Studies on the Effect of Picolines on the Stereochemistry of Lanthanide(III) Nitrates Coordination Compounds of 4[N-Furfural)amino]antipyrine semicarbazone and antibacterial activities

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ABSTRACT. In the present studies the effect of α-, β- and γ picolines on the stereochemistry of the coordination compounds of lanthanides(III) nitrates derived from 4[N-(furfural)amino]antipyrine semicarbazone (FFAAPS) has been studied. The general composition of the present coordination compounds is [Ln(FFAAPS)(NO$_3$)$_3$Pic] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho and Pic = α-, β- or γ-picolines). All these coordination compounds have been characterized by elemental analyses, molecular weight, molar conductance, magnetic susceptibility, infrared and electronic spectra. The infrared studies suggest that the FFAAPS behaves as a neutral tridentate ligand with N, N, O donor while α-, β- or γ-picoline is coordinated to the lanthanides(III) ion *via* hecterocyclic N-atom. Nitrates are bicovalently bonded in these compounds. From the electronic spectral data, nephelauxetic effect (β), covalence factor (b$^{1/2}$), Sinha parameter (δ%) and the covalence angular overlap parameter (η) have been calculated. Thermal stabilities of these complexes have been studied by thermogravimetric analysis. The coordination number of lanthanides(III) in the present compound is found to be ten. The antibacterial studies screening of the primary ligand FFAAPS and the complexes showed that the present complexes have moderate antibacterial activities.

Key words: Lanthanides, Lanthanides(III) semicarbazone, Semicarbazone complexes, Coordination compounds, Antibacterial properties.

INTRODUCTION

Initially coordination chemistry of lanthanides was limited to strongly chelating ligands with oxygen as donor atoms.[1-3] With the development of new complexing compounds, a significant number of lanthanide complexes with various types of ligands were synthesized and characterized. The chemistry of metal complexes with heterocyclic compounds containing nitrogen, sulfur and oxygen as complexing ligands has attracted increasing attention. It is well known that heterocyclic compounds are widely distributed in nature and essential to many biochemical processes. These compounds are of worth attention for many reasons due to their biological activities while many drugs involve heterocycles, sulfur, oxygen, nitrogen, amino-nitrogen, azomethine nitrogen and alcoholic or phenolic oxygen are some of the donor atoms of interest. Pyrazolone (N-heterocyclic compounds) is an active moiety as a pharmaceutical ingredient, especially in non-steroidal anti-inflammatory agents used in the treatment of arthritis and other musculoskeletal and joint disorders. Earlier work reported that some drugs showed increased activity when administered as metal chelates rather than as organic compounds. The coordinating behaviour of 4-aminoantipyrine has been modified into a flexible ligand system by condensation with a variety of reagents like aldehyde, ketone, semicarbazide[4], thiosemicarbazide, *etc.*[5-7] Several biological effects of lanthanides have been developed and recognized for decades and used as tools in biomedical studies in the last century.[8-17] In recent years, new experimental methods have been developed due to which new data on the role of lanthanides in the biochemical processes operating in cellular membranes, organelles and cytoplasm have been obtained.[8-17] In pursuit of better understanding of the chelating behaviour of some N, N, O and N, N, S donor semicarbazones and thiosemicarbazones in metal complexes our[4-7,18-29] and other[30-31] research groups have

acquired more information about their nature of coordination behaviour, structures, spectral[4-7,18-29] and biological properties.[6,24-29] In continuation of our study, in present communication we studied the effect of picolines on the stereochemistry of lanthanide(III) nitrates coordination compounds of 4[N-(furufral)amino]antipyrine semicarbazone (Fig. 1) and their biological properties.

EXPERIMENTAL

Materials

The lanthanide(III) nitrates were obtained from Rare Earth Products Ltd. (India) and were used without further purification. α-, β- and γ-picolines, 4-aminoantipyrine and furfural were purchased from S.D. Fine Chemicals (India). The ligand 4[N-(furfural)amino]antipyrine semicarbazone was synthesized by reported method.[4,18] All the solvents were obtained from BDH, E-Merck and S.D. Fine Chemicals (India). These solvents were used as such or after distillation if felt necessary.

Synthesis of the complexes

All the complexes of lanthanide(III) nitrato complexes were synthesized by mixing the methanolic solution of respective lanthanide(III) nitrate, FFAAPS and picolines in the molar ratio 1:1:1 and refluxing the reaction mixture for *ca*. 2 h. The resulting solution was concentrated by evaporation on a water bath. It was then washed repeatedly with methanol and then extracted with anhydrous diethyl ether to get the solid complex. The coloured complexes were filtered and dried *in vacuo* over P_4O_{10}.

Composition and analytical estimations

The lanthanide content in the complexes was estimated as their oxides by direct combustion in a platinum crucible. The estimation was further confirmed by dissolving

the product of direct combustion in dil. HCl. The acid solution of the decomposed complexes was transferred into a flask. Its pH was adjusted to 5.8-6.4 using acetic acid-sodium acetate buffer and was then titrated against 0.1 M EDTA using xylenol orange indicator. The results from both the methods were in excellent agreement within the experimental error. The nitrogen contents in the compounds were estimated by Kjeldahl method. The molecular weights of the complexes were determined cryoscopically in freezing nitrobenzene (PhNO$_2$) using a Beckmann thermometer of accuracy ± 0.01 ºC.

Physical measurements and antibacterial studies

The conductivity measurements were carried out at room temperature in PhNO$_2$ using a Toshniwal conductivity Bridge (type CL01/01) and a dip type cell operated at 220 volts. All the measurements were done at room temperature. A Gouy's balance was used for the magnetic measurements at room temperature where Hg[Co(SCN)$_4$] was used as a calibrant. The infrared spectra of the lanthanide(III) complexes were recorded, on a Perkin-Elmer spectrophotometer model 521, in KBr in the range of 4000-200 cm^{-1}. The visible spectra of different Pr^{3+}, Nd^{3+} and Sm^{3+} complexes were recorded using a Hilger Uvispek spectrophotometer with 1 cm quartz cell. The red shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these complexes. From the β-values the covalence factors (b$^{1/2}$), Sinha paramter *i.e.* metal-ligand covalency per cent (δ%) and the covalency angular overlap parameter (η) have been calculated by following equations.[32,33]

$$b^{1/2} = \frac{1}{2}[(n-\beta)^{1/2}]$$

$$\delta\,(\%) = \left\{\frac{(1-\beta)}{\beta}\right\} \times 100$$

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

The thermogravimetric analysis of lanthanide(III) complexes was carried out in static air with open sample holder and a small platinum boat, the heating rate was 6 ºC/min.

The antibacterial activity of some of the lanthanide(III) complexes were screened by agar-cup method in DMF solvents at a concentration of 50 µg mL^{-1} and the results were checked against gram positive bacteria *Bacillus subtilis* (*B. subtilis*) and *Staphylococcus aureus* (*S. aureus*) and gram negative bacteria *Escherichia coli* (*E. coli*) and *Salmonella typhi* (*S. typhi*).[6,28]

RESULTS AND DISCUSSION

The reaction of methanolic solutions of lanthanide(III) nitrates with 4[N-(furufral)amino]antipyrine semicarbazone (FFAAPS) and α-, β- or γ-picolines (α, β, γ-pic) resulting in the formation of complexes of the general composition [Ln(FFAAPS)(NO$_3$)$_3$Pic] where Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho. The analytical data of the present compounds are given in Table 1. The complexes are generally stable and could be stored for a long time and are non-hygroscopic in nature. Majority of the complexes do not possess sharp melting point and decomposed around 250ºC. The analytical data presented in Table 1 indicate that the complexes are generally pure and need no further purification.

The molar conductance values (Table 1) in PhNO$_2$ are too low to account for any dissociation, therefore these coordination compounds considered to be non-electrolytes.[34] The ratio of molecular weight observed to that calculated was ~ 0.98. It clearly shows that the complexes are monomeric in solution. The magnetic moment values calculated in 4f-metal complexes are also given in Table 1 which shows that the lanthanum complexes are diamagnetic in nature. The same is expected from its closed shell electronic configuration and absence of unpaired electrons. The remaining tripositive lanthanide(III) complexes

are paramagnetic due to the presence of 4f-electrons, which are effectively shielded by $5s^2$ and $5p^6$ electrons. The comparison of these observed values with those observed for 8-hydrated sulphate[35] and those calculated for uncomplexed ions, indicates that the 4f-electrons do not participate in any coordination bond formation in these complexes. The magnetic moments of these complexes are well within the range predicted and observed in the compounds of paramagnetic ions as reported earlier.[36-38]

Infrared spectra

The main infrared bands of the free ligands (FFAAPS and picolines) and their lanthanide(III) nitrates complexes are given in Table 2. As expected the $\nu(NH_2)$ of the hydrazinic nitrogen of semicarbazide ($\sim$1622 cm^{-1}) is absent in the infrared spectra of FFAAPS.[37,38] It has also been observed that the amide-II band is shifted towards the lower energy side compared to that of the semicarbazone. The effect is due to the electron density drift from the hydrazinic nitrogen.[37,38] The characteristics absorption of the carbonyl group in FFAAPS is observed at *ca*. 1700 cm^{-1} [39]. In the complexes, this band is shifted to lower energy region 1655-1645 cm^{-1} as shown in Table 2. The amide-II band in FFAAPS has been observed at 1565 cm^{-1}, this band is also shifted towards lower wave numbers by $\sim$35 cm^{-1} *i.e.* 1630 cm^{-1}. This observation suggests that the coordination is through the carbonyl oxygen atom. The strong band at *ca*. 1600 cm^{-1} in the present semicarbazone apparently has a large contribution from the $\nu(C=N)$ band in all the complexes as compared to the free ligand. Another strong band was observed at 1610 cm^{-1} due to azomethine (C=N) absorption. On complexation this band is shifted towards the lower frequency region, clearly indicating the coordination through the azomethine N-atom.[37,38] In far infrared region the bands due to $\nu(Ln-N)/\nu(Ln-O)$ are also observed.[37,38,40,41]

In the spectra of picolines, strong absorptions occur in range 1650-1435 cm^{-1} due to C=C, C=N stretching and ring vibrations.[42,43] Out of these, the absorptions associated with the cyclic ring are apparently unaffected on complexation, while those arising from the heterocyclic rings are shifted to higher frequencies due to tightening of the ring on coordination. This is suggestive of the view that the picolines is bonded with Ln^{3+} ion through the hetero-N atom.[42-44]

In all the nitrato complexes, the occurrence of two strong absorptions at 1525-1500 cm^{-1} and 1300-1285 cm^{-1} region (Table 3) is attributed to ν_4 and ν_1 modes of vibration of the covalently bonded nitrate group, respectively suggesting that the nitrate groups lie inside the coordination sphere.[45] Other absorptions associated with the covalent nitrate groups are also observed in the spectra of the metal complexes. If the (ν_4-ν_1) difference is taken as an approximate measure of the covalency of the nitrate group[45], a value of ~ 200 cm^{-1} for the complexes studied herein suggest strong covalency for the metal-nitrate bonding. According to Lever *et al.*[46] bidentate coordination involves a greater distortion from D$_{3h}$ symmetry than monodentate coordination. To identify the monodentate or bidentate nature, we applied Lever separation method which states that a separation of 40-50 cm^{-1} in the combination bands in the 1800-1700 cm^{-1} region conclude the bidentate nitrate coordination.[46] The bidentate character of the nitrate groups has been established by X-ray[47] and neutron diffraction studies.[48] Hence the nitrate groups in the present complexes are of bidentate nature.
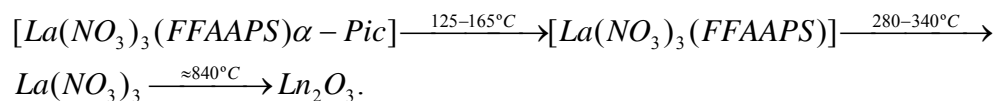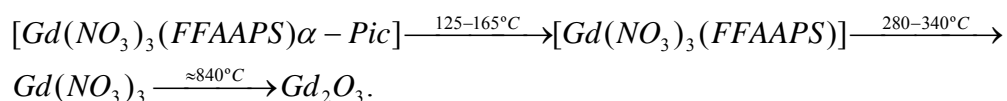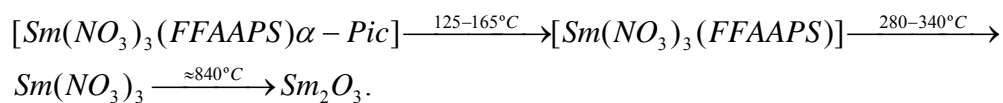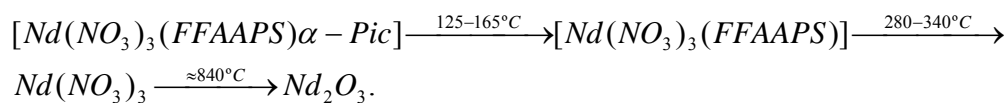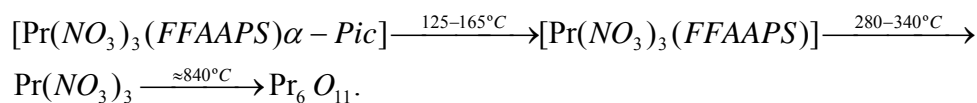
Electronic spectra studies

The electronic spectral data of typical complexes in acetonitrile were recorded and are shown in Table 4. The electronic spectral data for an aqueous salt solution are also given in Table 4. Lanthanum(III) does not show any significant absorption in the visible region. However, praseodymium(III), neodymium(III), samarium(III), gadolinium(III)

and dysprosium(III) has the absorption bands of in the visible and near infrared region. These bands appear due to transitions from the ground levels $^3H_4$, $^4I_{9/2}$, $^6W_{5/2}$, $^8S_{7/2}$ and $^6H_{15/2}$ to the excited J-levels of 4f-configuration, respectively. These red shift or nephelauxetic effect is also observed in acetonitrile solution of the complexes. The red shift is usually accepted as evidence of a higher degree of covalency than existing in the aquo compounds.[32] The marked enhancement in the intensity of the band in all the complexes has been observed which were utilized to calculate the nephelauxetic effect (β) in the complexes. Using the β-values the covalence factor ($b^{1/2}$), Sinha parameter *i.e.* metal-ligand covalency per cent (δ %) and the covalency angular overlap parameter (η) have been calculated (*cf. vide infra*). The positive value for (1-β) and δ % in these chelate complexes (Table 4) suggest that the bonding between the lanthanide(III) and the ligands is more covalent with respect to the bonding in the lanthanide(III) aquo ion. The positive values of $b^{1/2}$ and η support covalent bonding.

Thermogravimetric studies

Thermoanalytical results of typical Ln(NO$_3$)$_3$(FFAAPS)α-Pic] (Ln = La, Pr, Nd, Sm or Gd) are shown presented in Table 5. The pyrolysis curves of these complexes indicate virtually no change in weight up to 120ºC. At 125-160ºC, a loss of 11.87-12.20% has been observed, which corresponds to the evaporation of one α-picoline ligand. Further a loss of 53.49-54.60% in 280-340ºC temperature region show the loss of FFAAPS ligand. The lanthanide oxide (La$_2$O$_3$, Pr$_6$O$_{11}$, Nd$_2$O$_3$, Sm$_2$O$_3$ or Gd$_2$O$_3$) is the final product at ~ 850 ºC as shown in the following equations.[49]

$$[La(NO_3)_3(FFAAPS)\alpha - Pic] \xrightarrow{125-165°C} [La(NO_3)_3(FFAAPS)] \xrightarrow{280-340°C}$$
$$La(NO_3)_3 \xrightarrow{\approx 840°C} Ln_2O_3.$$

$$[Pr(NO_3)_3(FFAAPS)\alpha - Pic] \xrightarrow{125-165°C} [Pr(NO_3)_3(FFAAPS)] \xrightarrow{280-340°C}$$

$$Pr(NO_3)_3 \xrightarrow{\approx 840°C} Pr_6 O_{11}.$$

$$[Nd(NO_3)_3(FFAAPS)\alpha - Pic] \xrightarrow{125-165°C} [Nd(NO_3)_3(FFAAPS)] \xrightarrow{280-340°C}$$

$$Nd(NO_3)_3 \xrightarrow{\approx 840°C} Nd_2 O_3.$$

$$[Sm(NO_3)_3(FFAAPS)\alpha - Pic] \xrightarrow{125-165°C} [Sm(NO_3)_3(FFAAPS)] \xrightarrow{280-340°C}$$

$$Sm(NO_3)_3 \xrightarrow{\approx 840°C} Sm_2 O_3.$$

$$[Gd(NO_3)_3(FFAAPS)\alpha - Pic] \xrightarrow{125-165°C} [Gd(NO_3)_3(FFAAPS)] \xrightarrow{280-340°C}$$

$$Gd(NO_3)_3 \xrightarrow{\approx 840°C} Gd_2 O_3.$$

Antimicrobial studies

Several biological activities of lanthanide(III) complexes have been identified and used as tools in biomedical studies. Their potential pharmaceutical values has received attention as well.[8-17] The antibacterial activities of the present lanthanide(III) complexes and tetracycline standard drug were also screened by agar-cup method in DMF solvent at a concentration of 50 μg mL^{-1}.[6,28] The results were checked against gram positive bacteria *B. subtilis* and *S. aureus* and gram negative bacteria *E. coli* and *S. typhi* and reported in Table 6. The diameters of zone of inhibition (in mm) of the standard drug tetracycline against gram positive bacteria *B. subtilis* and *S. aureus* and gram negative bacteria *E. coli* and *S. typhi* were found to be 18, 17, 21 and 22, respectively. Under identical conditions, Table 6 shows that the lanthanide(III) complexes of FFAAPS and α-picoline have moderate antibacterial activities against these bacteria.

CONCLUSION

The isolated complexes have been characterized by elemental analyses, molar mass, molar conductance, magnetic susceptibility, infrared and electronic spectral studies. The

conductance and the molecular weight determination of these coordination compounds in nitrobenzene indicates their non-ionic nature. Hence all the three nitrate groups are present inside the coordination sphere. Infrared data reveals the bidentate (O, O donor) nature of NO_3^-. FFAAPS is acting as neutral tridentate (N,N,O-donor) and α-, β- and γ-picolines is coordinating *via* its heterocyclic N-atom. The overall experimental evidence showed that these metal ions display a coordination number ten. The lanthanide(III) ions are surrounded by 7-oxygen atoms (6-oxygens of 3-bidentate nitrate ions, 1-oxygen from amide groups of FFAAPS), 2-nitrogen atoms of azomethine groups of FFAAPS and 1-nitrogen atom of heterocyclic ligand and thus products a coordination number of ten for the central lanthanide(III) ion (Fig. 2).[50]
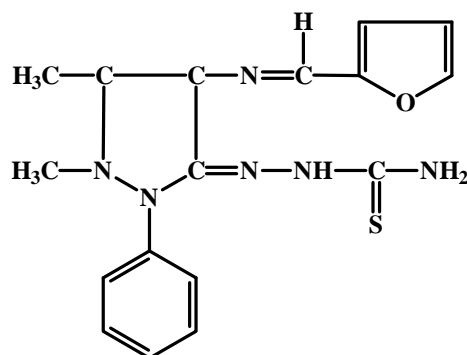
4[N-(furfural)amino]antipyrine semicarbazone (FFAAPS)
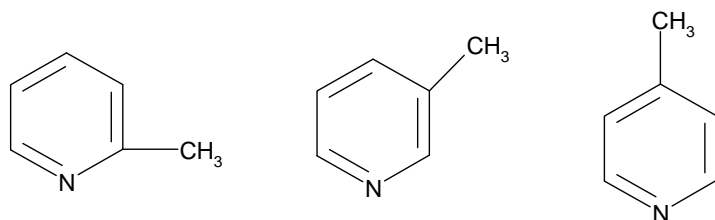
α-Picoline   β-Picoline   γ-Picoline

Fig. 1: Structures of 4[N-(furfural)amino]antipyrine semicarbazone (FFAAPS) and α-, β- and γ-Picolines.
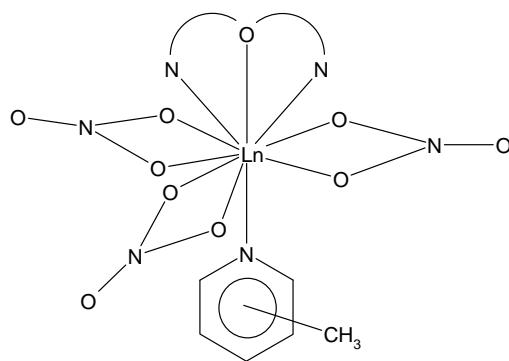
Fig. 2: Proposed structure of [Gd(FFAAPS)(NO$_3$)$_3$γ-Pic], Ln = La,Pr, Nd, Sm, Gd, Tb, Dy or Ho) and Pic = α-, β- or γ-Picolines (C.N. = 10)

Table 1. Analytical, conductivity, molecular weight and magnetic moment data of mixed ligand complexes of lanthanide(III) with FFAAPS as primary ligand and α-, β- and γ-picolines as secondary ligand.

Complex	Yield (%)	Analysis Found (Calcd) (%)				Mol. wt. Found (Calcd.)	Ω_m (ohm^{-1} cm^{-2} mol^{-1})	μ_{eff} (BM)
		Ln	C	H	N			
[La(FFAAPS)(NO$_3$)$_3$α-Pic]	80	18.26 (18.38)	36.31 (36.50)	3.23 (3.30)	12.86 (12.96)	751 (756)	1.8	Diamag
[Pr(FFAAPS(NO$_3$)$_3$α-Pic]	78	18.49 (18.60)	36.23 (36.41)	3.23 (3.29)	12.82 (12.92)	753 (758)	1.7	3.50
[Nd(FFAAPS)(NO$_3$)$_3$α-Pic]	76	18.79 (18.92)	36.08 (36.26)	3.22 (3.28)	12.77 (12.87)	755 (761)	1.6	3.51
[Sm(FFAAPS)(NO$_3$)$_3$α-Pic]	77	19.43 (19.55)	35.71 (35.98)	3.19 (3.25)	12.68 (12.77)	763 (767)	1.9	1.64
[Gd(FFAAPS)(NO$_3$)$_3$α-Pic]	75	20.14 (20.28)	35.49 (35.65)	3.17 (3.23)	12.57 (12.66)	769 (774)	1.6	7.93
[Tb(FFAAPS)(NO$_3$)$_3$α-Pic]	82	20.31 (20.48)	35.43 (35.56)	3.16 (3.22)	12.53 (12.62)	771 (776)	1.7	9.52
Dy(FFAAPS)(NO$_3$)$_3$α-Pic]	80	20.67 (20.84)	35.28 (35.40)	3.14 (3.20)	12.48 (12.57)	774 (779.5)	1.3	10.60
[Ho(FFAAPS)(NO$_3$)$_3$α-Pic]	78	20.83 (21.09)	35.10 (35.29)	3.14 (3.19)	12.45 (12.53)	776 (782)	1.8	10.42
[La(FFAAPS)(NO$_3$)$_3$β-Pic]	79	18.27	36.30	3.24	12.85	750	1.3	Diamag

		(18.38)	(36.50)	(3.30)	(12.96)	(756)		
[Pr(FFAAPS)(NO$_3$)$_3$β-Pic]	76	18.47 (18.60)	36.24 (36.41)	3.23 (3.29)	12.80 (12.92)	752 (758)	1.4	3.52
[Nd(FFAAPS)(NO$_3$)$_3$β-Pic]	78	18.77 (18.92)	36.09 (36.26)	3.22 (3.28)	12.75 (12.87)	757 (761)	1.5	3.50
[Sm(FFAAPS)(NO$_3$)$_3$β-Pic]	79	19.44 (19.55)	35.73 (35.98)	3.19 (3.25)	12.67 (12.77)	762 (767)	1.6	1.65
[Gd(FFAAPS)(NO$_3$)$_3$β-Pic]	80	20.13 (20.28)	35.48 (35.65)	3.17 (3.23)	12.56 (12.66)	770 (774)	0.9	7.94
[Tb(FFAAPS)(NO$_3$)$_3$β-Pic]	82	20.32 (20.48)	35.42 (35.56)	3.16 (3.22)	12.52 (12.62)	771 (776)	1.1	9.53
[Dy(FFAAPS)(NO$_3$)$_3$β-Pic]	81	20.65 (20.84)	35.26 (35.40)	3.15 (3.20)	12.47 (12.57)	775 (779.5))	1.3	10.59
[Ho(FFAAPS)(NO$_3$)$_3$β-Pic]	80	20.82 (21.09)	35.11 (35.29)	3.14 (3.19)	12.43 (12.53)	777 (782)	1.5	10.40
[La(FFAAPS)(NO$_3$)$_3$γ-Pic]	79	18.24 (18.38)	36.33 (36.50)	3.23 (3.30)	12.83 (12.96)	751 (756)	1.6	Diamag
[Pr(FFAAPS)(NO$_3$)$_3$γ-Pic]	80	18.45 (18.60)	36.22 (36.41)	3.24 (3.29)	12.81 (12.92)	753 (758)	1.8	3.54
[Nd(FFAAPS)(NO$_3$)$_3$γ-Pic]	78	8.73 (18.92)	36.10 (36.26)	3.24 (3.28)	12.73 (12.87)	756 (761)	1.6	3.51
[Sm(FFAAPS)(NO$_3$)$_3$γ-Pic]	77	19.43	35.75	3.19	12.67	763	1.8	1.66

		(19.55)	(35.98)	(3.25)	(12.77)	(767)		
[Gd(FFAAPS)(NO$_3$)$_3$γ-Pic]	81	20.12 (20.28)	35.46 (35.65)	3.18 (3.23)	12.55 (12.66)	770 (774)	1.7	7.95
[Tb(FFAAPS)(NO$_3$)$_3$γ-Pic]	80	2033 (20.48)	35.40 (35.56)	3.16 (3.22)	12.52 (12.62)	771 (776)	1.8	9.55
[Dy(FFAAPS)(NO$_3$)$_3$γ-Pic]	78	20.66 (20.84)	35.25 (35.40)	3.14 (3.20)	12.46 (12.57)	775 (779.5)	1.3	10.58
[Ho(FFAAPS)(NO$_3$)$_3$γ-Pic]	81	20.83 (21.09)	35.13 (35.29)	3.14 (3.19)	12.43 (12.53)	777 (782)	1.5	10.47

Table 2. Key infrared spectral bands (cm^{-1}) of mixed lignad complexes of lanthanides(III) nitrate with FFAAPS and α-, β- and γ-picolines.

Compound	ν(C=N) azomethine	ν(C=N) hydrazine	ν(C=O) I	II	III	ν(C=C), ν(C=N) and ring coordination	ν(Ln−O)/ν(Ln−N)
α-Pic	—	—	—	—	—	1588sh, 1585s, 1578s, 1483s, 1440s	—
β-Pic	—	—	—	—	—	1590w, 1587s, 1575s, 1480s,1437s	—
γ-Pic	—	—	—	—	—	1592sh, br, 1590s, 1578m, 1483m, 1442s	—
FFAAPS	1610s	1600m	1700m	1565s	1340m	—	—
[La(FFAAPS)(NO₃)₃α-Pic]	1580m	1630m	1645m	1532m	1320m	1633s, 1610vs, 1510vs, 1468vs	450m, 392w
[Pr(FFAAPS(NO₃)₃α-Pic]	1582m	1632m	1650m	1530m	1325m	1630s, 1603vs, 1518vs, 1468vs	452m, 395w
[Nd(FFAAPS)(NO₃)₃α-Pic]	1585m	1625m	1652m	1533m	1322m	1645s, 1605vs, 1492vs, 1482vs	460m, 402w
[Sm(FFAAPS)(NO₃)₃α-Pic]	1583m	1620m	1650m	1530m	1320m	1635s, 1605vs, 1520vs, 1470vs	455m, 390w
[Gd(FFAAPS)(NO₃)₃α-Pic]	1581m	1632m	1652m	1532m	1318m	1640s, 1610vs, 1503vs, 1484vs	445m, 392w
[Tb(FFAAPS)(NO₃)₃α-Pic]	1578m	1630m	1648m	1530m	1322m	1645s, 1605vs, 1499vs, 1485vs	450m, 398w
Dy(FFAAPS)(NO₃)₃α-Pic]	1578m	1632m	1650m	1533m	1325m	1630sh, 1582s, 1575s, 1470s	452m, 395w
[Ho(FFAAPS)(NO₃)₃α-Pic]	1580m	1630m	1652m	1535m	1320m	1635s, 1612vs, 1520vs, 1470vs	440m, 390w
[La(FFAAPS)(NO₃)₃β-Pic]	1582m	1631m	1653m	1530m	1315m	1645s, 1610vs, 1520s, 1468m	442m, 392w
[Pr(FFAAPS)(NO₃)₃β-Pic]	1585m	1632m	1655m	1532m	1320m	1642s, 1600vs, 1525vs, 1472m	460m, 400w
[Nd(FFAAPS)(NO₃)₃β-Pic]	1587m	1630m	1645m	1533m	1321m	1648s, 1608vs, 1525vs, 1473vs	443m, 398w
[Sm(FFAAPS)(NO₃)₃β-Pic]	1582m	1628m	1647m	1532m	1322m	1638s, 1612vs, 1518vs,	460m, 395w

							1470vs	
[Gd(FFAAPS)(NO$_3$)$_3\beta$-Pic]	1585m	1635m	1645m	1533m	1323m	1637sh, 1615vs, 1520vs, 1472vs	462m, 380w
[Tb(FFAAPS)(NO$_3$)$_3\beta$-Pic]	1583m	1632m	1640m	1532m	1320m	1642s, 1612vs, 1498vs, 1480s	465m, 392w
[Dy(FFAAPS)(NO$_3$)$_3\beta$-Pic]	1582m	1637m	1652m	1533m	1322m	1630s, 1615vs, 1505s, 1482m	470m, 395w
[Ho(FFAAPS)(NO$_3$)$_3\beta$-Pic]	1585m	1635m	1650m	1632m	1322m	1637s, 1608vs, 1518vs, 1472m	472m, 398w
[La(FFAAPS)(NO$_3$)$_3\gamma$-Pic]	1588m	1628m	1652m	1530m	1320m	1639s, 1612vs, 1522vs, 1480m	450m, 395w
[Pr(FFAAPS)(NO$_3$)$_3\gamma$-Pic]	1587m	1630m	1650m	1532m	1321m	1638s, 1608s, 1515vs, 1482m	445m, 392w
[Nd(FFAAPS)(NO$_3$)$_3\gamma$-Pic]	1585m	1632m	1652m	1533m	1322m	1632s, 1610s, 1518vs, 1482s	465m, 398w
[Sm(FFAAPS)(NO$_3$)$_3\gamma$-Pic]	1580m	1633m	1648m	1530m	1320m	1635s, 1612vs, 1522vs, 1470vs	470m, 399w
[Gd(FFAAPS)(NO$_3$)$_3\gamma$-Pic]	1582m	1635m	1640m	1532m	1322m	1645s, 1612vs, 1522s, 1468m	472m, 400w
[Tb(FFAAPS)(NO$_3$)$_3\gamma$-Pic]	1585m	1637m	1645m	1530m	1320m	1637s, 1610s, 1525s, 1470m	470m, 400w
[Dy(FFAAPS)(NO$_3$)$_3\gamma$-Pic]	1583m	1638m	1642m	1532m	1321m	1640s, 1615vs, 1518s, 1472m	465m, 398w
[Ho(FFAAPS)(NO$_3$)$_3\gamma$-Pic]	1582m	1840m	1640m	1530m	1320m	1642s, 1620s, 1520s, 1475m	460m, 400w

Table 3. Infrared absorption frequencies (cm^{-1}) of NO_3^- ion in Gd(FFAAPS)(NO$_3$)$_3$$\alpha$-, β- or γ-picolines.

Complexes	$(\nu_2 + \nu_5)$	$(\nu_2 + \nu_6)$	$(\nu_2 + \nu_5) - (\nu_2 + \nu_6)$	ν_4	ν_1	ν_2	ν_6	ν_3	ν_5
[La(FFAAPS)(NO$_3$)$_3$$\alpha$-Pic]	1782vw	1740vw	42	1500s,br	1295m	1030m	825m	740m	700w
[Pr(FFAAPS(NO$_3$)$_3$$\alpha$-Pic]	1790vw	1745vw	45	1520m, 1515w	1292m	1028m	817m	735m	—
[Nd(FFAAPS)(NO$_3$)$_3$$\alpha$-Pic]	1785vw	1740vw	45	1518m	1298m	1032m	822m	742m	698w
[Sm(FFAAPS)(NO$_3$)$_3$$\alpha$-Pic]	1780vw	1738vw	42	1525m	1300m	1025m	823m	738m	690w
[Gd(FFAAPS)(NO$_3$)$_3$$\alpha$-Pic]	1790vw	1740vw	50	1515m	1302m	1028m	825m	737m	685sh
[Tb(FFAAPS)(NO$_3$)$_3$$\alpha$-Pic]	1782vw	1732vw	50	1512m	1290m	1025m	820m	740m	690w
Dy(FFAAPS)(NO$_3$)$_3$$\alpha$-Pic]	1785vw	1742vw	43	1498s,br	1285m	1030m	822m	735m	700w
[Ho(FFAAPS)(NO$_3$)$_3$$\alpha$-Pic]	1792vw	1742vw	50	1510sh, 1490m	1300m	1032m	825m	738m	—
[La(FFAAPS)(NO$_3$)$_3$$\beta$-Pic]	1790vw	1745vw	45	1515m	1302m	1028m	822m	737m	702sh
[Pr(FFAAPS)(NO$_3$)$_3$$\beta$-Pic]	1792vw	1752vw	40	1525m 1510w	1295m	1030m	830m	735m	710sh
[Nd(FFAAPS)(NO$_3$)$_3$$\beta$-Pic]	1795vw	1750vw	45	1510sh, 1490m	1292m	1032m	827m	740m	698w
[Sm(FFAAPS)(NO$_3$)$_3$$\beta$-Pic]	1790vw	1745vw	45	1515m 1510w	1295m	1025m	828m	738m	690w
[Gd(FFAAPS)(NO$_3$)$_3$$\beta$-Pic]	1792vw	1742vw	50	1520m	1300m	1027m	832m	735m	695w

				1508m					
[Tb(FFAAPS)(NO$_3$)$_3$β-Pic]	1795vw	1745vw	50	1510sh, 1490m	1302m	1028m	830	742m	690sh
[Dy(FFAAPS)(NO$_3$)$_3$β-Pic]	1785vw	1740vw	45	1522m, 1510w	1298m	1030m	830m	740m	692sh
[Ho(FFAAPS)(NO$_3$)$_3$β-Pic]	1790vw	1745vw	45	1525m	1295m	1032m	832m	735m	685w
[La(FFAAPS)(NO$_3$)$_3$γ-Pic]	1788vw	1744vw	44	1520m	1298m	1028m	830m	742m	690w
[Pr(FFAAPS)(NO$_3$)$_3$γ-Pic]	1792vw	1742vw	50	1518m 1503w	1302m	1030m	828m	738m	692w
[Nd(FFAAPS)(NO$_3$)$_3$γ-Pic]	1787vw	1747vw	40	1522m 1510w	1299m	1032m	832m	737m	695w
[Sm(FFAAPS)(NO$_3$)$_3$γ-Pic]	1790vw	1750vw	47	1525m 1510w	1302m	1035m	837m	738m	698w
[Gd(FFAAPS)(NO$_3$)$_3$γ-Pic]	1792vw	1752vw	40	1520m	1295m	1028m	833m	740m	700w
[Tb(FFAAPS)(NO$_3$)$_3$γ-Pic]	1782vw	1735	47	1515m	1292m	1032m	835m	742m	702sh

Table 4. Electronic spectral data (cm^{-1}) and related bonding parameters of mixed ligand complexes of lanthanide(III) nitrate with FFAAPS and α-, β- and γ-picolines.

Complex	Ln(NO$_3$)$_3$ spectral bands in aqueous solution	Complex electronic spectral band in acetonitrile	Energy levels	$(1-\beta)$	β	$b^{1/2}$	$\delta\%$	η
[Pr (FFAAPS)(NO$_3$)$_3$α-Pic]	22470	22320	$^3H_4 \rightarrow 3P_2$	0.0066	0.9934	0.0408	0.6715	0.0033
	21280	21100	$\rightarrow 3P_1$	0.0084	0.9916	0.0459	0.8613	0.0042
	20830	20650	$\rightarrow 3P_0$	0.0086	0.9914	0.0464	0.8715	0.0043
	16950	16750	$\rightarrow 1D_2$	0.0118	0.9882	0.0543	1.1930	0.0056
[Nd (FFAAPS)(NO$_3$)$_3$α-Pic]	19420	19250	$^4I_{9/2} \rightarrow {}^2G_{9/2}, {}^2G7_{7/2}$	0.0087	0.9913	0.4670	0.8827	0.0044
	17390	17200		0.0109	0.9871	0.0522	1.1040	0.0055
	13420	13200	$\rightarrow {}^4G_{5/2}, {}^4F_{7/2}$	0.0164	0.9836	0.0640	1.6663	0.0082
	12500	12450	$\rightarrow {}^2S3_{3/2}, {}^4H_{9/2}$	0.0120	0.9888	0.0547	1.2145	0.0060
			$\rightarrow {}^4F_{5/2}$					
[Sm(FFAAPS)(NO$_3$)$_3$α-Pic]	24850	24720	$^4H_{9/2} \rightarrow {}^4F_{9/2}$	0.0052	0.9948	0.0361	0.5257	0.0026
	24100	23820	$\rightarrow {}^6P_{5/2}$	0.0116	0.9884	0.0538	1.1746	0.0058
	21600	21450	$\rightarrow {}^4I_{13/2}$	0.0069	0.9931	0.0416	0.6988	0.0035
[Pr(FFAAPS)(NO$_3$)$_3$β-Pic]	22470	22300	$^3H_4 \rightarrow {}^3P_2$	0.0076	0.9924	0.0436	0.7658	0.0038
	21280	21050	$\rightarrow {}^3P_1$	0.0108	0.9892	0.0520	1.0918	0.0054
	20830	20600	$\rightarrow {}^3P_0$	0.0114	0.9889	0.0534	1.1528	0.0055
	16950	16750	$\rightarrow {}^1D_2$	0.0118	0.9900	0.0543	1.1919	0.0059
[Nd(FFAAPS)(NO$_3$)$_3$β-Pic]	19420	19250	$^4I_{9/2} \rightarrow {}^2G_{9/2},$	0.0088	0.9912	0.0469	0.8878	0.0119

	17390	17200	$^2G_{7/2}$	0.0109	0.9891	0.0523	1.1050	0.0055
	13420	13220	$\rightarrow ^4G_{5/2},\ ^4F_{7/2}$	0.0149	0.9851	0.0510	1.5125	0.0076
	12500	12350	$\rightarrow ^2S_{3/2},\ ^4H_{9/2}$	0.0120	0.9880	0.0548	1.2146	0.0060
			$\rightarrow ^4F_{5/2}$					
[Sm(FFAAPS)(NO$_3$)$_3$β-Pic]	24850	24710	$^4H_{9/2} \rightarrow ^4F_{9/2}$	0.0056	0.9944	0.0374	0.5632	0.0028
	24100	23800	$\rightarrow ^6P_{5/2}$	0.1245	0.9876	0.558	1.2606	0.0062
	21600	21400	$\rightarrow ^4I_{13/2}$	0.0093	0.9974	0.0482	0.9324	0.0046
[Pr(FFAAPS)(NO$_3$)$_3$γ-Pic]	22470	22300	$^3H_4 \rightarrow ^3P_2$	0.0076	0.9924	0.0436	0.7658	0.0038
	21280	21000	$\rightarrow ^3P_1$	0.0132	0.9868	0.0574	1.3336	0.0066
	20830	20600	$\rightarrow ^3P_0$	0.0110	0.9890	0.0524	1.1122	0.0055
	16950	16700	$\rightarrow ^1D_2$	0.0147	0.9853	0.0606	1.4919	0.0075
[Nd (FFAAPS)(NO$_3$)$_3$γ-Pic]	19420	19200	$^4I_{9/2} \rightarrow ^2G_{9/2},\ ^2G_{7/2}$	0.0113	0.9887	0.0531	1.1429	0.0057
	17390	17200	$\rightarrow ^4G_{5/2},\ ^4F_{7/2}$	0.0109	0.9891	0.0522	1.1020	0.0055
	13420	13200	$\rightarrow ^2S_{3/2},\ ^4H_{9/2}$	0.0164	0.9836	0.0640	1.6673	0.0083
	12500	12300	$\rightarrow ^4F_{5/2}$	0.0160	0.9840	0.0632	1.6260	0.0081
[Sm(NO$_3$)$_3$(FFAAPS)(NO$_3$)$_3$γ-Pic]	24850	24700	$^4H_{9/2} \rightarrow ^4F_{9/2}$	0.0060	0.9940	0.0387	0.6036	0.0060
	24100	23800	$\rightarrow ^6P_{5/2}$	0.0125	0.9876	0.0560	1.2657	0.0062
	21600	21420	$\rightarrow ^4I_{13/2}$	0.0083	0.9917	0.0456	0.8370	0.0042

Table 5. Thermoanalytical results of some mixed ligand complexes of lanthanide(III) nitrate with FFAAPS and α-picolines.

Complex	Sample wt (mg)	Residual wt. (mg)	Ligand mass loss (%)				Residual (%) ~ 850°C	
			125-165°C		280-340°C			
			Theor.[a]	Exp	Theor.[b]	Exp	Theor.[c]	Exp
[La(FFAAPS)(NO$_3$)$_3$α-Pic]	15.60	3.31	12.30	12.20	54.89	54.38	21.56	21.73
[Pr(FFAAPS)(NO$_3$)$_3$α-Pic]	18.10	4.09	12.26	12.16	54.74	54.60	22.47	22.63
[Nd(FFAAPS)(NO$_3$)$_3$α-Pic]	20.10	4.09	12.22	12.11	54.53	54.36	22.07	22.36
[Sm(FFAAPS)(NO$_3$)$_3$α-Pic]	22.30	5.11	12.12	12.00	54.10	53.87	22.68	22.94
[Gd(FFAAPS)(NO$_3$)$_3$α-Pic]	24.10	5.69	12.01	11.87	53.61	53.49	23.38	22.63

[a]Calculated for loss of α-Pic
[b]Calculated for loss of FFAAPS
[c]Calculated for lanthanide oxides (La$_2$O$_3$, Pr$_6$O$_{11}$, Nd$_2$O$_3$, Sm$_2$O$_3$, Gd$_2$O$_3$)

Table 6. Antibacterial activity of FFAAPS and [Ln(FFAAPS)(NO$_3$)$_3\alpha$-Pic].

Compound	*E. coli*	*S. aureus*	*B. subtilis*	*S. typhi*
FFAAPS	+ +	+	+ +	+ +
[La(FFAAPS)(NO$_3$)$_3\alpha$-Pic]	+ +	+ +	+ + +	−
[Pr(FFAAPS)(NO$_3$)$_3\alpha$-Pic]	+ + +	+ +	+ + +	+ + +
[Nd(FFAAPS)(NO$_3$)$_3\alpha$-Pic]	+ +	+ +	+ + +	+ +
[Sm(FFAAPS)(NO$_3$)$_3\alpha$-Pic]	+ + +	+ +	+ + +	+ + +
[Tb(FFAAPS)(NO$_3$)$_3\alpha$-Pic]	+ +	+ +	+ + +	+ +
Tetracycline	+ + + +	+ + +	+ + + +	+ + + +

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