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Synthesis of lanthanon complexes with β–diketones and study of their spectral and electrochemical behavior

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ABSTRACT

In the present paper, we have discussed the preparation of ligand and complex formation with lanthanides and their characterization. Reagents of analytical quality (Merck) were used. They included the following: $YCl_3.6H_2O$; $La(NO_3)_3.6H_2O$; $Nd(NO_3)_3.5H_2O$; $Sm(NO_3)_3.5H_2O$; $Pr(NO_3)_3.5H_2O$; 1–Phenyl–3–methyl pyrazolone–5, acetyl chloride, 95% ethanol, dioxane and petroleum ether (40–60 ℃). The lignad 1–Phenyl–3–Methyl–4–Acetoxime Pyrazolone–5(PMAP) was prepared from 1–phenyl–3–methyl pyrazolone–5 and acetyl chloride using a modified procedure and its complexes with lanthanides (rare earth chelates) are characterized by electronic spectra, IR spectra, Proton Magnetic Resonance (PMR) Spectra and electronic spectral studies. Complexes of schiff bases with lanthanons has drawn much attention due to their importance in biological, pharmacological and biochemical processes.

Key words: Lanthanides, PMAP, β–diketones

INTRODUCTION

Lanthanons are remarkable similar in their chemical properties which is due to the nearly identical configurations of the electrons available for bond formation. The coordination chemistry of trivalent lanthanide ions has extended rapidly during the last three decades. Lanthanon chelates of ligands possessing oxygen and nitrogen donor atoms find application as bactericides and fungicides. A number of mixed ligand complexes of lanthanides containing acetate groups, □diketones and amines have earlier been prepared and characterized. Metal extraction from aqueous solution with 1phenyl3methyl4benzoyl 5pyrazolone (PMBP) has been studied extensively. PMBP is an excellent complexing agent of metals due to the great reactivity of its (CO) group and stability of its complex. It is well known that the size of a tetravalent ion of the lanthanide series continuously decreases as the 4̃fsub shell is filled up with electrons and this shrinkage (the so called lanthanoid contraction) plays an important role in the coordination chemistry of lanthanide elements. Since the bonding between such an ion and common ligands are predominantly electrostatic, they will be in general strengthened by this shrinkage.

EXPERIMENTAL SECTION

Reagents: Reagents of analytical quality(Merck): $YCl_3.6H_2O$; $La(NO_3)_3.6H_2O$; $Nd(NO_3)_3.5H_2O$; $Sm(NO_3)_3.5H_2O$; $Pr(NO_3)_3.5H_2O$; 1–Phenyl–3–methyl pyrazolone–5, acetyl chloride, 95% ethanol, dioxane and petroleum ether (40–60°C).

Preparation of Ligand:

The ligand PMAP was prepared from 1–phenyl–3–methyl pyrazolone–5 and acetyl chloride using a modified Jensen procedure(1). Into a one litre–3–necked flask containing dioxane (100 ml) carrying a dropping funnel, a mechanical stirrer and a reflux condenser was placed (17.0 g). A solution was obtained by gentle heating and stirring calcium hydroxide (10g) was added and acetyl chloride (15ml) was added drop wise with in about 2–3 minutes. The reaction was exothermic and the reaction mixture became a paste. The mixture was allowed to cool and then refluxed with stirring for one hour on a heating mantle, during which period the bright yellow complex formed initially turned yellowish brown. The complex was decomposed by pouring the reaction mixture into stirred hydrochloric acid (500 ml–3N). A yellowish off solid settled and was filtered 95% ethanol recrystallised twice from white crystals m.pt. 112°C ($C_{12}H_{12}N_2O_2$). Its oxime was prepared by reacting with hydroxyl amine hydrochloride m.pt. 118° ($C_{12}H_{13}N_3O_2$).

Preparation of Lanthanon Chelates:

Ligand PMAP (5 mM) dissolved in minimum quantity of ethanol by warming was added with stirring to a solution of the lanthanon nitrate or chloride (1 mM) in the minimum quantity of the same solvent. The reaction mixture was heated for 10 minute and the yellow solution poured into excess water (600 ml). Creamish precipitates deposited and were filtered under suction. The solids then dried in air under suction and transferred into a large volume (300 ml) of petroleum ether (boiling range 40–60°C) contained in a 600 ml beaker. The suspension obtained was heated with stirring. Unreacted ligand dissolved colouring the petroleum ether yellow while the complex remained undissolved. The solution of the excess ligand was decanted. The process was repeated until colouration of the petroleum ether was no longer observed. The precipitate were then filtered under suction and dried over phosphorous pentoxide.

RESULTS AND DISCUSSION

Both lanthanum (atomic number 57) and yttrium (atomic number 39) are included, since they are broadly indistinguishable from the lanthanides in so many respects. Table 1 contains a list of the complexes prepared together with some physical properties and micro analytical data.

Electronic Spectra:

Table 2 gives the UV-spectral data for ligand PMAP and its rare earth chelates in 95% ethanol. No absorption was observed in the visible for any of the compounds. In the absence of quantum mechanical calculations it is not possible to assign the absorption bands to definite electronic transitions with complete certainty.

TABLE 1: Analytical Data of Rare Earth Chelates of PMAP

S. No.	Molecular Formula	C% Calcd. (Found)	H% Calcd. (Found)	N% Calcd. (Found)	Metal	Deco mopo sition T	Molar Conductance Δ_M ohm^{-1} cm^2 mol^{-1}	Colour	μ_{eff} (B.M.)
1.	Y(PMAP)$_3$	55.32 (55.46)	4.50 (4.62)	16.10 (16.17)	11.30 (11.44)	160	30.10	White	Diamagnetic
2.	La(PMAP)$_3$	52.0 (52.11)	4.20 (4.34)	15.02 (15.20)	16.60 (16.75)	143	28.12	Cream	Diamagnetic
3.	Ce(PMAP)$_3$	51.90 (52.04)	4.20 (4.33)	15.03 (15.17)	16.70 (16.87)	170	25.05	Cream	2.50
4.	Pr(PMAP)$_3$	51.82 (51.99)	4.20 (4.33)	15.0 (15.16)	16.80 (16.95)	163	24.30	Cream	2.52
5.	Nd(PMAP)$_3$	51.62 (51.78)	4.20 (4.31)	15.0 (15.10)	17.10 (17.28)	170	18.10	Cream	3.25
6.	Sm(PMAP)$_3$	51.10 (51.28)	4.10 (4.27)	14.80 (14.95)	17.70 (17.84)	163	20.05	Cream	3.28

However it appears reasonable to assign the bands to $\pi^*\leftarrow\pi$ transitions. The spectra of the complexes are similar in character to the spectrum of the ligand, the absorption maxima of the ligand remain either unchanged or suffer slight hypsochromic shifts in the chelates. However the molar extinction coefficients measured at identical wavelengths show significant differences. It is pertinent to mention that no charge transfer band was observed in any of the chelate spectrum.

TABLE 2: UV–Spectral Data of ligand and chelates

S.No.	Compound	λ_1 max (nm)	(ε)	λ_2 max (nm)	(ε)	λ_3 max (nm)	(ε)
1.	$(C_{12}H_{13}N_3O_2)$	215.6	(31,315)	238	(36,890)	277	(36,880)
2.	Y(PMAP)$_3$	210	(59,480)	236	(55,265)	275	(57,545)
3.	La(PMAP)$_3$	212	(95,450)	235	(106,800)	276	(106,800)
4.	Ce(PMAP)$_3$	211	(74,000)	233	(78,880)	276	(74,000)
5.	Pr(PMAP)$_3$	210.5	(59,850)	235	(63,140)	276	(63,140)
6.	Nd(PMAP)$_3$	211	(74,000)	232.5	(78,870)	276	(74,000)
7.	Sm(PMAP)$_3$	210	(54,940)	235	(56,610)	276	(59,940)

The fact that both the ligand and complexes have virtually identical absorption maxima indicates that the π–bonding system in each ligand anion is almost intact, only the δ–orbitals of the oxygen atoms (one orbital being non bonding and other having lost a proton) being substantially involved in bonding with the metal ion.

Infrared Spectra:

The IR–spectra of metal 1,3–diketonates in general and rare earth 1,3–diketonates in particulars have received considerable attention as well as some controversy(2-6). The ligand PMAP is known to exhibit tautomerism and at least two of its tautomers have been isolated, but since the preparation of the chelates was carried out in ethanolic medium, the IR of the tautomer usually isolated from ethanol could be considered as reference. Since these chelates have similar

IR–spectra, only the spectral data of the ligand and representative complexes are displayed in Table 3, the detailed vibrational frequencies with possible assignments being given.

The main changes found after chelation are:

(1) The disappearance of the OH—O, absorption band centered at 2600 cm^{-1}.

(2) ν(C=N) of the pyrazolone ring existing around 1570 cm^{-1} in the ligand, do not get shifted to lower frequency band in the complexes, suggesting the non involvement of tertiary ring N atom

(3) Ligand show medium to strong bands in the region 3000 –3400 cm^{-1}, assignable to ν(OH) oxime. The broad nature of the bands suggest Hydrogen bonding$^{(7)}$.

(4) The ν(C=N) (Oxime linkage) mode in the ligand is possibly submerged by the other strong band at around 1615 cm^{-1}.

(5) The ν(N–O) mode for the ligand was observed as a strong band at 940 cm^{-1}.

(6) The ν(C–O) phenolic of the ligand observed at 1510 cm^{-1}, which shifted to 1540 cm^{-1} in the metal complexes$^{(8)}$. This along with the disappearance of bands for ν(O–H) (enolic = C–OH) suggests deprotonation and complexation of enolic (–OH) oxygen during complex formation.

(7) The bands due to ν(C=N) oxime shifted to lower frequencies by about 15–25 cm^{-1} compared to free ligand values indicating bonding through nitrogen atom$^{(9)}$.

(8) A medium peak assigned to ν(N–O) in the ligand gets transferred to 990–1000 cm^{-1} band. This confirms the donation of a lone pair of electrons from the azomethine N to the metal.

(9) Spectra of the ligand show ν(C–OH) in the region 1540–1580 cm^{-1}, suggesting their existence in the enolic form in the solid state$^{(10)}$.

(10) IR data gave further useful information on the structure of the ligand clearly indicating the presence of H–N and O–H, stretching bands$^{(11)}$ at 3412, and 3182 cm^{-1}, respectively (C=N) and (N–O) vibrations at 1574 and 1012 cm^{-1}.

(11) The IR–spectra of the complexes, the (C=N) higher frequency indicates the formation of coordination bonds between the metal and nitrogen atom of the ligand. The values are in harmony with the previously reported diamino glyoxime derivatives$^{(12)}$.

(12) Despite complications due to the appearance of several bands in the IR spectra of the ligand in the region 500–400 cm^{-1}, the bidentate pyrazolonates exhibit new vibrational frequency bands near 480 and 500 cm^{-1} assigned to ν(Ln–O) and ν(Ln–N) respectively.

TABLE 3: Diagnostatic IR–Frequency Bands (cm^{-1}) of lanthanons

S. No.	**Compounds**	**ν (C=N) (Pyrazolone)**	**ν (C=N) (Oxime)**	**ν (N–O)**	**Py– ring stretch**	**CH_3– rock out of plan4e**	**ν (C–C_6H_5)**	**ν (M–N)**	**ν (M–O)**
1.	Y$(PMAP)_3$	1535s	1650m	980sh	1395s	1025m	948s	445w	510m
2.	La$(PMAP)_3$	1540s	1655m	980m	1390s	1020m	950s	450w	520m
3.	Ce$(PMAP)_3$	1520sh	1650b	995m	1395s	1025m	945s	440w	520m
4.	Pr$(PMAP)_3$	1530s	1650	995m	1380s	1030m	920sh	450m	510m
5.	Nd$(PMAP)_3$	1535s	1640m	990m	1370s	1020m	930sh	450m	580m
6.	Sm$(PMAP)_3$	1528s	1640m	995m	1390s	1025m	920sh	445w	525m

Proton Magnetic Resonance (PMR) Spectra:

Amongst the rare earth ions whose chelates were studied, La^{3+} and Y^{3+} are diamagnetic, while the other Ln^{3+} ions, containing unpaired 4f electrons are all paramagnetic. As a result of the paramagnetism of some of the complexes and accompanying isotropic shifts of the nuclear resonances, the PMR spectra cover a range of ~30 ppm at 32°C. In these tris chelates cis and trans isomerism are possible(13,14). Here cis and trans refer to facial and meridional arrangements of like donor atoms in the octahedral coordination sphere. Cis isomers would have a threefold symmetry axis (C_3) relating corresponding nuclei and only one resonance signal for each kind of ligand nucleus would be expected. On the other hand, trans isomers have no symmetry and up to three resonance signals for each kind of ligand nucleus may occur. The simplicity of the spectra of the free ligand and the chelates permits general assignments of the proton signals. Table 4 gives the PMR spectral data for PMAP and some of its rare earth chelates in $CDCl_3$. The PMR spectrum of PMAP shows a sharp singlet at +2.10 ppm (relative to TMS) which from the position and integrated intensity of the signal is assigned to the three methyl protons of the free ligand, a multiplet (+7.20 to +8.07 ppm) ascribed to the ten phenyl protons, and a broad peak at +9.27 attributable to a deshielded hydroxyl proton indicating that the ligand exists as an enol in $CDCl_3$. In the lanthanon (4f°) chelate both the methyl and the phenyl protons suffer upfield shifts. The methyl signal has shifted from +2.10 to +1.43 ppm while the phenyl multiplet has now shifted to (+6.6 to +7.8 ppm), and the hydroxyl signal has disappeared. Apart from these shifts there is some slight broadening of the signals. It is significant to mention that although La^{3+} is diamagnetic shifts and a slight broadening has been observed. With the Neodymium ($4f^3$) chelate both the methyl and the phenyl signals have suffered greater shifts and broadening. The methyl signal has now shifted from + 2.10 ppm in the lignad to +1.00 ppm in the chelate and the broadening extends from +0.3 to +1.5 ppm while the phenyl multiplet now extends from +5.00 to 7.80 ppm. The observation is not surprising. The shifts may be attributed to contact and pseudo-contact interactions while the broadening may be ascribed to spin–spin relaxation processes. The hydroxyl proton resonance is also absent. The broadening is obvious while the hydroxyl proton signal has disappeared. Y^{3+} chelate exhibited a singlet for the methyl protons at +1.4 ppm and the phenyl multiplet at +6.6 to +8.0 ppm.

Table 4: Proton NMR spectral data of Ligand and chelates (chemical shifts is δ ppm relative to TMS)

Compound	**Methyl protons**	**Phenyl protons**	**Hydroxyl proton**
($C_{12}H_{13}N_3O_2$) (Ligand)	2.10 (sh,s)	7.20–8.07(m)	9.27(hr,s)
$Y(PMAP)_3$	1.40(sh,s)	6.60–8.00(m)	–
$La(PMAP)_3$	1.43(br,s)	6.60–7.80(m)	–
$Nd(PMAP)_3$	1.00(br,s)	5.00–7.80(br,m)	–
$Pr(PMAP)_3$	1.50(br,s)	6.40–8.40(br,m)	–

Sh – Sharp; br – broad; s – singlet; m–multiplet

It is clear from the PMR spectra of these complexes that the hydroxyl proton has been lost and that the OH of the enolic form of the ligand was involved in chelation.

Even though it would appear from the PMR spectra obtained at 32°C that the chelates isolated have the cis arrangement since only one set of signals were obtained, it is much more likely that a very rapid equilibrium mixture of both forms is present, and a time-averaged spectrum is being observed.

Electronic spectral studies:

Electronic absorption spectra of lanthanide ion have been subjected to several investigations(15-19). The f–electronic transitions of the lanthanides are found to be sharp and line like and these can be characterized by the total angular quantum number (J). On complexation, the spectra tend to show the band energy shift as compared to the spectra of Ln(III) aquo ions due to the nephelauxetic effect. The magnitude of the red shift depends on the change in the electronic repulsion parameters in the complexes(20). Nephelauxetic (β) ratio is equal to ν_c/ν_f, where ν_c and ν_f are energy in cm^{-1} of the transitions in complex and free metal ion respectively. Nephelauxetic ratio is a measure of covalency in metal–ligand bond. It depends on the expansion of electron cloud present in the shell by the ligand and denoted by B this parameter is expressed in the form(21).

$$\frac{(1-\beta) = \bar{\nu}_{aquo} - \bar{\nu}_{complex}}{\bar{\nu}_{aquo}} \tag{1}$$

$$\delta\% = \frac{1-\beta}{\beta} \text{ x } 100 \tag{2}$$

Where $\bar{\nu}$ refers to wave number of corresponding band. The bonding parameters ($b^{1/2}$,) and covalency–angular overlap parameter (η) are related to B as follows(22,23).

$$b^{1/2} = \left[\frac{1}{2}(1-\beta)\right]^{1/2} \tag{3}$$

$$\eta = \frac{(1 - \beta^{1/2})}{\beta^{1/2}} \tag{4}$$

Korraker and others(24,25) showed that the coordination number of lanthanide element can be predicted from the shape, intensity and wavelength of the hypersensitive transition in the visible region. It was also noted that if the coordination number decreases, intensity of hypersensitive band increases.

In the electronic spectra of Ce(III), Pr(III), Nd(III) and Sm(III) complexes recorded in DMF shows bands, in comparison to the spectra of pure salt lanthanide(III) chloride/nitrate.

Ce(III) Complexes:

Ce(III) complexes display five bands in the region 22,480–22,520, 23,650–23,680, 32,580–32,610, 45,380–45,420 and 47,900–47,920 cm^{-1}. The first three bands are assigned to Laporte–Allowed lattice 4f→5d transition and the last two bands correspond to transitions:

$${}^2F_{5/2} \rightarrow {}^2D_{3/2} \quad \text{and} \quad {}^2F_{5/2} \rightarrow {}^2D_{5/2}$$

Pr(III), Nd(III) and Sm(III) Complexes:

The electronic spectral bands of Pr(III), Nd(III) and Sm(III) complexes are due to the transition from the ground levels, ${}^3H_4$, ${}^4I_{9/2}$ and ${}^6H_{5/2}$ to the excited J levels of 4f–configuration respectively.

Pr(III) Complexes:
In Pr(III) complexes four bands in 16,700–16,750, 20,700–20,760, 21,480–21,510 and 22,400–22,460 cm^{-1} have been observed which are assigned to the following transitions:
$^3H_4 \rightarrow {}^1D_2$, $^3H_4 \rightarrow {}^3P_0$; $^3H_4 \rightarrow {}^3P_1$ and $^3H_4 \rightarrow {}^3P_2$

The hypersensitive nature of some transitions is due to the heterogeneity of the solvent. The reason of hypersensitivity is possibly due to the electronic quadrupole rather than electronic dipole.The magnetic moments of the complexes shows little deviations from van vleck values(26) and those of hydrated sulphates. This indicates that 4f–electrons do not take part in bonding, due to very effective shielding by $5S^2$ $5p^6$ electrons.

The electronic absorption bands(27) of Pr(III), Nd(III) and Sm(III) appear due to the transitions from the ground levels $^3H_4$, $^4I_{9/2}$, $^6H_{5/2}$ to the excited J–Levels of 4f–configuration respectively. Pr(III) complex shows bands around 17,300, 20,800, 22,000 and 23,000 cm^{-1} corresponding to the transitions from $^3H_4$ to $^4D_2$, $^2P_0$, $^3P_1$ and $^3P_2$ energy levels, respectively.

Nd(III) complexes show bands around 12,000, 12,800, 13,000, 13,500, 18,500, 19,500, 20,800 and 23,000 cm^{-1} assignable to transitions from $^4I_{9/2}$ level to $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^2S_{3/2}$, $^4G_{7/2}$, $^2G_{9/2}$, $^4G_{9/2}$ $^2P_{1/2}$ energy levels respectively(28).

Sm(III) complexes show bands around 17,500, 18,900, 20,000, 20,500, 21,500, 23,800 and 25,000 cm^{-1} corresponding to the energy levels $^4G_{5/2}$, $^4F_{3/2}$, $^4G_{7/2}$, $^4I_{9/2}$, $^4I_{13/2}$, $^6P_{5/2}$ and $^4F_{9/2}$ respectively. It has been observed that on complexation the electronic spectral bands of Pr(III), Nd(III) and Sm(III) shift to lower energy side. The slight shift in the bands have been attributed by Jorgenson to the effect of crystal fields upon the inter electronic(29-31) repulsions between the 4f–electrons i.e. to lowering of inter-electron repulsion parameter in the complexes. Further a marked enhancement in the intensity of the bands upon complexation is also observed. Values of β for the present derivatives are calculated. From the mean β–values, the covalency parameter (δ) and bonding parameter (b1/2) were determined using the standard procedures. The values of β–which are less than unity and positive values of δ–and b1/2–support partial covalent nature of bonding between metal and the ligand. The magnitudes of covalency parameter and bonding parameter increases from Pr(III) to Sm(III) indicating that the extent of covalent character of metal–ligand bond increases with the increase in atomic number which is in conformity with the lanthanide contraction.(32-37)

CONCLUSION

(1) The micro analytical data indicates that the chelates are tris.
(2) The complexes are anhydrous and therefore 6–coordination is indicated.
(3) IR spectral data of the complexes indicate (a) the absence of the OH…O broad absorption band which is centered at 2600 cm^{-1} in the ligand and (b) the shift of the C=O stretching frequency from 1640 cm^{-1} in the ligand to ~1608 cm^{-1} in the complex. The inference therefore is that the OH of an enol form of the ligand and C=O are involved in bonding.
(4) UV data reveal that there is no π–bond interaction involving chelate rings of the tris complex indicating that attachment of the ligand anions to the metal involves δ–bonds.

(5) In spite of NMR data, from arguments given above, it appears likely that a very rapid equilibrium mixture of both the cis– and trans–isomers is present.

REFERENCES

[1] B.S. Jensen, *Acta Chem. Scand*; 13 (**1959**) 1668.
[2] I.J. Bellamy and R.F. Branch, *J. Chem. Soc*; 4491 (**1954**).
[3] K.E. Lawson, *Spectrochim. Acta* 17 (**1961**) 248.
[4] N. Nakamoto, Y. Morimoto and A.F.Martell, *J. Phys. Chem*; 66 (**1967**) 346.
[5] S.Pinchas, B.L. Silver and I. Laulicht, *J. Chem. Phys*. 46 (**1967**) 1506.
[6] H.Junge and H.Musso, *Spectrochim Acta 24A* (**1968**) 1219.
[7] J.C. Robles, Y. Matsuzaka, et al *Inorg. Chem*; 32 (**1993**) 13.
[8] K. Dey, K.K. Nandi and G.B. Kaufman, *Polyhedron* 13 (**1994**) 2047.
[9] U.Avetata, N. Demirhan and M.Teker, *J. Incl. Phen* M 26 (**1996**) 27.
[10] U. Avetata, et al Synth. React. *Inorg. Met. Org. Chem*; 28 (**1998**) 393.
[11] U.Avetata, et al, Synth. React. Inorg. *Met. Org. Chem*; 29 (**1999**) 827.
[12] N. Demirhan, et al Synth. React. *Inorg. Met. Org. Chem*; 32 (**2002**) 1567.
[13] U. Avetata, N. Demirhan and A. Gul, *Monatsh Chem*. 129 (**1998**).
[14] J.R. Hutchison, J.G. Gordon and R.H. Holm, *Inorg. Chem*. 10 (**1971**) 1004.
[15] L.M. Jackman and F.A. Cotton, Dynamic Nuclear Magnetic Resonance pp 347–358 Academic Press (**1975**).
[16] W.T. Carnell, P.R. Fields and Rajnak, *J. Chem. Phys*. 49 (**1968**) 4413.
[17] S.P. Tandon and P.C. Mehta, *J. Chem. Phys*. 52 (**1970**) 4313.
[18] S.S.L. Suroma, et al, *J. Inorg. Nucl. Chem*; 42 (**1980**) 610.
[19] Megh Singh, G.K. Joshi, et al, *Ind. J. Pure Appl. Phys*; 17 (**1979**) 610.
[20] R.D. Peacock, J. Chem. Soc. (A) (1971) 2038 *Mole. Phys*. 25 (**1973**) 817.
[21] C.K. Jorgenson, Modern aspects of ligand field theory (North Hall Amsterdam).
[22] C.K. Jorgenson and B.R. Judd, *Mol. Phys*. 8 (**1964**) 28.
[23] D.E. Henric and G.R. Coppin, *J. Chem. Phys*; 49 (**1968**) 477.
[24] M.Singh, S.N. Mishra and R.D. Verma, *J. Inorg. Nucl. Chem*; 40 (**1978**) 1939.
[25] D.G. Karraker, *Inorg. Chem*; 6 (**1967**) 1863.
[26] S.P. Tandon and P.C. Mehta, *J. Chem. Phys*; 52 (**1970**) 5416.
[27] J.H. Van Vleck and A. Frank, *Phys. Rev*; 34 (**1929**) 494.
[28] D.M. Yost, H. Russel and C.S. Garner, The rare earth elements and their compounds (Wiley, New York) **1957**.
[29] C.K. Jorgensen, *Acta Chem. Scand* 11 (**1957**) 1981.
[30] S.P. Sinha, *J. Inorg. Nucl. Chem*; 33 (**1971**) 2205.
[31] A.d. Garnovskii and I.S. Vailchenko, *Russ. Chem. Rev*; 71 (**2002**) 943.
[32] P.A. Vigato and S. Tamburini, *Coord. Chem. Rev*; 248 (**2004**) 1717.
[33] S.A. Cotton, C.R. *Chimic* 8 (**2005**) 129.
[34] K. Mohanan and S.N. Devi, *J. Ind. Chem. Soc*; 83 (**2006**) 31.
[35] K.M. Khan, et al, *J. Enz. Inh. Med. Chem*; 21 (**2006**) 139.
[36] K. Mohanan and S.N. Devi, *Russian J. Coord. Chem*; 32 (**2006**) 600.
[37] K. Mohanan, S.N. Devi and B. Murukan, *Synth. React. Inorg. Met. Org. Met. Chem*; 36 (**2006**) 441.