{/}$ as given by

$$P = \sum_{\lambda=2,4,6} T_\lambda \sigma(f^N \psi J \parallel U^{(\lambda\lambda} \parallel f^N \psi' J')^2 \qquad (8)$$

Where $U^{(\lambda)}$ is matrix element of rank λ. The three quantitiesT_2,$T_4$and T_6 are related to the radial parts of the $4f^N$ wave functions, the wave functions of perturbing configurations of which the nearest is $4f^{N-1}5d$.

The measured intensity of an absorption band is related to the probability (P) for the absorption of radiant energy (oscillator strength) by the expression:

$$P = \frac{2303mc^2}{N\pi e^2} \int \varepsilon_i(\sigma) d\sigma$$

or

$$P = 4.318 \times 10^{-9} \int \varepsilon_i(\sigma) d\sigma \qquad (9)$$

Where ε is the molar absorptivity at the energy σ (cm^{-1}) and other symbols have their usual meaning. From these values the value of T_2,$T_4$and T_6 are calculated by using

$$\frac{P_{obs}}{\nu} = [(U^2)]^2 T_2 + [(U^4)]^2 T_4 + [(U^6)]^2 T_6 \qquad (10)$$

RESULTS AND DISCUSSION

Figure 1 shows the comparative absorption spectra of Pr(III) and Pr(III) with different urea and thiourea in DMF as solvent while **Figure 2** shows the comparative absorption spectra of Pr(III) with pu in methanol, acetonitrile, dioxane and DMF. Pr(III) ions observed four energy bands ($^3H_4 \rightarrow {}^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$) in the visible spectral region. These transitions do not obey the selection rules for hypersensitive transition, yet, they have been found to exhibit substantial sensitivity towards even minor coordination changes around Ln(III) ion, due to the difference in the binding behaviour and changes in the immediate coordination environment around Ln(III) ion. Such transitions are regarded as ligand mediated pseudo hypersensitive transitions [15] . Karraker [16] shows the interrelation between the coordination number with the shape, energy and oscillator strengths of hypersensitive and pseudo-hypersensitive transitions.

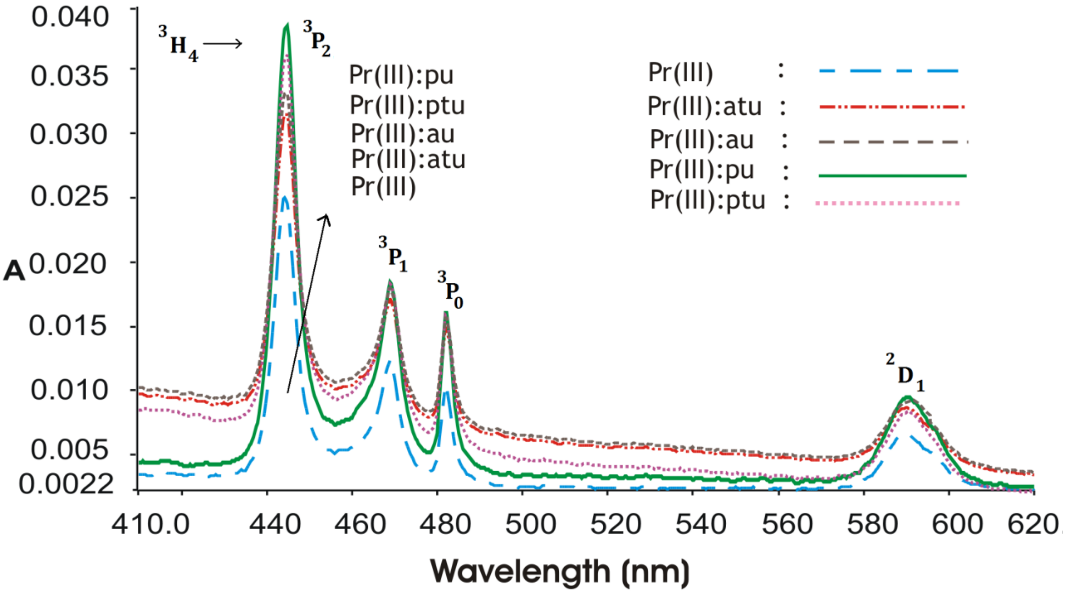

Figure 1 Comparative absorption spectra of Pr(III), Pr(III):atu, Pr(III):au:, Pr(III):ptu, Pr(III):pu in DMF

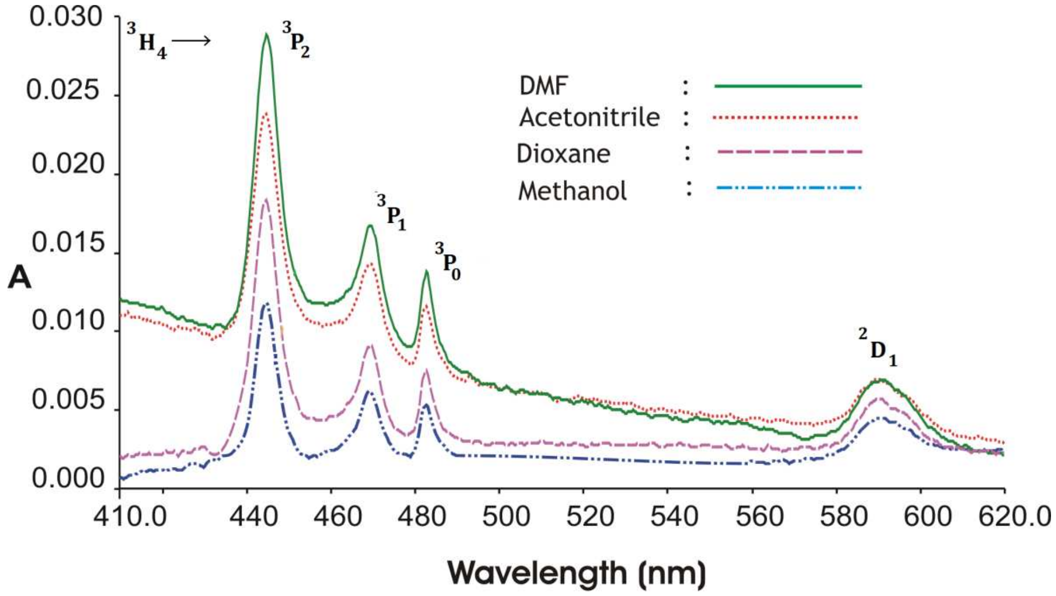

Figure 2 Comparative absorption spectra of Pr(III):pu in Methanol, Acetonitrile, dioxane and DMF

On complexation of Pr (III) with the ureas and thioureas, we observed reduction in the values of interelectronic repulsion parameters, Slator–Condon and spin–orbit coupling constant (**Table 1**). This phenomenon is referred to as nephelauxetic effect. Nephelauxetic effect is taken as a measure of metal–ligand covalent bonding. This effect may be visualized to be due to an expansion of the wave functions which results from interaction between the metal cations and neighbouring ligands. The Nephelauxetic effect increases as the co-ordination number decreases. For spectral studies on the structures of coordination compounds of lanthanides in solution, any evidence of the relationship between the Nephelauxetic band shift and the structure is of special interest. The variation in the value of E^k (k = 2, 4, 6) corresponds to that in the value of (F_k), since they are interrelated. Misra *et al.* [17-18] observed a general decrease in the value of F_k, E^k and ξ_{4f} parameters as compared to corresponding parameters of the free ion. The values of Nephelauxetic effect (β) in all the system is less than unity and the values of the bonding parameter ($b^{1/2}$) are positive which indicates covalent bonding. The marginal decrease in the values of F_k and ξ_{4f} indicating complexation leads to the increase in the values of Nephelauxetic ratio and percentage covalency (**Table 1**). From the table the decrease in the bonding parameter is found to be lowest for phenyl urea(pu) when DMF is the solvent.

Table 1 Computed value of energy interaction Slater Condon F_k (cm^{-1}), Spin orbit interaction ξ_{4f} (cm^{-1}), Racah energy E^K (cm^{-1}), Nephelauxetic ratio (β), bonding ($b^{1/2}$) and covalency (δ) parameters of Pr(III), Pr(III):atu, Pr(III):au, Pr(III) : ptu and Pr(III): pu systems in different organic solvents :

System	F_2	F_4	F_6	ξ_{4f}	E^1	E^2	E^3	β	$b^{1/2}$	δ
1. CH_3CN										
Pr(III)	309.1868	42.6842	4.6687	722.4906	3510.7080	23.7576	586.6717	0.9468	0.1630	5.6156
Pr(III) : atu	309.1774	42.6819	4.6686	722.4497	3510.6020	23.7568	586.6539	0.9468	0.1631	5.6203
Pr(III) : au	309.1696	42.6809	4.6685	722.4255	3510.5120	23.7562	586.6390	0.9468	0.1632	5.6234
Pr(III) : ptu	309.1546	42.6701	4.6682	722.4352	3510.3124	23.7555	586.6100	0.9452	0.1633	5.6239
Pr(III): pu	309.1473	42.6778	4.6681	722.4191	3510.2600	23.7545	586.5967	0.9468	0.1633	5.6245
2. DMF										
Pr(III)	309.0868	42.6694	4.6672	721.5003	3509.5730	23.7499	586.4819	0.9460	0.1643	5.7076
Pr(III) : atu	309.0503	42.6644	4.6667	721.2606	3509.1580	23.7471	586.4126	0.9458	0.1646	5.7319
Pr(III) : au	309.0295	42.6615	4.6663	720.9412	3508.9220	23.7455	586.3732	0.9455	0.1650	5.7598
Pr(III) : ptu	308.9701	42.6533	4.6654	721.1192	3508.2470	23.7409	586.2604	0.9456	0.1650	5.7559
Pr(III): pu	308.9810	42.6410	4.6641	721.0352	3508.1235	23.7310	586.1523	0.9452	0.1652	5.7623
3. Dioxane										
Pr(III)	309.1618	42.6798	4.6683	722.4318	3510.4240	23.7556	586.6241	0.9468	0.1632	5.6242
Pr(III) : atu	309.1415	42.6770	4.6680	722.3118	3510.1940	23.7541	586.5858	0.9466	0.1633	5.6367
Pr(III) : au	309.1308	42.6755	4.6679	722.1599	3510.0720	23.7533	586.5654	0.9465	0.1635	5.6500
Pr(III) : ptu	309.0771	42.6681	4.6671	722.1616	3509.4630	23.7491	586.4636	0.9464	0.1636	5.6586
Pr(III): pu	308.9852	42.6512	4.6652	722.1421	3509.1256	23.7482	586.4123	0.9463	0.1637	5.6599
4. CH_3OH										
Pr(III)	309.1904	42.6837	4.6688	722.5815	3510.7490	23.7578	586.6785	0.9469	0.1629	5.6081
Pr(III) : atu	309.1825	42.6826	4.6687	722.5599	3510.6590	23.7572	586.6635	0.9469	0.1630	5.6110
Pr(III) : au	309.1075	42.6723	4.6675	722.6085	3509.8080	23.7515	586.5212	0.9468	0.1631	5.6195
Pr(III) : ptu	309.0376	42.6626	4.6665	722.5609	3509.0140	23.7461	586.3886	0.9467	0.1633	5.6346
Pr(III): pu	309.0012	42.6523	4.6652	722.5512	3508.9854	23.7421	586.3421	0.9466	0.1635	5.6496
5. CH_3CN + DMF										
Pr(III)	309.1614	42.6797	4.6683	722.3155	3510.4200	23.7556	586.6235	0.9467	0.1633	5.6331
Pr(III) : atu	309.1370	42.6764	4.6680	722.1230	3510.1430	23.7537	586.5772	0.9465	0.1635	5.6518
Pr(III) : au	309.1064	42.6721	4.6675	722.1057	3509.7950	23.7514	586.5190	0.9464	0.1636	5.6581
Pr(III) : ptu	309.0852	42.6912	4.6669	722.0852	3509.0012	23.7496	586.4123	0.9465	0.1637	5.6679
Pr(III): pu	309.0305	42.6617	4.6664	722.0054	3508.9330	23.7456	586.3750	0.9463	0.1639	5.6782
6. CH_3CN:Dioxane										
Pr(III)	309.1532	42.6786	4.6682	722.1235	3510.3260	23.7550	586.6079	0.9465	0.1635	5.6491
Pr(III) : atu	309.0968	42.6708	4.6674	722.1799	3509.6870	23.7507	586.5009	0.9465	0.1636	5.6540
Pr(III) : au	309.0672	42.6667	4.6669	722.1083	3509.3500	23.7484	586.4446	0.9464	0.1637	5.6643
Pr(III) : ptu	308.5461	42.6521	4.6654	722.2101	3509.4521	23.7412	586.6210	0.9461	0.1632	5.6601
Pr(III): pu	308.9135	42.6455	4.6646	722.4971	3507.6050	23.7366	586.1531	0.9464	0.1637	5.6597
7. DMF : Dioxane										
Pr(III)	309.1219	42.6743	4.6677	722.0259	3509.9720	23.7526	586.5486	0.9464	0.1637	5.6617
Pr(III) : atu	309.0830	42.6689	4.6672	721.7743	3509.5300	23.7496	586.4748	0.9462	0.1640	5.6873
Pr(III) : au	309.0283	42.6614	4.6663	721.5342	3508.9098	23.7454	586.3709	0.9459	0.1644	5.7146
Pr(III) : ptu	308.9825	42.6410	4.6651	721.1230	3508.7801	23.7352	586.3189	0.9412	0.1658	5.7612
8. CH_3OH + CH_3CN										
Pr(III)	309.1539	42.6787	4.6682	722.0024	3510.3340	23.7550	586.6029	0.9464	0.1636	5.6583
Pr(III) : atu	309.0649	42.6664	4.6669	722.4288	3509.3240	23.7482	586.4403	0.9466	0.1634	5.6402
Pr(III) : au	309.0807	42.6686	4.6671	722.1069	3509.5030	23.7494	586.4703	0.9464	0.1637	5.6622
Pr(III) : ptu	309.0199	42.6602	4.6662	722.0146	3508.8130	23.7447	586.3549	0.9463	0.1639	5.6792
Pr(III): pu	308.9751	42.6512	4.6645	721.9852	3508.5421	23.7412	586.1254	0.9459	0.1652	5.6801
9. CH_3OH+DMF										
Pr(III)	309.1438	42.6773	4.6681	722.2325	3510.2190	23.7543	586.5900	0.9466	0.1634	5.6423
Pr(III) : atu	309.1194	42.6739	4.6677	722.0470	3509.9430	23.7524	586.5438	0.9464	0.1637	5.6605
Pr(III) : au	308.9857	42.6555	4.6657	721.0687	3508.4240	23.7421	586.2900	0.9456	0.1650	5.7572
Pr(III) : ptu	308.9805	42.6549	4.6656	721.1256	3508.8951	23.7417	586.2841	1.2543	0.1676	5.7210
Pr(III): pu	308.9781	42.6544	4.6656	721.7072	3508.3380	23.7415	586.2757	0.9460	0.1643	5.7096
10. CH_3OH + Dioxane										
Pr(III)	309.1648	42.6802	4.6684	722.3130	3510.4580	23.7559	586.6299	0.9467	0.1633	5.6328
Pr(III) : atu	309.1525	42.6785	4.6682	722.2290	3510.3180	23.7549	586.6065	0.9466	0.1634	5.6412
Pr(III) : au	309.0875	42.6695	4.6672	722.0999	3509.5800	23.7499	586.4832	0.9464	0.1637	5.6627
Pr(III) : ptu	309.0452	42.6656	4.6665	722.1213	3509.9861	23.7475	586.4123	0.9462	0.1637	5.6656
Pr(III): pu	309.0242	42.6608	4.6663	722.1413	3508.8610	23.7451	586.3630	0.9461	0.1638	5.6688

Tables 2 gives the computed and observed values of energies for the various transition bands and root mean square (RMS) deviation showing the correctness of the various energy parameters. For Pr(III), the values of Eobs is larger than that of Ecal and with the addition of ligands there is decrease in the values of the energies showing there is complexation. The estimated r. m. s values for Pr(III) for these complexes indicated the accuracy of the method to be sufficient for parametric calculation.

Table 2 Computed and Observed values of Energies(cm^{-1}) and R.M.S. values for Pr(III), Pr(III):atu, Pr(III):au, Pr(III) : ptu and Pr(III): pu in different organic solvents

System	$^3H_4 \rightarrow$	$^3P_2$	$^3H_4 \rightarrow$	$^3P_1$	$^3H_4 \rightarrow$	$^3P_0$	$^3H_4 \rightarrow$	$^1D_2$	R.M.S
	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	Eobs	Ecal	
1. CH_3CN									
Pr(III)	22511.37	22462.58	21327.87	21251.54	20746.46	20746.46	16971.88	17141.19	100.00
Pr(III) : atu	22510.86	22461.74	21326.96	21250.72	20746.03	20689.79	16970.72	17140.64	100.32
Pr(III) : au	22509.85	22461.09	21326.05	21250.07	20745.60	20689.20	16970.44	17140.21	100.19
Pr(III) : ptu	22509.64	22460.85	21325.85	21249.01	20744.98	20688.52	16970.12	17139.01	100.23
Pr(III): pu	22509.34	22459.75	21325.14	21248.65	20743.88	20687.70	16969.00	17139.29	100.58
2. DMF									
Pr(III)	22506.81	22450.85	21321.05	21240.60	20744.74	20681.63	16946.28	17133.72	110.36
Pr(III) : atu	22496.68	22447.17	21320.60	21237.08	20743.02	20678.61	16943.41	17131.34	110.56
Pr(III) : au	22490.61	22444.16	21319.69	21234.36	20743.02	20676.54	16938.82	17129.46	112.03
Pr(III) : ptu	22489.52	22442.52	21318.45	21262.45	21741.23	20674.23	16937.99	17128.56	112.01
Pr(III): pu	22487.58	22441.04	21317.87	21230.90	20737.85	20672.71	16937.38	17127.24	111.83
3. DXN									
Pr(III)	22512.89	22460.59	21325.60	21249.55	20745.17	20688.66	16967.85	17139.87	101.62
Pr(III) : atu	22510.36	22458.62	21324.69	21247.66	20744.31	20687.01	16964.97	17138.59	102.52
Pr(III) : au	22508.84	22457.13	21324.23	21246.30	20744.31	20685.97	16961.80	17137.66	103.77
Pr(III) : ptu									
Pr(III): pu	22504.78	22453.52	21322.42	21242.55	20740.43	20682.21	16958.35	17135.20	104.49
4. CH_3OH									
Pr(III)	22517.96	22463.28	21329.24	21252.15	20746.46	20690.96	16969.00	17141.62	102.24
Pr(III) : atu	22517.45	22462.63	21328.33	21251.51	20746.03	20690.36	16968.42	17141.19	102.29
Pr(III) : au	22516.44	22457.82	21329.24	21246.45	20740.43	20685..19	16959.21	17137.89	106.38
Pr(III) : ptu	22509.85	22452.86	21324.23	21241.37	20735.70	20680.20	16956.34	17134.54	106.01
Pr(III): pu									
5. CH_3CN:DMF									
Pr(III)	22508.84	22459.98	21325.14	21249.06	20745.60	20688.41	16968.42	17139.52	100.89
Pr(III) : atu	22503.26	22457.37	21323.33	21246.59	20744.74	20686.34	16966.12	17137.84	101.11
Pr(III) : au	22500.73	22455.21	21322.87	21244.37	20742.58	20684.15	16963.53	17136.38	101.89
Pr(III) : ptu	22499.21	22449.58	21319.69	21238.66	20737.85	20678.63	16954.32	17132.60	105.26
Pr(III): pu									
6. CH_3CN:DXN									
Pr(III)	22511.37	22458.46	21327.87	21247.72	20746.03	20687.47	16960.08	17138.58	105.49
Pr(III) : atu	22508.84	22454.94	21326.51	21244.00	20741.72	20683.63	16956.05	17136.15	106.68
Pr(III) : au	22506.30	22452.58	21324.23	21241.64	20740.00	20681.41	16953.75	17134.58	107.05
Pr(III) : ptu	22503.26	22444.15	21312.42	21232.42	20727.54	20671.37	16950.30	17128.65	105.90
Pr(III): pu									
7. DMF : Dioxane									
Pr(III)	22507.32	22455.86	21324.69	21245.15	20744.31	20685.09	16958.64	17136.86	105.17
Pr(III) : atu	22498.20	22451.97	21322.87	21241.42	20742.58	20681.88	16955.47	17134.34	105.41
Pr(III) : au	22494.66	22447.06	21319.23	21236.63	20740.00	20677.59	16948.00	17131.13	107.84
Pr(III) : ptu	22488.59	22439.43	21311.06	21228.68	20731.83	20669.55	16942.26	17125.91	108.18
Pr(III): pu	22482.42	22435.23	21301.52	21212.52	20725.52	20661.56	16939.45	17122.87	107.21
8. CH_3OH +CH_3CN									
Pr(III)	22515.42	22457.90	21327.87	21247.29	20746.89	20687.29	16955.19	17138.26	108.25
Pr(III) : atu	22511.88	22454.03	21326.96	21242.75	20738.28	20681.86	16954.32	17135.41	107.72
Pr(III) : au	22506.30	22453.48	21326.51	21242.58	20740.86	20682.35	16954.04	17135.20	107.33
Pr(III) : ptu	22500.22	22448.91	21322.42	21237.95	20736.99	20677.91	16950.59	17132.13	107.49
Pr(III): pu	22498.22	22445.41	21320.31	21221.24	20714.52	20672.25	16948.23	17130.45	108.21
9. CH_3OH : DMF									
Pr(III)	22508.33	22458.38	21326.05	21247.50	20744.74	20687.02	16964.11	17138.46	102.95
Pr(III) : atu	22501.74	22455.80	21322.42	21245.06	20743.88	20684.96	16963.82	17136.81	101.85
Pr(III) : au	22497.70	22441.84	21319.69	21231.79	20739.57	20673.71	16930.79	17127.81	116.19
Pr(III) : ptu	22488.08	22444.54	21309.24	21233.80	20735.70	20674.39	16955.47	17129.32	101.94
Pr(III): pu	22481.12	22435.12	21301.52	21225.81	20731.52	20647.12	16949.52	17132.56	112.52
10. CH_3OH : Dioxane									
Pr(III)	22513.90	22460.20	21326.05	21249.29	20746.03	20688.65	16964.97	17139.66	103.18
Pr(III) : atu	22512.38	22458.95	21324.69	21248.10	20745.60	20687.62	16963.53	17138.85	103.47
Pr(III) : au	22510.86	22453.90	21322.87	21243.03	20741.72	20682.81	16954.32	17135.49	107.13
Pr(III) : ptu	22504.78	22449.84	21318.33	21238.76	20736.99	20678.45	16953.46	17132.70	105.95
Pr(III): pu	22503.41	22447.72	21316.64	21237.15	20735.12	20676.52	16949.54	17130.89	107.59

Table 3 Experimental values of oscillator strength (P x 10^6) (observed and calculated) and Judd-Ofelt parameter (T_λ x 10^{10}) cm^{-1} for Pr(III), Pr(III):atu, Pr(III):au, Pr(III) : ptu and Pr(III): pu complexes in different organic solvents

System	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}			
1. CH_3CN											
Pr(III)	0.8754	0.8754	0.3892	0.5621	0.7465	0.5709	3.1291	3.1291	-8.5797	1.5681	9.8394
Pr(III) : atu	0.9202	0.9202	0.4088	0.5914	0.7860	0.6006	3.2489	3.2489	-6.4838	1.6498	10.2098
Pr(III) : au	0.9659	0.9659	0.4209	0.6031	0.7976	0.6125	3.1369	3.1369	11.2974	1.6822	9.8386
Pr(III) : ptu	0.9786	0.9786	0.4199	0.6013	0.7991	0.6129	3.1489	3.1489	12.8974	1.6872	9.8745
Pr(III): pu	0.9903	0.9903	0.4195	0.6041	0.8009	0.6134	3.1579	3.1579	15.3466	1.6849	9.9002
2. Dioxane											
Pr(III)	0.5566	0.5566	0.5733	0.6044	0.6454	0.6138	2.5737	2.5737	-44.5426	1.6861	7.9864
Pr(III) : atu	0.6312	0.6312	0.4355	0.6066	0.7897	0.6160	2.8463	2.8463	-80.8040	1.6921	8.8796
Pr(III) : au	0.6752	0.6712	0.4495	0.7000	0.8621	0.7001	3.0012	3.0012	-45.2356	1.8523	9.2531
Pr(III) : ptu	0.7274	0.7274	0.4679	0.7024	0.9513	0.7132	3.5963	3.1996	-47.0844	1.9594	9.9649
Pr(III): pu	0.7894	0.7894	0.5093	0.7244	0.9539	0.7356	3.5963	3.5963	-59.2524	2.0206	11.2508
3. DMF											
Pr(III)	0.6176	0.6176	0.3918	0.5459	0.7107	0.5543	2.7538	2.7538	-42.3365	1.5227	8.6220
Pr(III) : atu	0.6077	0.6077	0.3948	0.5586	0.7336	0.5672	3.1254	3.1254	-68.9790	1.5227	8.6220
Pr(III) : au	0.7037	0.7037	0.4570	0.6500	0.8559	0.6600	3.1811	3.1811	-51.0522	1.8134	9.9539
Pr(III) : ptu	0.7256	0.7256	0.4653	0.6312	0.8752	0.6852	3.2897	3.2897	-52.0897	1.9235	9.9952
Pr(III): pu	0.8055	0.8055	0.4512	0.6264	0.8138	0.6360	3.3069	3.3069	-36.1076	1.7474	10.3844
4. CH_3OH											
Pr(III)	0.4214	0.4214	0.3661	0.4727	0.5884	0.4801	2.4373	2.4373	-65.8177	1.3186	7.6357
Pr(III) : atu	0.5237	0.5237	0.3952	0.5000	0.6152	0.5086	2.7196	2.7190	99.2080	1.3971	0.5181
Pr(III) : au	0.5244	0.52444	0.3808	0.4995	0.6279	0.5073	2.6391	2.6391	-55.6982	1.3934	8.2768
Pr(III) : ptu	0.5156	0.5156	0.3845	0.5012	0.6301	0.5100	2.6412	2.6412	-57.2589	1.4001	8.2878
Pr(III): pu	0.5058	0.5058	0.3895	0.5055	0.6310	0.5132	2.6459	2.6459	-60.4543	1.4095	8.2957
5. Dioxane+CH_3CN											
Pr(III)	0.5963	0.5963	0.3538	0.4983	0.6513	0.5049	2.5753	2.5753	-35.2774	1.3868	8.0723
Pr(III) : atu	0.6192	0.6192	0.3749	0.5273	0.6902	0.5355	2.6514	2.6514	-35.1697	1.4708	8.3003
Pr(III) : au	0.7103	0.7103	0.3875	0.5386	0.7004	0.5470	2.5840	2.5840	-10.1250	1.5023	8.0698
Pr(III) : ptu	0.7241	0.7241	0.3899	0.5412	0.7013	0.5512	2.5941	2.5941	-11.5231	1.5236	8.052
Pr(III): pu	0.6935	0.6935	0.3733	0.5294	0.6962	0.5377	2.5740	2.5740	-13.2616	1.4767	8.0446
6. DMF+Dioxane											
Pr(III)	0.6183	0.6183	0.3455	0.4830	0.6302	0.4905	2.5851	2.5851	-30.9118	1.3476	8.1164
Pr(III) : atu	0.6097	0.6097	0.3515	0.4904	0.6391	0.4980	22 2.5817	2.5817	-32.7068	1.3683	8.1032
Pr(III) : au	0.7563	0.7563	0.4071	0.6003	0.8058	0.6096	2.4997	2.4997	5.6078	1.6748	7.7536
Pr(III) : ptu	0.7712	0.7712	0.4123	0.6123	0.8512	0.7213	2.5114	2.5114	3.5621	1.6941	7.8512
Pr(III): pu	0.6667	0.6667	0.3493	0.5074	0.6758	0.5152	2.5214	2.5215	-15.8335	1.4156	7.8935
7. CH_3OH+DMF											
Pr(III)	0.7630	0.7630	0.3853	0.5394	0.7056	0.5488	2.6414	2.6414	-2.0257	1.5075	8.2579
Pr(III) : atu	0.7849	0.7849	0.3911	0.5619	0.7439	0.5705	2.6942	2.6942	-0.6643	1.5675	8.4176
Pr(III) : au	0.7986	0.7986	0.3146	0.5287	0.7543	0.5369	2.5987	2.5987	9.1357	1.4750	8.1306
Pr(III) : ptu	0.8413	0.8413	0.3542	0.5364	0.7613	0.5512	2.6012	2.6012	10.1589	1.5891	8.2351
Pr(III): pu	0.8687	0.8687	0.3960	0.5774	0.7705	0.5863	2.7176	2.7176	16.7818	1.6108	8.4842
8. DMF+CH_3CN											
Pr(III)	0.7378	0.7378	0.3857	0.5546	0.7347	0.5632	2.7172	2.7172	-12.7957	1.5471	8.4957
Pr(III) : atu	0.7961	0.7961	0.3697	0.5549	0.7515	0.5634	2.7498	2.7498	-1.7890	1.5480	8.6046
Pr(III) : au	0.7885	0.7885	0.3988	0.5684	0.7493	0.5771	2.7508	2.7508	-3.4056	1.5855	8.5988
Pr(III) : ptu	0.8056	0.8056	0.4112	0.5912	0.7985	0.6012	2.7612	2.7645	-4.23	1.6213	8.6123
Pr(III): pu	0.8221	0.8221	0.4237	0.6124	0.8135	0.6219	2.7757	2.7757	2.3603	1.7085	8.6483
9. CH_3OH+Dioxane											
Pr(III)	0.7400	0.7400	0.3645	0.5236	0.6933	0.5313	2.4675	2.4675	4.2511	1.4606	7.6983
Pr(III) : atu	0.7479	0.7479	0.3735	0.5494	0.7366	0.5579	2.4887	2.4887	4.5695	1.5326	7.7491
Pr(III) : au	0.8094	0.8094	0.3732	0.5553	0.7488	0.5639	2.4847	2.4847	18.8669	1.5489	7.7311
Pr(III) : ptu	0.9562	0.8562	0.3799	0.5612	0.75864	0.5741	2.5123	2.5123	19.5231	1.5752	7.8621
Pr(III): pu	0.8988	0.8988	0.3898	0.5732	0.7684	0.5821	2.5544	2.5544	34.4843	1.5989	7.9458
10. CH_3OH+CH_3CN											
Pr(III)	0.6921	0.6921	0.3570	0.4953	0.6434	0.5030	2.5327	2.5327	-10.6821	1.3815	7.9326
Pr(III) : atu	0.7262	0.7262	0.3649	0.5064	0.6580	0.5143	2.5508	2.5508	-4.1833	1.4125	7.9836
Pr(III) : au	0.7398	0.7398	0.3671	0.5041	0.6510	0.5119	2.5349	2.5349	-0.1516	1.4060	7.9334
Pr(III) : ptu	0.7521	0.8521	0.6723	0.5212	0.6912	0.5623	2.5512	2.5512	2.3546	1.4231	7.9921
Pr(III): pu	0.7794	0.7794	0.3830	0.5499	0.7280	0.5585	2.5776	2.5776	5.9954	1.5338	8.0383

The absorption intensity data for 4f – 4f transitions in a series of Pr(III) complexes of ureas/ thioureas in different organic solvents are reported in **Table 3**. These are analyzed in terms of oscillator strength, Judd Ofelt intensity parameters T_λ (λ = 2,4,6) and changes in the ligands and solvent composition. The addition of ligands (urea/thiourea) to Pr(III) brings about a noticeable enhancement in the oscillator strength of pseudohypersensitive

4f–4f bands (irrespective of solvent nature). Consequently, marked variation in the experimentally determined Judd–Ofelt (T_λ) intensity parameters was found. This intensification of 4f–4f bands can be interpreted in terms of interaction of 4f-orbital with ligand wave function. The intensification of bands and red shift were taken as an evidence for the involvement of ligand in complexation. This intensification of 4f–4f bands became more prominent for phenyl than ally urea/thiourea.

In general comparing the variation observed in the energy interaction parameter (Fk and ξ_{4f}) with variation of oscillator strength and Judd Ofelt parameter (intensity parameter) towards minor coordination changes induced by the bonding of these different ureas and thioureas, it is because of this reason that the discussion of energy interaction parameter and energy parameter has been reduced merely to a minimum while main emphasis has been given for using intensity data for structural elucidation. The significant changes in the T_λ parameters in absence of significant nephelauxetic effect (as observed in present study) also show that the unsymmetrical part of the field has major influence on these parameters. Regarding this, Reisfeld [19] has argued that an increase in covalency is not the sole factor that influences T_λ parameters. The nephelauxetic effect, which is caused by lowering of the excited states of lanthanide ion by the surrounding crystal field, is influenced mainly by the asymmetric part of the crystal field. The values of T_λ parameters change significantly on varying the composition of solvents. T_2 is found to be negative so it is meaningless in the present study. T_4 and T_6 are affected significantly. Both parameters are related not only to the immediate coordination changes but also to changes in symmetry properties of the complex species [20]. The different potential donor sites are responsible for the distortion of the polyhedron of oxygen/sulphur around Pr(III), lowering the site symmetry and increasing the probability of the 4f – 4f transition.

Absorption spectra of Pr(III) complex in different organic solvents (**Figure 2**) clearly shows the affinity of solvents towards the Pr(III) coordination environment. The small differences in the 4f–4f band shape in the different solvents may be related to differences in how the donor groups interact with f-electrons of the lanthanide ion. DMF appears to have strongest influence on Pr(III):pu followed by dioxane and least in acetonitrile. This means that DMF is effective in promoting 4f– 4f electric dipole intensity [21-23], and to cause alternation in strength and symmetry of field about Pr(III). Changes in symmetry around Pr(III) along with invasion of solvent type lead to the intensification of 4f–4f bands.

CONCLUSION

From the above study it can be concluded that (i) The relative sensitivities of different 4f-4f transition bands towards these minor coordination changes and their correlation in terms of different T_λ-parameters also indicated clearly that all the T_λ parameters are exhibiting sensitivities towards the structural changes. In case of Pr(III) , T_6 is most significant followed by T_4 while T_2 is invalid because sometimes its values is coming negative. ii) Maximum intensification was induced by phenyl urea while ally thiourea imparted lowest intensity to the 4f – 4f bands. They are observed in the order atu < au < ptu < pu. iii) The solvent also induced varying intensification to the pseudohypersensitive bands; DMF induced maximum intensification followed by solvent mixture comprising of DMF and methanol. Urea in general have been found to be better ligand as compared to analogous thiourea ligands , due to the higher affinity of O-donor atom of ureas by the hard metal ion Ln(III) then S-donor atoms of thioureas . Moreover, the π- electron density have also played a major role towards the intensification of bands.

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