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Investigation on the Lanthanoid Chelates of 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone. An Examination of the Phenomenon of Hypersensitivity

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1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (Hpmbp) form complexes with lanthanoids of the type $Ln(pmbp)_3\cdot nH_2O$ ($n=4$ for La—Sm, and $n=1$ for Eu—Yb and Y), $Ln(pmbp)_3\cdot 2pyridine\cdot 2H_2O$, $Ln(pmbp)_3\cdot$(2,2′-bipyridine/1,10-phenanthroline)$\cdot C_2H_5OH$, $NH_4[Ln(pmbp)_4]\cdot C_2H_5OH$ and $Q^+[Ln(pmbp)_4]\cdot C_2H_5OH$, where Q^+ is the quaternary ammonium cation of piperidine, pyrrolidine or morpholine. These compounds have been characterized from physicochemical studies. The electronic spectra of the Nd(III) complexes have been studied in detail to investigate the phenomenon of hypersensitivity with respect to the coordination environment and solvent medium. In these compounds solvent does not play a significant role to cause variation in hypersensitivity. The oscillator strengths of the hypersensitive transition in these compounds show the following trend: $Q^+[Nd(pmbp)_4] > Nd(pmbp)_3\cdot phen > Nd(pmbp)_3\cdot bpy > Nd(pmbp)_3\cdot 2py\cdot 2H_2O > Nd(pmbp)_3\cdot 2H_2O$. In the Pr(III) complexes the band due to $^3H_4 \rightarrow {}^1D_2$ transition has been found to be hypersensitive, and the gradation of intensity due to this band follows almost the same trend as in the corresponding Nd(III) complexes.

Since the introduction of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (Hpmbp) as a chelate-forming extractant by Jensen[1] extensive studies have been made on the use of this reagent for solvent extraction and separation of various metal ions[2,3]. The versatility of Hpmbp is comparable to the more popular extractant thenoyltrifluoroacetone (Htta).[4] In previous publications[5,6] we have reported solvent extraction behavior of the entire lanthanoid series using Hpmbp as the extractant and have noted the "tetrad effect" in the series.

Although composition and stability constants of extracted binary or ternary complexes (formed in the presence of Lewis bases during synergistic extraction) of Hpmbp with various metal ions have been determined, characterization of these compounds in the solid state have been scarcely made. To our knowledge only Cu(II) and VO^{2+} chelates have been investigated so far.[7] We wish to report here synthesis and characteristics of several types of lanthanoid chelates with Hpmbp. Our interest in these compounds stems from a desire to investigate the phenomenon of hypersensitivity which is a subject of considerable interest.

Experimental

Materials. Lanthanoids oxides (99.9% pure) were obtained from Johnson Matthey (U.K.) and A.D. Mackay (U.S.A.). Hpmbp was prepared by a modified procedure[8] of Jensen.[1] The compound in its keto form was obtained by recrystallization from (1 : 4) ethanol-water mixture (mp 120 °C, lit, 122 °C) and in the enol form from heptane (mp 91 °C, lit, 92 °C).

Preparation of the Chelates. The method adopted for the preparation of a particular type of lanthanoid chelate is the same for all the metal ions. Here preparations are described with respect to neodymium.

$Nd(pmbp)_3\cdot 4H_2O$: Hydrated neodymium nitrate (1 mmol) and Hpmbp (3 mmol) were dissolved separately in ethanol (10 ml), then mixed together and stirred for a few minutes. Water was slowly added to the solution until precipitation of the compound occurred. After stirring the mixture for 30 min, the compound was filtered and washed thoroughly with water and petroleum ether. The compound was recrystallized from ethanol-water mixture (1 : 1).

$Nd(pmbp)_3\cdot 2py\cdot 2H_2O$: One g (*ca.* 1 mmol) of $Nd(pmbp)_3\cdot 4H_2O$ was dissolved in 30 ml ethanol. To it 1 g (12 mmol) of pyridine was added and the solution was refluxed on a water bath for 4 h. After filtration, the filtrate was concentrated to a small volume. The compound separated was filtered, and was washed with cold ethanol and petroleum ether.

$Nd(pmbp)_3(bpy/phen)\cdot C_2H_5OH$: To an ethanolic solution (10 ml) of hydrated neodymium nitrate (1 mmol) an ethanol solution (15 ml) containing 3 mmol of Hpmbp, 1 mmol of 2,2′-bipyridine (or 1,10-phenanthroline) and 3 mmol of sodium hydroxide was added in a dropwise manner with stirring. The mixture was stirred for 30 min and the volume was then reduced to about 5 ml, cooled and filtered. The product was washed with water, a small amount of cold ethanol and finally with benzene. The compound was recrystallized from (1 : 1) ethanol-water mixture.

*$Q^+[Nd(pmbp)_4]\cdot C_2H_5OH$**:* To a stirred ethanol solution (25 ml) containing 1 mmol of hydrated neodymium nitrate and 4 mmol of Hpmbp was slowly added 4 mmol of the heterocyclic base (diluted in 5 ml of ethanol). The mixture was stirred for 30 min, evaporated to ≈10 ml, filtered, and the product was washed with petroleum ether and water. It was recrystallized from (2 : 1) ethanol-water mixture.

$NH_4[Nd(pmbp)_4]\cdot C_2H_5OH$: In the above preparation instead of adding a heterocyclic base ammonia gas was passed through the solution for 30 min. The mixture was filtered and the filtrate was evaporated almost to dryness. The compound separated was collected and recrystallized from (1:1) ethanol-water mixture.

All these compounds were obtained in high yield, 70—90%.

Analyses. Carbon, hydrogen and nitrogen were analysed in the microanalytical laboratory of this Institute. Lanthanoids were estimated after decomposing the compounds with acid mixtures (HNO_3-$HClO_4$) and titrating with Na_2H_2-edta using Xylenol Orange as the indicator.[9]

Physical Measurements. Conductivity measurements were carried out using a Philips PR 9500 conductivity bridge. Infrared spectra were recorded on Perkin-Elmer 225/621 spectrometers in KBr pellets (in the range 4000—400 cm^{-1}). and in nujol or hexachlorobutadiene mulls (between 700—200 cm^{-1}). Electronic spectral measurements were carried

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** Q^+ is the quaternary ammonium cation of morpholine, piperidine or pyrrolidine.

TABLE 1. ANALYTICAL DATA

Compound	C% Calcd	C% Found	H% Calcd	H% Found	N% Calcd	N% Found	M% Calcd	M% Found
Hpmbp	73.38	73.27	5.40	5.18	10.07	10.01	—	—
Nd(pmbp)$_3$·4H$_2$O	58.45	58.63	4.49	4.72	8.02	7.95	15.75	15.40
Nd(pmbp)$_3$·2H$_2$O	60.53	59.96	4.25	4.41	8.31	8.25	14.24	14.10
Nd(pmbp)$_3$·py$_2$·2H$_2$O	62.62	62.08	4.53	4.82	9.58	9.45	12.32	12.18
Nd(pmbp)$_3$·bpy·C$_2$H$_5$OH	64.24	63.92	4.54	4.42	9.51	9.37	12.24	12.37
Nd(pmbp)$_3$·phen·C$_2$H$_5$OH	64.86	64.70	4.41	4.29	9.93	9.21	11.99	11.80
Hpiper[Nd(pmbp)$_4$]·C$_2$H$_5$OH	65.01	64.86	5.06	4.95	9.10	9.20	10.40	11.25
Hpyrrol[Nd(pmbp)$_4$]·C$_2$H$_5$OH	64.82	64.70	4.96	4.81	9.20	9.35	10.52	10.65
Hmorph[Nd(pmbp)$_4$]·C$_2$H$_5$OH	64.00	63.87	4.51	4.40	9.09	9.00	10.39	10.52
NH$_4$[Nd(pmbp)$_4$]·C$_2$H$_5$OH	63.84	63.80	4.71	4.78	9.58	9.53	10.94	10.86
Eu(pmbp)$_3$·H$_2$O	61.12	61.16	4.10	4.26	8.39	8.27	15.18	15.11
Y(pmbp)$_3$·H$_2$O	64.71	64.50	4.33	4.45	8.88	8.65	10.47	10.42
Sm(pmbp)$_2$·bpy·C$_2$H$_5$OH	63.90	63.81	4.48	4.37	9.47	9.41	12.68	12.75
Su(pmbp)$_3$·bpy	63.81	63.70	4.10	4.15	9.76	9.65	13.08	13.01
Gd(pmbp)$_3$·phen·C$_2$H$_5$OH	64.25	64.42	4.37	4.28	9.23	9.15	12.93	12.82
Hpiper[Pr(pmbp)$_4$]·C$_2$H$_5$OH	64.16	65.08	5.07	5.00	9.12	9.12	10.21	10.30
Hpiper[Pr(pmbp)$_4$]	65.61	65.60	4.79	4.71	9.44	9.52	10.32	10.24
Hpyrrol[Er(pmbp)$_4$]·C$_2$H$_5$OH	63.74	63.31	4.88	4.74	9.04	9.08	11.99	11.87
Hmorph[Yb(pmbp)$_4$]·C$_2$H$_5$OH	62.76	62.25	4.80	4.74	8.91	8.85	12.23	12.30

py, pyridine; bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline; piper, piperidine; pyrrol, pyrrolidine; morph, morpholine.

out either on a Spectro MOM 201 or a Hilger UV-spek spectrophotometer. For measurements in the visible range, the solutions used mostly had a concentration $\approx 1\times10^{-2}$ M. The oscillator strength (P) was determined from the relation[10]

$$P = 4.31\times10^{-9}\left[\frac{9n}{(\eta+2)^2}\right]\varepsilon_i(\nu_i)d,$$

where n is the refractive index of the medium, ε_i is the molar extinction coefficient and ν_i is the energy of transition in cm^{-1}. The band areas were measured by a planimeter.

Results and Discussion

The analytical data of the lanthanoid complexes are summarized in Table 1. In general, the compounds are freely soluble in acetone, ethanol and chloroform, less soluble in benzene, and insoluble in hydrocarbon solvents. These compounds are generally light yellow in color, but the neodymium compounds show dichroic behavior; violet in the day light and greenish-yellow under a fluorescent lamp. The compounds of the type, Q$^+$[Ln(pmbp)$_4$] and [Ln(pmbp)$_3$L] (where L is 2,2′-bipyridine or 1,10-phenanthroline) contain one molecule of ethanol as the solvent of crystallization which can be removed by heating at *ca.* 60 °C for an hour. The tris-chelates of the lower lanthanoids (La—Sm) having the composition Ln(pmbp)$_3$.4H$_2$O contain two coordinated water molecules. The two solvated water molecules may be removed by heating at 100 °C for 2 h. Thermal analysis shows that Ln(pmbp)$_3$.2H$_2$O is stable up to 200°C, and beyond this temperature further loss of water molecules cause decomposition of the compound. On the other hand, the tris-chelates of the higher lanthanoids (Eu onward), Ln(pmbp)$_3$·H$_2$O do not contain any water of crystallization. Conductivity measurements of the tetrakis-chelates in nitrobenzene show that Λ_M values are in the range 20—25 ohm^{-1} cm^2 mol^{-1} which are consistent with the 1:1 electrolytic behavior of the compounds.[11]

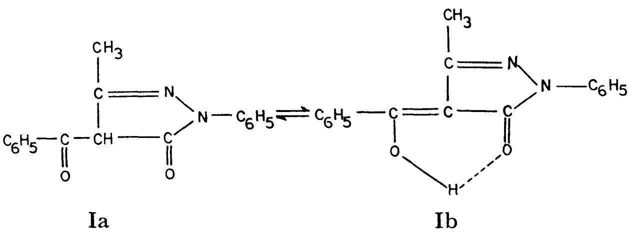
Hpmbp can be isolated both in keto and enol forms (Ia, Ib). The reagent is comparatively a strong acid, (pK_a=4.10[5]) and although its distribution constrants in various solvents have been determined[2], no information regarding the keto-enol equilibrium in organic solvents is known. Unfortunately, the reagent does not have enough solubility in major organic solvents suitable for studying NMR spectra. In an attempt to study this equilibrium the electronic spectra of Hpmbp in several organic solvents have been recorded. The pertinent data summarized in Table 2 show that the reagent has two absorption bands, but neither of these can be related to a particular tautomer. On the contrary, both the bands are composite type, having significant contribution of the either forms. It may be mentioned that the enol form is obtained by recrystallization from heptane.[1–4] On this basis one may expect that in heptane the reagent remains at least 98% in the enol form, if not exclusively. It follows from Table 2 that the decreased order of molar absorptivity of the lower wavelength band with respect to solvent is, heptane>methanol>ethanol>chloroform; whereas the corresponding order for the higher wavelength band is, chloroform>heptane>carbon tetrachloride>methanol>ethanol. It is well-known that an enol content increases with the decrease in dielectric constant of a solvent. On this basis the higher wavelength band gives an indication of the decreased order of the enol content, although the position of chloroform is confusing. Attempt was also made to determine keto-enol ratio by Meyer's bromine absorption method.[12] However, this approach was unsuccessful because bromine nonselectively gets absorbed both by

Table 2. Electronic spectral data of Hpmbp

Solvent	λ_{max} (nm)	ε
Methanol	236	16840
	273	17300
Ethanol	238	16190
	278	15080
Heptane	242	19200
	289	17570
Chloroform	246	15350
	287	17950
Carbon tetrachloride	—	—
	291	17490

the double bond and the phenyl rings.

The IR spectrum of the enolic form of the ligand shows a broad band at 2540 cm^{-1} which is evidently due to hydrogen bonded OH. Hpmbp contains a large number of bands in the region 1700—200 cm^{-1} which rendered frequency assignments somewhat difficult. It is possible, however, to obtain some useful information regarding the metal–ligand bonding. For example, the ligand bands at 1662 and 1638 cm^{-1} are considerably shifted to lower frequency $\approx$1610 cm^{-1} in the metal chelates and thus can be related to the C=O stretching. On the other hand, a band at 1590 cm^{-1} in the ligand remains unaltered in the chelates and is therefore due to phenyl ring stretching. Similarly, another unaffected band at 1575 cm^{-1} appears to be due to C=C/C=N stretchings. The ligand band at 1545 cm^{-1} which gets displaced to 1525—1500 cm^{-1} in the complexes has major contribution due to C=O stretching. The remaining large number of bands which are mostly composite type do not undergo major shift in frequency in the complexes. A broad band in the complexes observed at 3400—3300 cm^{-1} is either due to the water molecules (in the tris-chelates) or the ethanol molecule (in the tetrakis- or the adduct type chelates). It has been observed that although the ligand has a weak band at 410 cm^{-1}, in the tris- or the adduct type chelates another new band appears at 400 cm^{-1}. In the tetrakis-chelates this band is observed at 435—440 cm^{-1}. We infer this band as due to Ln–O stretching. Indeed Liang *et al.*[13] also observed that Ln–O stretching vibration appears at 400—420 cm^{-1} in a large number of lanthanoid β-diketonates of both tris- and tetrakis-type.



Ia　　Ib

The electronic spectral characteristics of the compounds under discussion have been studied in detail with respect to those derived from Nd(III) and to a limited extent for the Pr(III) complexes. Admittedly useful information could have been obtained for the Ho(III) and Er(III) complexes but their hypersensitive bands appear in the region where there is considerable absorbance due to ligand/or charge-transfer tail.

Table 3 lists the oscillator strengths for several non-hypersensitive transitions in the neodymium complexes in several solvents. It may be noted from a comparison of these values with those of neodymium perchlorate[14] that the coordination environment or the solvent medium have little effect on the variation of band intensities. This is in accordance with the model proposed by Judd[15] and Oflet[16] for the intensities of f-f transitions.

In Table 4 the oscillator strengths (P) for the hypersensitive transition in the Nd(III) complexes have been summarized. It may be noted that in the Q^+[Nd(pmbp)$_4$] type complexes P values are independent of the Q^+ cations and there is a marginal variation in hypersensitivity with respect to the solvent medium. Interestingly, in Q^+[Nd(sdbm)$_4$] chelates (Hsdbm=1,3-diphenyl-3-thioxo-1-propanone) we noted[17] that while Q^+ ions had no effect, however, the oscillator strengths in acetone were significantly higher than in chloroform and benzene. We rationalized this variation by invoking a difference in symmetry of the dissociated (in acetone) and undissociated (in chloroform or benzene) form of the complexes. The fact that the Q^+[Nd(pmbp)$_4$] complexes do not show such a behavior implies that dissociation of these complexes do not profoundly affect their symmetries. According to Henrie *et al.*[18] symmetry does have implication on the overall intensity but hypersensitivity *per se* can not be classified as being due to a symmetry phenomenon.

Table 4 reveals that the gradation of hypersensitivity in the compounds is Q^+[Nd(pmbp)$_4$]>Nd(pmbp)$_3$·phen > Nd(pmbp)$_3$·bpy > Nd(pmbp)$_3$·2py·2H$_2$O>Nd(pmbp)$_3$·2H$_2$O. The greater hypersensitivity of the tetrakis complexes over the tris species can be rationalized by invoking an important observation made by Barnes and Pincott[19] that not only are the energies of the lanthanoid charge-transfer transitions dependent on the ligand but also they increase in a stepwise manner with the stepwise addition of ligands. Similar observation as the present one was made by us[17,20] previously for β-thioxo ketonates and also by Poluektov *et al.*[21] for a number of phenolic ligands.

Table 4 shows that the addition of heterocyclic donors to the tris-chelate do as not profoundly increase hypersensitivity in the adducts. Sinha *et al.*[22] observed that hypersensitivity in neodymium complexes shows the trend phen>bpy>H$_2$O, but the differences are not much. Our results also show a similar trend. Sinha *et al.*[22] related the above trend to the poor donor capacity of nitrogen atom toward lanthanoid ions which indeed is an estabilshed fact.[23] Sinha and Green reported[24] that the formation constants of lanthanoid-phen or bpy complexes are extremely low, log $K_1 \approx 1$.

Literature shows[25–27] that the increased order of hypersensitivity in tris-β-diketonates is hexafluoroacetylacetone < trifluoroacetylacetone < acetylacetone <benzoylacetone< thenoyltrifluoroacetone < dibenzoylmethane. In the corresponding β-thioxo ketonates also the following trend was observed by us[17,20] 4-phenyl-4-thioxo-2-butanone<4-thenoyl-4-thioxo-1,1,1-trifluoro-2-butanone < 1,3-diphenyl-3-thioxo-1-propanone. These results combined together imply that hypersensitivity

TABLE 3. OSCILLATOR STRENGTH (P) OF SOME NON-HYPERSENSITIVE TRANSITION IN NEODYMIUM COMPLEXES

Compound	Solvent	$P\times 10^6$		
		$^4I_{9/2}$ $^4F_{3/2}$ (10800—11800 cm^{-1})	$^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$ (11800—13000 cm^{-1})	$^4I_{9/2} \rightarrow {}^4F_{7/2}, {}^4S_{3/2}$ (13000—14100 cm^{-1})
$Nd(ClO_4)_3$	$DClO_4$-HClO	2.57[a]	8.54[a]	8.78[a]
$Nd(pmbp)_2 \cdot 2H_2O$	Chloroform	2.84	11.51	9.89
	Acetone	2.30	10.44	10.86
	Benzene	2.92	10.17	10.70
	Methanol	2.77	11.44	11.12
$Nd(pmbp)_3 \cdot py_2 \cdot 2H_2O$	Chloroform	2.75	10.77	8.92
$Nd(pmbp)_3 \cdot bpy \cdot C_2H_5OH$	Chloroform	3.16	11.20	11.22
	Methanol	3.28	11.11	11.45
	Acetone	3.22	11.35	11.17
	Benzene	2.67	11.05	10.37
$Nd(pmbp)_3 \cdot phen \cdot C_2H_5OH$	Chloroform	2.86	11.13	10.86
$NH_4[Nd(pmbp)_4 \cdot C_2H_5OH$	Chloroform	2.75	11.13	9.89
$Hpiper[Nd(pmbp)_4] \cdot C_2H_5OH$	Chloroform	2.48	11.47	11.47
$Hpyrrol[Nd(pmbp)_4] \cdot C_2H_5OH$	Chloroform	2.88	11.39	10.70
$Hmorph[Nd(pmb)_4] \cdot C_2H_5OH$	Chloroform	2.85	11.47	11.08
	Methanol	3.38	11.12	11.05
	Acetone	3.46	8.87	9.85
	Benzene	2.68	11.05	10.73

a) Data taken from Ref. 14.

TABLE 4. OSCILLATOR STRENGTH OF HYPERSENSITIVE TRANSITION IN NEODYMIUM COMPLEXES

Compound	$P\times 10^6$ ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) 16250—18250 cm^{-1}				
	Acetone	Benzene	Chloroform	Dioxane	Methanol
$Nd(pmbp)_3 \cdot 2H_2O$	57.4	59.2	56.8	57.7	51.1
$Nd(pmbp)_3 \cdot py_2 \cdot 2H_2O$	—	—	62.1	—	—
$Nd(pmbp)_3 \cdot bpy \cdot C_2H_5OH$	62.1	65.9	66.7	63.8	57.2
$Nd(pmbp)_3 \cdot phen \cdot C_2H_5OH$	—	—	71.3	—	—
$NH_4[Nd(pmbp)_4] \cdot C_2H_5OH$	—	—	74.9	—	—
$Hpiper[Nd(pmbp)_4] \cdot C_2H_5OH$	—	—	78.2	—	—
$Hpyrrol[Nd(pmbp)_4] \cdot C_2H_5OH$	—	—	75.6	—	—
$Hmorph[Nd(pmbp)_4] \cdot C_2H_5OH$	77.2	76.3	74.9	73.1	71.7

of lanthanoid complexes generally increases with the increases in pK_a value of the ligand. However, there are exceptions to this generality. For example, pK_a of Hdbm is greater than Hsdbm, but the neodymium complex of Hsdbm shows greater band intensification.[17] This is due to more covalent interaction in the thio compound as sulfur acts as a softer base. A comparison of the oscillator strengths of Hpmbp complexes (Table 4) with the β-diketonates reported in literature[25—27] reveals that in spite of weaker basicity, the oscillator strengths of Hpmbp complexes are rather high. Moreover, lanthanoid–pmbp complexes have relatively high formation constants (log $\beta_3 \approx 12$—13)[28] which indicate that probably the complexes are stabilized to a great extent through covalent interaction. Menzel *et al.*[7] also indicated higher covalency in Cu-(pmbp)$_2$ compared to Cu(II) acetylacetonate.

Henrie *et al.*[18] have recently proposed a mechanism to explain the phenomenon of hypersensitivity which suggests that hypersensitive transitions aries from metal-ligand covalency *via* charge-transfer levels. The greater the covalent interaction greater will be the hypersensitivity. On this premise Henrie *et al.*[18] further proposed a correlation between P and pK_a. From the present study we conclude that hypersensitivity indeed increases with greater covalent interaction, but a linear correlation between hypersensitive band intensity and ligand basicity appears to be an overemphasized one.

The electronic spectral characteristics of the Pr(III) complexes in chloroform have been investigated. The hypersensitive transition, $^3H_4 \rightarrow {}^3F_2$ (*ca.* 5.2×10^3 cm^{-1}) was beyond the range of measurement. Although $^3H_4 \rightarrow {}^3P_2$ and $^3H_4 \rightarrow {}^1D_2$ transitions have been reported[29] to exhibit hypersensitivity, they do not obey quadrupole selection rules. In the Pr(III)–pmbp complexes, $^3H_4 \rightarrow {}^3D_2$ transition is completely swamped by the ligand/or charge-transfer tail, which also considerably modified the bands due to $^3H_4 \rightarrow {}^3P_1$, $^1I_6$ ($\approx 21.2\times 10^3$ cm^{-1}) transitions. The molar extinction coefficients of $^3H_4 \rightarrow {}^1D_2$ transition ($\approx 17.6\times 10^3$ cm^{-1}) in the complexes on comparison with the corresponding value for the aquated Pr^{3+} ion reveal that there is significant increase in intensity in the complexes. In fact, the gradation in intensity is almost similar to the one observed in the Nd(III) complexes. In view of the exceptional behavior of Pr(III) in its hypersensitivity which still remains as one of the major problems in lanthanoid intensity theory,[30] no attempt has been made to evaluate the oscillator strengths for $^3H_4 \rightarrow {}^1D_2$ transition.

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References

1) B. S. Jensen, *Acta Chem. Scand.*, **13**, 1668 (1959).
2) O. Navratil, *Chem. Listy*, **68**, 470 (1974). A review.
3) G. N. Rao and J. S. Thakur, *J. Sci. Indust. Res. (India)*, **34**, 110 (1975). A review.
4) Yu. A. Zolotov, "Extraction of Chelate Compounds" (Engl. Translation), Ann Arbor-Humphrey Science Publishers (1970), p. 227.
5) A. Roy and K. Nag, *Indian J. Chem.*, **15A**, 474 (1977).
6) A. Roy and K. Nag, *J. Inorg. Nucl. Chem.*, **40**, 331 (1978).
7) E. R. Menzel, D. R. Lorenz, J. R. Wasson, K. R. Radigan, and B. J. McCormick, *J. Inorg. Nucl. Chem.*, **38**, 993 (1976).
8) Yu. A. Zolotov, V. G. Lambrev, and M. K. Chamutova, *Dokl. Akad. Nauk SSSR*, **165**, 117 (1965).
9) S. J. Lyle and M. Rehman, *Talanta*, **10**, 1177 (1963).
10) D. M. Gruen, C. W. Dekock, and R. L. McBeth, *Adv. Chem. Ser.*, **71**, 102 (1967).
11) W. J. Geary, *Coord. Chem. Rev.*, **7**, 1177 (1971).
12) K. Meyer, *Chem. Ber.*, **45**, 2843 (1912).
13) C. Y. Liang, E. J. Schmitschek, and T. A. Trias, *J. Inorg. Nucl. Chem.*, **32**, 811 (1970).
14) W. R. Carnall, P. R. Fields, and B. G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965).
15) B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).
16) G. S. Oflet, *J. Chem. Phys.*, **37**, 511 (1962).
17) K. Nag and M. Chaudhury, *Inorg. Chem.*, **15**, 2291 (1976).
18) D. E. Henrie, R. L. Fellows, and G. R. Choppin, *Coord. Chem. Rev.*, **18**, 199 (1976).
19) J. C. Barnes and H. Pincott, *J. Chem. Soc. A*, **1966**, 842.
20) K. Nag and M. Chaudhury, *Inorg. Nucl. Chem. Lett.*, **12**, 307 (1976).
21) N. S. Poluektov, M. A. Tishchenko, and G. E. Gerasimenko, *Dokl. Akad. Nauk SSSR*, **213**, 1334 (1973).
22) S. P. Sinha, P. C. Mehta, and S. S. L. Surana, *Mol. Phys.*, **23**, 807 (1972).
23) J. H. Forsberg, *Coord. Chem. Rev.*, **10**, 195 (1973).
24) S. P. Sinha and R. D. Green, *Spectrosc. Lett.*, **4**, 399 (1971).
25) D. G. Karraker, *Inorg. Chem.*, **6**, 1863 (1967).
26) P. C. Mehta and S. P. Tandon, *J. Chem. Phys.*, **53**, 414 (1970).
27) L. I. Kononenko, M. A. Tishchenko, and U. N. Drobyazko, *Zh. Anal. Khim.*, **26**, 729 (1971).
28) A. Roy and K. Nag, unpublished result.
29) R. D. Peacock, *Chem. Phys. Lett.*, **7**, 187 (1970).
30) R. D. Peacock, *Struct. Bonding*, **22**, 83 (1975).