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Comparison of Electric-dipole Intensity Parameter for a Series of Structurally Related Pr(III) Complexes with Ureas and Thioureas in Non-aqueous Media

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Absorption difference and comparative absorption spectrophotometric studies involving 4*f*–4*f* transitions on praseodymium(III) and different ureas—phenyl urea, biphenyl urea, allyl urea, ethylene urea tetramethyl urea and thioureas—phenyl thiourea, biphenyl thiourea, allyl thiourea, ethylene thiourea and tetramethyl thiourea have been carried out in DMF and CH_3OH as well as in DMF-CH_3OH, DMF-CH_3CN, DMF-dioxane, CH_3OH-CH_3CN and CH_3CN-dioxane mixtures. The small chemical and structural differences due to the ligands and solvents are shown to produce significant variation in the intensities of observed 4*f*–4*f* absorption bands and their relative perturbation on 4*f*–4*f* transition intensities are readily apparent in the Judd-Ofelt electric dipole (T_λ, $\lambda = 2, 4, 6$) parameters determined for these complexes. Some correlations have also been made from the plots of oscillator strengths of different transitions against T_λ parameters which represent the relative sensitivities of different 4*f*–4*f* transitions.

Key Words: Praseodymium(III), Complexes, Ureas, Thioureas, Hypersensitive, Pseudohypersensitive.

INTRODUCTION

The 4*f*–4*f* absorption spectra of most lanthanide complexes in solution (both aqueous and non-aqueous) exhibit absorption bands assigned to specific ground multiplet to excited multiplet transition manifolds. Each multiplet to multiplet transition manifolds is generally comprised of a few unresolved transitions between individual crystal field levels of ground and excited multiplets. The 4*f*–4*f* transitions observed in the absorption spectra of trivalent lanthanide ions are induced electric dipole or magnetic dipole transitions. These electric dipole transitions of $4f^n$ configuration are parity forbidden, however, as a result of interaction between central lanthanide ion and surrounding ligands mixing into

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$4f^n$ configuration with configuration of opposite parity substantially relaxes the parity restriction.

The oscillator strength (P) of a $4f^n$–$4f^n$ electric dipole transition can be expressed as

$$P = \nu \sum_{\lambda = 2, 4, 6} T_\lambda \langle f^n \psi J || U^{(\lambda)} || f^n \psi' J' \rangle^2 \tag{1}$$

where ν is the $\psi J \rightarrow \psi' J'$ transition energy expressed in cm^{-1} and $U^{(\lambda)}$ is the unit tensor operator of the rank which connects the initial $\langle f^n \psi J|$ and the final $|f^n \psi' J'\rangle$ state through three phenomenological parameters T_λ ($\lambda = 2, 4, 6$). These parameters are related predominantly to the radial part of the $4f^n$ wave function of the perturbing configuration and the ligand field parameters that characterize the environment[1, 2].

Devlin *et al.*[3, 4] have made extensive absorption spectral studies on a series of Nd(III), Ho(III) and Er(III) complexes derived from structurally related ligands in aqueous medium and have shown that the minor structural differences are reflected through the significant variation of electric dipole intensity parameters.

The ligands used in the present study are substituted ureas and substituted thioureas which differ only with respect to their coordinating donor atom (oxygen in ureas and sulphur in thioureas).

EXPERIMENTAL

Pr(III) perchlorate (hydrated) was dissolved in isopropanol and a little amount of benzene was added. The mixture was shaken thoroughly and the ternary azeotrope of benzene, water and isopropanol was distilled out under reduced pressure. This process of azeotropic dehydration was repeated four times to yield anhydrous Pr(III) perchlorate.

The reactions of Pr(III) perchlorate and ureas/thioureas in 1 : 10 molar ratio were carried out in anhydrous solvent. The reaction mixture was heated under reflux for 24 h. The reaction resulted in separation of solid with the stoichiometry $[Pr(urea/thoiurea)_6(solv.)_3](ClO_4)_3$.

Absorption spectra were recorded on a Perkin-Elmer Lambda-35 UV-Visible spectrophotometer modified to record the spectra with much improved resolution. The concentration of Pr(III) in the final solution kept at 10 mM and the spectra were recorded at 298K. The spectra obtained over 25000–12500 cm^{-1} region which showed four bands, originating from the ground multiplet $^3H_4$, as $^3P_2 \leftarrow {}^3H_4$, $^3P_1 \leftarrow {}^3H_4$, $^3P_0 \leftarrow {}^3H_4$ and $^1D_2 \leftarrow {}^3H_4$, of which the second band is a combination of $^3P_1 \leftarrow {}^3H_4$ and $^1I_6 \leftarrow {}^3H_4$ transitions.

The spectra were first analyzed by linear curve analysis followed by Gaussian curve analysis of the individual absorption band. The experimental oscillator strengths are obtained by using the equation

$$P = (4.32 \times 10^{-9}) \int \varepsilon_{max}(\nu)\, d\nu \tag{2}$$

where ε_{max} is the molar extinction coefficient and ν is the energy of the band in cm^{-1}.

The calculated oscillator strength can be expressed in terms of T_λ parameters as

$$\frac{P_{cal.}}{\nu} = [U^{(2)}]^2 \cdot T_2 + [U^{(4)}]^2 \cdot T_4 + [U^{(6)}]^2 \cdot T_6 \qquad (3)$$

The transition energies and the intra-configurational $U^{(\lambda)}$ matrix elements[5] used for the intensity analysis[5] are given in Table-1. The oscillator strength (P) and Judd-Ofelt (T_λ) parameters used in the discussions have usual significance and their evaluation method has been discussed earlier[2, 6–9].

TABLE-1

TRANSITION ENERGIES AND INTRACONFIGURATIONAL $U^{(\lambda)}$ MATRIX ELEMENT[5] FOR Pr(III)

Level	Approx ν (cm^{-1})	$[U^{(2)}]$	$[U^{(4)}]$	$[U^{(6)}]$
$^1D_2$	16780	0.0029	0.0192	0.0618
$^3P_0$	20770	0.0000	0.1719	0.0000
$^3P_1$	21360	0.0000	0.1708	0.0000
$^1I_6$	21400	0.0087	0.0482	0.0220
$^3P_2$	22500	0.0000	0.0366	0.1247

All transitions originate from $^3H_4$ ground multiplet.

RESULTS AND DISCUSSION

Ureas and thioureas, though ambidentate ligands, bind to metal usually as unidentate neutral ligand corresponding to Pr(III) through oxygen and sulphur donor atoms. The complexes investigated are of the type $PrL_6L'_3$, where L is urea or thiourea and L′ is solvent. These complexes provide a nona-coordinated environment around Pr(III) where the L donor atoms of the ligands are located at the vertices of a trigonal prism where three L′ donor atoms of the solvent molecules occupy the capping position on normal to the rectangular faces of the prism. Thus the major structural differences are found in: (i) the nature of L donor atom and the type of substituent on the urea and thiourea moiety, and (ii) the nature of L′ of the solvent.

Exceptional behaviour of praseodymium and ligand mediated pseudohypersensitivity:

Generally out of several 4*f*–4*f* bands observed in lanthanide absorption spectra, some of them exhibit extremely high sensitivity towards even minor coordination changes around lanthanide and they are characterized by large values of $U^{(2)}$ matrix elements and contributed significant variation of T_2 parameter. Such transitions are considered hypersensitive transitions[10] and they are found to obey

TABLE-2

EXPERIMENTAL VALUES OF OSCILLATOR STRENGTH ($P \times 10^6$) (OBSERVED AND CALCULATED) AND JUDD-OFELT PARAMETER ($T_\lambda \times 10^{10}$) cm^{-1} FOR Pr(III)-UREA COMPLEXES IN DIFFERENT SOLVENTS

Compound	$^3H_4 \rightarrow {^3P_2}$		$^3H_4 \rightarrow {^3P_1}$		$^3H_4 \rightarrow {^3P_0}$		$^3H_4 \rightarrow {^1D_2}$		T_2	T_4	T_6	$T_{(\lambda)}$ (complex)/ $T_{(\lambda)}$ (aquo)		r.m.s.
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}				$\lambda = 4$	$\lambda = 6$	
1. Solvent: DMF														
Pr(III)-au	17.562	17.56	7.043	3.19	4.983	4.98	5.016	5.02	–352.87	14.52	57.80	3.405	1.870	1.920
Pr(III)-pu	21.874	21.87	11.630	14.56	7.706	7.71	8.408	8.41	–20.95	23.25	70.47	5.050	2.289	1.460
Pr(III)-tmu	21.276	21.28	8.133	13.54	7.227	7.23	8.875	8.87	114.50	18.84	69.68	4.017	2.271	2.700
Pr(III)-eu	20.282	20.28	7.061	0.64	3.165	3.16	5.223	5.22	–517.13	11.98	68.16	2.667	2.224	3.210
Pr(III)-dpu	22.172	22.17	8.711	5.08	4.979	4.98	6.662	6.66	–381.17	16.30	73.57	3.575	2.398	1.810
2. Solvent: DMF + CH_3OH														
Pr(III)-au	10.886	10.89	2.265	0.62	2.386	2.39	3.297	3.30	–180.87	5.87	36.79	1.215	1.205	0.820
Pr(III)-pu	13.822	13.82	3.458	3.13	2.670	2.67	4.675	4.67	–135.84	7.45	46.66	1.601	1.525	0.165
Pr(III)-tmu	13.120	13.12	3.969	0.46	2.151	2.15	3.301	3.30	–350.36	7.26	44.24	1.630	1.443	1.760
Pr(III)-eu	11.081	11.08	3.934	2.23	1.649	1.65	3.355	3.35	–185.72	6.51	37.25	0.937	1.241	0.855
Pr(III)-dpu	20.024	20.02	9.704	8.79	5.611	5.61	6.691	6.69	–214.14	18.24	65.40	3.998	2.127	0.450
3. Solvent: DMF + Dioxane														
Pr(III)-au	14.234	14.23	7.831	11.99	4.206	4.21	6.091	6.09	106.78	14.27	46.10	3.140	1.496	2.080
Pr(III)-pu	18.464	18.46	13.356	13.11	5.223	5.22	6.360	6.36	–161.99	21.58	58.91	4.845	1.903	0.130
Pr(III)-tmu	17.494	17.49	7.825	8.20	4.227	4.23	6.161	6.16	–125.13	14.29	57.62	3.144	1.875	0.190
Pr(III)-eu	15.681	15.68	7.714	6.78	4.315	4.31	5.181	5.18	–179.32	14.29	51.22	3.138	1.664	0.460
Pr(III)-dpu	20.628	20.63	10.858	10.87	5.634	5.63	7.164	7.16	–169.16	19.50	67.19	4.304	2.182	0.060

Compound	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6	$T(\lambda)$ (complex)/ $T(\lambda)$ (aquo)		r.m.s.
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}				$\lambda = 4$	$\lambda = 6$	
4. Solvent: DMF + CH_3CN														
Pr(III)-au	11.919	11.92	5.690	9.67	4.059	4.06	5.239	5.24	116.47	11.77	38.67	2.550	1.261	1.990
Pr(III)-pu	15.194	15.19	7.874	9.66	5.089	5.09	5.771	5.87	–28.20	15.55	49.12	3.393	1.600	0.890
Pr(III)-tmu	14.115	14.11	6.620	7.80	4.369	4.37	5.220	5.22	–52.89	13.21	45.99	2.877	1.500	0.590
Pr(III)-eu	14.065	14.06	6.916	5.30	4.163	4.16	4.427	4.43	–202.70	13.23	45.81	2.955	1.489	0.810
Pr(III)-dpu	17.159	17.16	6.761	2.86	8.619	4.62	4.861	4.86	–352.76	13.71	56.62	2.978	1.848	1.950
5. Solvent: CH_3OH														
Pr(III)-au	5.584	5.58	3.742	8.92	2.476	2.48	3.385	3.38	234.00	7.48	17.53	1.368	0.814	2.590
Pr(III)-pu	12.207	12.21	4.790	3.44	3.118	3.12	3.847	3.85	–174.74	9.50	40.36	2.070	1.319	0.670
Pr(III)-tmu	11.595	11.59	3.984	3.71	3.031	3.03	3.385	3.38	–219.03	8.51	38.46	1.837	1.259	1.130
Pr(III)-eu	9.315	9.31	3.020	4.15	2.533	2.53	3.535	3.53	–17.53	6.78	30.19	0.853	1.042	0.560
Pr(III)-dpu	14.039	14.04	8.175	6.86	3.318	3.32	4.509	4.51	–185.68	13.39	45.69	8.324	1.488	0.650
6. Solvent: CH_3OH + CH_3CN														
Pr(III)-au	8.022	8.02	4.933	7.32	2.610	2.61	3.452	3.45	63.28	8.93	25.72	4.459	0.835	1.190
Pr(III)-pu	10.872	10.87	6.037	9.22	3.960	3.96	4.664	4.66	82.72	12.01	34.89	2.617	1.136	1.590
Pr(III)-tmu	9.547	9.54	3.426	3.79	2.692	2.69	3.401	3.40	–60.35	7.44	31.53	5.503	1.031	0.180
Pr(III)-eu	9.231	9.23	4.057	5.00	3.068	3.07	3.465	3.46	–25.79	8.65	30.08	5.239	0.981	0.470
Pr(III)-dpu	12.744	12.74	5.162	6.40	3.880	3.88	4.755	4.75	–10.23	10.96	41.81	2.367	1.365	0.610

TABLE-3

EXPERIMENTAL VALUES OF OSCILLATOR STRENGTH ($P \times 10^6$) (OBSERVED AND CALCULATED) AND JUDD-OFELT PARAMETER ($T_\lambda \times 10^{10}$) cm^{-1} FOR Pr(III)-THIOUREA COMPLEXES IN DIFFERENT SOLVENTS

Compound	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6	$T_{(\lambda)}$ (complex)/ $T_{(\lambda)}$ (aquo)		r.m.s.
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}				$\lambda = 4$	$\lambda = 6$	
1. Solvent: DMF														
Pr(III)-atu	16.542	16.54	8.022	7.01	4.064	4.06	5.455	5.45	–191.60	14.27	54.27	3.297	2.106	0.50
Pr(III)-ptu	20.311	20.31	8.022	2.80	4.647	4.65	5.580	5.58	–150.58	15.10	67.35	3.308	2.195	2.61
Pr(III)-tmtu	20.222	20.22	8.939	6.26	5.154	5.15	6.262	5.26	–312.24	16.78	66.54	3.679	2.166	1.34
Pr(III)-etu	19.786	19.79	7.832	2.48	4.614	4.61	5.354	5.35	–156.01	14.84	65.59	3.250	2.137	2.70
Pr(III)-dptu	20.686	20.69	8.691	2.91	4.679	4.68	4.560	5.56	–183.33	15.85	68.47	3.490	2.230	2.89
2. Solvent: DMF + CH_3OH														
Pr(III)-atu	13.628	13.63	5.922	10.18	4.044	4.04	5.904	5.90	115.88	12.00	44.65	2.610	1.457	2.13
Pr(III)-ptu	15.423	15.42	8.957	9.30	4.543	4.54	5.455	5.45	–107.86	15.00	49.82	3.531	1.619	0.17
Pr(III)-tmtu	15.108	15.11	6.546	5.88	4.217	4.22	5.053	5.05	–161.14	12.92	49.61	2.818	1.619	0.34
Pr(III)-etu	13.776	13.78	6.291	9.73	4.334	4.33	5.729	5.73	71.26	12.80	44.94	2.783	1.466	1.72
Pr(III)-dptu	16.235	16.23	6.582	4.73	4.792	4.79	5.106	5.11	–234.14	13.76	53.32	2.977	1.778	0.89
3. Solvent: DMF + CH_3CN														
Pr(III)-atu	12.330	12.33	6.032	9.24	4.428	4.43	5.173	5.17	71.65	12.66	39.86	2.734	1.296	1.60
Pr(III)-ptu	14.037	14.04	6.237	4.05	3.978	3.98	4.257	4.26	–233.89	12.25	46.02	1.379	1.563	1.09
Pr(III)-tmtu	13.590	13.59	6.771	8.91	4.465	4.46	5.311	5.31	365.00	13.50	44.07	2.935	1.433	1.07
Pr(III)-etu	13.241	13.24	6.404	6.28	3.989	3.99	4.562	4.56	–115.37	12.44	43.14	2.931	1.392	0.06
Pr(III)-dptu	17.646	17.65	7.653	1.90	4.283	4.28	4.518	4.52	–455.93	14.18	58.22	10.11	1.895	2.87

Compound	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T_2	T_4	T_6	$T_{(\lambda)}$ (complex)/ $T_{(\lambda)}$ (aquo)		r.m.s.
	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}	P_{obs}	P_{cal}				$\lambda = 4$	$\lambda = 6$	
4. Solvent: DMF + Dioxane														
Pr(III)-atu	12.469	12.47	5.457	6.74	4.229	4.23	4.683	4.68	–33.81	11.77	40.62	2.537	1.326	0.64
Pr(III)-ptu	13.223	13.22	5.179	6.40	4.657	4.66	4.925	4.98	–43.75	12.08	43.18	2.574	1.409	0.61
Pr(III)-tmtu	11.277	11.38	4.396	4.19	2.980	2.98	3.880	3.88	–106.18	8.89	37.61	1.928	1.227	0.10
Pr(III)-etu	10.013	10.01	3.771	3.68	2.859	2.86	3.441	3.44	–88.20	8.04	33.01	1.734	1.078	0.04
Pr(III)-dptu	16.052	16.05	6.551	4.50	4.455	4.45	4.987	4.99	–243.75	13.25	52.82	2.669	1.778	1.02
5. Solvent: CH_3OH														
Pr(III)-atu	12.157	12.16	5.749	8.42	4.293	4.29	4.956	4.96	43.80	12.17	39.40	2.631	1.258	1.33
Pr(III)-ptu	15.641	15.64	5.809	5.04	4.451	4.45	5.198	5.20	–171.75	12.46	51.62	2.688	1.688	0.38
Pr(III)-tmtu	13.333	13.33	5.567	4.86	3.859	3.86	4.419	4.42	–148.99	11.37	43.77	2.467	1.430	0.35
Pr(III)-etu	13.048	13.05	5.900	7.72	4.281	4.28	5.026	5.03	–9.66	12.31	42.51	2.669	1.387	0.91
Pr(III)-dptu	15.880	15.88	6.086	4.24	3.922	3.92	4.979	4.98	–232.42	12.01	52.60	2.620	1.801	0.92
6. Solvent: $CH_3OH + CH_3CN$														
Pr(III)-atu	8.502	8.50	3.354	1.89	2.456	2.46	2.537	2.54	–149.02	7.03	27.98	1.518	0.921	0.73
Pr(III)-ptu	10.384	10.38	5.076	9.46	4.079	4.08	4.824	4.82	151.03	11.16	33.41	1.804	1.116	2.19
Pr(III)-tmtu	10.175	10.17	5.455	7.69	3.130	3.13	4.153	4.15	36.96	10.22	32.94	1.980	1.084	1.12
Pr(III)-etu	9.455	9.45	3.269	2.23	2.562	2.56	2.983	2.98	–135.09	7.09	31.32	1.524	1.022	0.52
Pr(III)-dptu	14.212	14.21	5.550	3.25	3.515	3.51	4.281	4.28	–242.29	10.86	47.03	2.367	1.532	—

the selection rules for quadrupole transitions. The other 4*f*–4*f* transitions are regarded only marginally sensitive or almost insensitive. It is expected that the intensities of hypersensitive transitions are modulated in large part by the variation of T_2 parameter. Pr(III), however, has been found to show exceptional behaviour. The transition $^3F_2 \leftarrow {}^3H_4$ (hypersensitive) occuring around 5200 cm^{-1} has not been observed in most of the spectral studies reported for Pr(III) complexes specially in solution. The values of T_2 parameters are often found to be negative which appears quite logical as the only transition having significant U^2 matrix ($^3F_2 \leftarrow {}^3H_4$) has not been included in the data available for spectral of any of the praseodymium complexes in solution. Therefore, to explain the spectra and structure relationship, in Pr(III) complexes, the T_6 and T_4 parameters along with the oscillator strengths of the observed four transitions are considered. In our absorption spectral studies involving Pr(III) and Nd(III), the unusual high sensitivity of $^3P_2 \leftarrow {}^3H_4$, $^3P_1 \leftarrow {}^3H_4$ and $^1D_2 \leftarrow {}^3H_4$ transitions of Pr(III) and $^4G_{7/2} \leftarrow {}^4I_{9/2}$, $^4F_{7/2} \leftarrow {}^4I_{9/2}$ and $^4F_{5/2} \leftarrow {}^4I_{9/2}$ transitions of Nd(III) in their complexes with ligands having different binding characteristics have been noted. We have considered these transitions as pseudohypersensitive transitions and used the name Ligand Medicated Pseudohypersensitive for such observation[11–13].

Comparative absorption spectra of Pr(III) complexes with substituted ureas/thioureas in non-aqueous media

Experimental oscillator strengths of different transitions and the determined values of Judd-Ofelt (T_λ) intensity parameters are given in Table-2. Comparative absorption spectra of Pr(III)-ureas in equimolar CH_3OH-dioxane mixture is given in Fig. 1. The figure clearly shows how the different substituents on urea affect the energies and oscillator strengths of the four pseudohypersensitive transitions. The

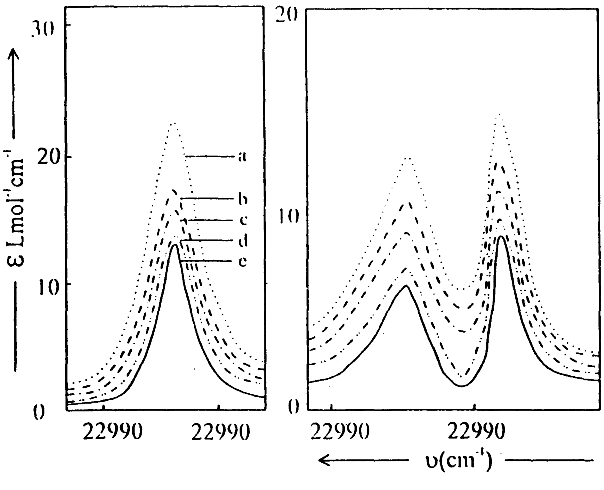

Fig. 1. Comparative absorption spectra of Pr(III) complexes with ureas: (a) biphenyl urea, (b) phenyl urea, (c) tetramethyl urea, (d) ethylene urea and (e) allyl urea in equimolar CH_3OH : dioxane

thiourea ligands also showed the same affinities towards Pr(III). The donor atoms (oxygen in ureas and sulphur in thioureas) are directly responsible for creating the immediate coordination environment around Pr(III). The substituent groups have only indirect effect on the coordination environment through the donor atoms of ureas and thioureas. In spite of this, we observed substantial changes in the spectral intensities, and consequently the Judd-Ofelt intensity parameters.

The comparative absorption spectrum of Pr(III)-biphenyl thiourea, given in Fig. 2, shows the effect of solvents. It is quite understandable that the solid complexes isolated by taking metal ion and excess of ligand were separated out as $Pr(urea)_6(solvent)_3$ or $Pr(thiourea)_6(solvent)_3$ and hence the difference in the spectral pattern, oscillator strengths and intensity parameters of different bands reflect the varying coordinating power of the solvent ligands. One interesting observation is that though all the observed absorption bands do not obey ΔJ selection rules, yet have shown significant variation in their oscillator strengths. Secondly, the sensitivity of each individual 4*f*–4*f* transitions towards the nature of the solvent or urea/thiourea ligands is different, hence suggesting that the relative sensitivity of 4*f*–4*f* transitions is different towards the coordination changes brought about by the nature of solvent or ligand molecules. Maximum intensification was induced by biphenyl urea and biphenyl thiourea followed by phenyl urea and phenyl thio urea. The generalized order of intensification of 4*f*–4*f* bands being:

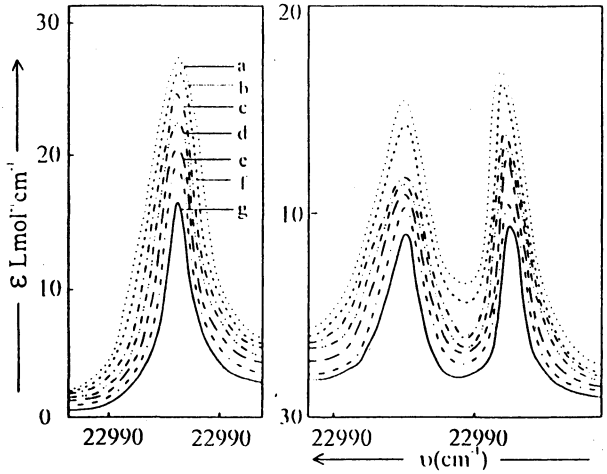

Fig. 2. Comparative absorption spectra of Pr(III)-biphenyl thiourea in different solvents: (a) DMF, (b) DMF : dioxane, (c) DMF : CH_3OH, (d) DMF : CH_3CN (e) CH_3OH : dioxane, (f) CH_3OH and (g) CH_3OH : CH_3CN

biphenyl urea > phenyl urea > tetramethyl urea > ethylene urea > allyl urea

biphenyl thiourea > phenyl thiourea > tetramethyl thiourea > ethylene thiourea > allyl thiourea

The solvents induced varying intensification to the pseudohypersensitive bands. DMF induced maximum intensification followed by solvent mixtures comprising DMF as one of the constituents. Ureas in general have been found to form complexes with Pr(III) with higher stability as compared to analogous thiourea ligands. This is reflected in the oscillator strengths and magnitude of T_λ parameters. Good ligating nature contributes enhanced intensities of absorption bands and higher values for Judd-Ofelt parameters.

Relative sensitivities of different 4*f*–4*f* transitions and their correlation with Judd-Ofelt intensity parameters

Generally, the variation of T_λ parameters is directly reflected in the relative magnitudes of the oscillator strengths of different 4*f*–4*f* transitions. In order to know the relative sensitivities of various 4*f*–4*f* transitions with respect to the variation of Judd-Ofelt electric dipole intensity parameters, the oscillator strengths of different transitions were plotted against T_4 and T_6 parameters (Fig. 3). For Pr(III), T_2 occasionally showed negative values and hence become meaningless. This is because only the $^3F_2 \leftarrow {}^3H_4$ transition occurring around 5200 cm^{-1} has a significant $U^{(2)}$ matrix element but it is generally not included in the data set of Pr(III) complexes, especially in solution. The sensitivity of these transitions was found to obey the order $^3P_2 \leftarrow {}^3H_4 > {}^3P_1 \leftarrow {}^3H_4 > {}^1D_2 \leftarrow {}^3H_4 > {}^3P_0 \leftarrow {}^3H_4$. Table-3 listing the slopes for the plots of oscillator strengths (P) of these four transitions against T_4 and T_6 as in Fig. 3 clearly shows that the relative sensitivities of these transitions follow the same order for both T_4 and T_6.

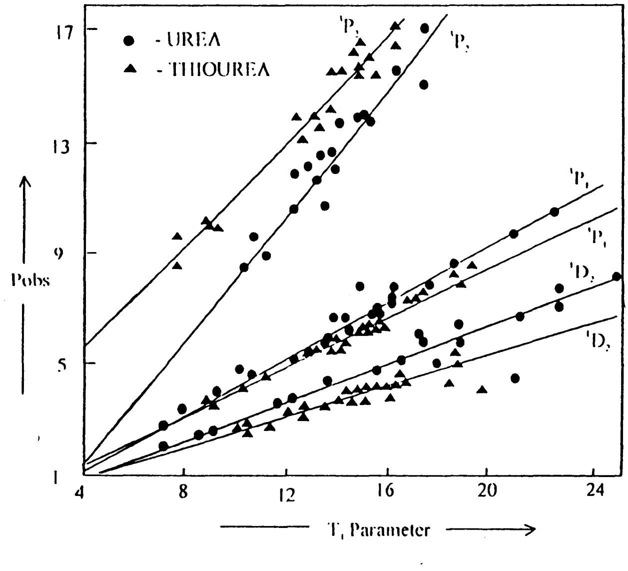

Fig. 3. Plot of oscillator strength (P) *vs.* T_4 parameter of Pr(III)-urea/thiourea complexes for different transitions showing relative sensitivities of various 4*f*–4*f* transitions with respect to the variation of Judd-Ofelt electric dipole intensity parameters

TABLE-4
SLOPES FOR THE PLOTS OF OSCILLATOR STRENGTH (P) FOR DIFFERENT 4F–4F TRANSITIONS OF Pr(III) AGAINST JUDD-OFELT T_λ ($\lambda = 2, 4, 6$) PARAMETERS

Transition	Pr(III)-Urea Complex		Pr(III)-Thio Urea Complex	
	T_4	T_6	T_4	T_6
$^3H_4 \rightarrow {}^3P_2$	1.095	0.445	0.906	0.326
$^3H_4 \rightarrow {}^3P_1$	0.510	0.210	0.486	0.149
$^3H_4 \rightarrow {}^3P_0$	0.286	0.133	0.228	0.071
$^3H_4 \rightarrow {}^1D_2$	0.341	0.137	0.279	0.083

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