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YTTRIUM AND LANTHANIDE NITRATE COMPLEXES OF 4-FORMYL-2,3-DIMETHYL-1-PHENYL-3-PYRAZOLIN-5-ONE

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ABSTRACT

Complexes of yttrium and lanthanide nitrates with 4-formyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (FDPP) having the general formula $[Ln(FDPP)_2(NO_3)_2]NO_3$, where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er have been synthesised and characterised by elemental analyses, molar conductance in non-aqueous solvents, electronic, infrared and proton NMR spectra as well as thermogravimetric analyses. FDPP acts as a neutral monodentate ligand, coordinating through the ring carbonyl oxygen and two of the nitrate ions are coordinated in a bidentate manner. A coordination number of six may be assigned to the metal ion in these complexes. The covalency parameters evaluated from the solid state electronic spectra suggest weak covalent character of the metal-ligand bond. The TG data of the lanthanide complexes indicate that the complexes are stable up to about 170° C and undergo decomposition in two stages forming the respective anhydrous lanthanide oxide as the final product.

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INTRODUCTION

In continuation of our earlier investigations on nitrate complexes of yttrium and lanthanides with antipyrine derivatives,[1-6] we report the synthesis and characterisation of a new series containing ten complexes of yttrium and lanthanide nitrates with 4-formyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (Fig. 1). The ligand being an antipyrine derivative, the present complexes would be expected to be of physiological importance.[7,8]

RESULTS AND DISCUSSION

The formation of yttrium and lanthanide nitrate complexes of FDPP may be represented as:

$$\mathrm{Ln(NO_3)_3 + 2FDPP \rightarrow Ln(FDPP)_2(NO_3)_3}$$

where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.

All the complexes are yellow, non-hygroscopic solids soluble in acetone, acetonitrile, ethanol, methanol, nitrobenzene, DMF and DMSO but insoluble in chloroform, benzene, toluene and carbon tetrachloride.

The analytical data (Table I) of the complexes indicate that all ten complexes have the general formula $\mathrm{Ln(FDPP)_2(NO_3)_3}$, where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.

Electrical Conductance

The molar conductance values (Table II) of the complexes in nitrobenzene and acetonitrile are in agreement with the values suggested for 1:1 electrolytes,[9] but in DMF the complexes exhibit a bit higher values than that expected for 1:1 electrolytes. This may be due to partial displacement of the coordinated nitrate groups by DMF molecules.[9] Thus, the complexes may

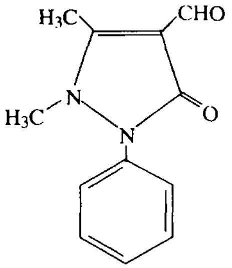


Fig. 1. 4-Formyl-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (FDPP)

be formulated as $[Ln(FDPP)_2(NO_3)_2]NO_3$, where Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho or Er.

Infrared Spectra

The infrared spectrum of FDPP exhibits two strong bands at 1664 and 1645 cm^{-1} attributable to the stretching vibrations of the aldehydic and ring carbonyl groups,[10] respectively. The infrared band observed at 1645 cm^{-1}, due to the stretching vibration of the ring carbonyl group, is shifted to around 1595 cm^{-1} in all these complexes, indicating that the ring carbonyl oxygen is coordinated[5] to the metal ion. However, the band at 1664 cm^{-1} remains at around 1661 cm^{-1}, indicating that the formyl oxygen is not coordinated.[10] Besides, the spectra of the complexes exhibit characteristic vibrational frequencies of both ionic and coordinated nitrate groups. A very strong band observed at around 1384 cm^{-1} indicates the presence of ionic nitrate group(s)[5,11] in these complexes and it is due to the ν_3 vibration of the nitrate group of D_{3h} symmetry. This is supported by another band of medium intensity appearing at around 820 cm^{-1}, attributable to the ν_2 vibration of the ionic nitrate.[11,12] The presence of coordinated nitrate groups is suggested by

Table I
Analytical Data[a] of Yttrium and Lanthanide Nitrate Complexes of FDPP

Complex[b]	Formula weight	% M	% C	% H	% N	Decomp. temp. (° C)	Yield, %
$[Y(FDPP)_2(NO_3)_2]NO_3$	707.4	12.61 (12.57)	40.53 (40.74)	3.38 (3.42)	13.81 (13.86)	210	80
$[La(FDPP)_2(NO_3)_2]NO_3$	757.4	18.41 (18.34)	37.80 (38.05)	3.15 (3.19)	12.90 (12.95)	223	85
$[Pr(FDPP)_2(NO_3)_2]NO_3$	759.4	18.57 (18.55)	37.65 (37.95)	3.19 (3.18)	12.97 (12.91)	222	85
$[Nd(FDPP)_2(NO_3)_2]NO_3$	762.7	18.86 (18.91)	37.92 (37.79)	3.20 (3.17)	12.90 (12.86)	219	85
$[Sm(FDPP)_2(NO_3)_2]NO_3$	768.8	19.50 (19.55)	37.34 (37.49)	3.18 (3.15)	12.83 (12.75)	212	80
$[Eu(FDPP)_2(NO_3)_2]NO_3$	770.5	19.71 (19.72)	37.20 (37.41)	3.10 (3.14)	12.78 (12.73)	206	85
$[Gd(FDPP)_2(NO_3)_2]NO_3$	775.7	20.22 (20.27)	36.91 (37.16)	3.08 (3.12)	12.56 (12.64)	170	80
$[Dy(FDPP)_2(NO_3)_2]NO_3$	781.0	20.73 (20.81)	36.78 (36.91)	3.14 (3.10)	12.63 (12.56)	192	80
$[Ho(FDPP)_2(NO_3)_2]NO_3$	783.4	21.14 (21.05)	36.69 (36.79)	3.11 (3.09)	12.60 (12.52)	188	85
$[Er(FDPP)_2(NO_3)_2]NO_3$	785.8	21.18 (21.29)	36.85 (36.68)	3.05 (3.08)	12.44 (12.48)	183	85

[a] Calculated values in parenthesis

[b] Empirical formula: $C_{24}H_{24}N_7O_{13}M$; where M = Y. La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, or Er.

Table II
Molar Conductance Data of Yttrium and Lanthanide Nitrate Complexes of FDPP

Complex	Molar conductance[a]		
	$C_6H_5NO_2$	CH_3CN	DMF
$[Y(FDPP)_2(NO_3)_2]NO_3$	19.94	121.88	138.50
$[La(FDPP)_2(NO_3)_2]NO_3$	22.71	116.34	132.96
$[Pr(FDPP)_2(NO_3)_2]NO_3$	21.60	110.80	121.88
$[Nd(FDPP)_2(NO_3)_2]NO_3$	24.37	113.57	127.42
$[Sm(FDPP)_2(NO_3)_2]NO_3$	23.27	127.42	116.34
$[Eu(FDPP)_2(NO_3)_2]NO_3$	22.16	135.73	124.10
$[Gd(FDPP)_2(NO_3)_2]NO_3$	18.84	108.03	130.19
$[Dy(FDPP)_2(NO_3)_2]NO_3$	20.50	132.96	124.65
$[Ho(FDPP)_2(NO_3)_2]NO_3$	20.22	127.42	132.96
$[Er(FDPP)_2(NO_3)_2]NO_3$	19.39	130.19	135.73

[a] 10^{-3} M solutions were used, in $ohm^{-1}cm^2mol^{-1}$

two bands observed around 1492 and 1306 cm^{-1} due to the v_4 and v_1 vibrations of the nitrate group of C_{2v} symmetry.[11] The medium band at 1031 cm^{-1} due to the v_2 vibration of the nitrate group (C_{2v}) stands as additional evidence for the presence of coordinated nitrate groups. The difference in wave numbers between the two highest frequency bands (v_4–v_1) of nitrate (C_{2v}) is about 186 cm^{-1}, indicating that the coordinated nitrate ions are bidentate.[13] The weak band observed at around 386 cm^{-1} is attributed to the Ln–O stretching vibration[13-15] in these complexes. The above spectral observations, together with the molar conductance data, confirm that two of

Table III

Important Infrared Spectral Bands (cm^{-1}) of FDPP and its Yttrium and Lanthanide Nitrate Complexes

Compound	ν(C=O) (aldehyde)	ν(C=O) (ring carbonyl)	ν(Ln–O)	NO_3 (coordinated)			NO_3 (ionic)	
				ν_4	ν_1	ν_2	ν_2	ν_3
FDPP	1664 s	1645 s	–	–	–	–	–	–
$[Y(FDPP)_2(NO_3)_2]NO_3$	1661 s	1595 m	386 w	1492 s	1306 s	1031 m	820 m	1384 vs
$[La(FDPP)_2(NO_3)_2]NO_3$	1662 s	1594 m	388 w	1490 s	1306 s	1032 m	820 m	1384 vs
$[Pr(FDPP)_2(NO_3)_2]NO_3$	1661 s	1592 m	386 w	1490 s	1306 s	1032 m	820 m	1385 vs
$[Nd(FDPP)_2(NO_3)_2]NO_3$	1661 s	1595 m	386 w	1492 s	1305 s	1031 m	821 m	1385 vs
$[Sm(FDPP)_2(NO_3)_2]NO_3$	1662 s	1594 m	387 w	1492 s	1305 s	1031 m	820 m	1386 vs
$[Eu(FDPP)_2(NO_3)_2]NO_3$	1661 s	1594 m	388 w	1492 s	1306 s	1032 m	820 m	1385 vs
$[Gd(FDPP)_2(NO_3)_2]NO_3$	1662 s	1595 m	386 w	1491 s	1306 s	1032 m	822 m	1384 vs
$[Dy(FDPP)_2(NO_3)_2]NO_3$	1662 s	1595 m	386 w	1492 s	1305 s	1032 m	820 m	1386 vs
$[Ho(FDPP)_2(NO_3)_2]NO_3$	1661 s	1595 m	388 w	1492 s	1306 s	1031 m	820 m	1386 vs
$[Er(FDPP)_2(NO_3)_2]NO_3$	1661 s	1595 m	386 w	1490 s	1306 s	1031 m	820 m	1384 vs

vs = very strong, s = strong, m = medium, w = weak the nitrate ions are coordinated to the metal ion in a bidentate fashion while the third nitrate ion remains uncoordinated in these complexes.

Proton NMR Spectra

The proton NMR spectrum of FDPP shows a resonance signal at δ 9.64 ppm with respect to TMS, corresponding to the aldehydic proton.[10] The position of this signal remains practically unchanged at δ 9.63 ppm in the spectra of both yttrium and lanthanum complexes indicating almost an identical environment around the aldehydic proton both in the ligand and the complexes. This may be due to the non-participation of the aldehydic group in coordination.[10] The other resonance signals corresponding to the phenyl, $N\text{-}CH_3$ and $C\text{-}CH_3$ groups are observed inthe regions δ 7.57–7.35 ppm (multiplet), δ 3.32 ppm (singlet) and δ 2.57 ppm (singlet), respectively, in the spectrum of the free ligand; and in the regions δ 7.58–7.35, 3.34 and 2.58 ppm, respectively, in the yttrium and lanthanum complexes.

Electronic Spectra

The electronic spectrum of FDPP shows two maxima at 33.89 kK and 39.52 kK corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In the complexes the $n \rightarrow \pi^*$ band is red-shifted and appears in the region 33.78–33.22 kK while the $\pi \rightarrow \pi^*$ band is blue-shifted and appears in the region 41.84–40.16 kK. The f–f bands are observed only in the Pr(III), Nd(III), Sm(III), Ho(III) and Er(III) complexes and are found to be red-shifted with respect to their aquo ions. The observed shift is a reflection of the "nephelauxetic effect." The interelectronic repulsion parameter (β), the percentage covalency (δ), the bonding parameter ($b^{1/2}$) and the covalency angular overlap parameter (η) were also calculated[16,17] (Table IV). The values

Table IV

f-f Transitions of the Nitrate Complexes of Pr, Nd, Sm, Ho, and Er with FDPP

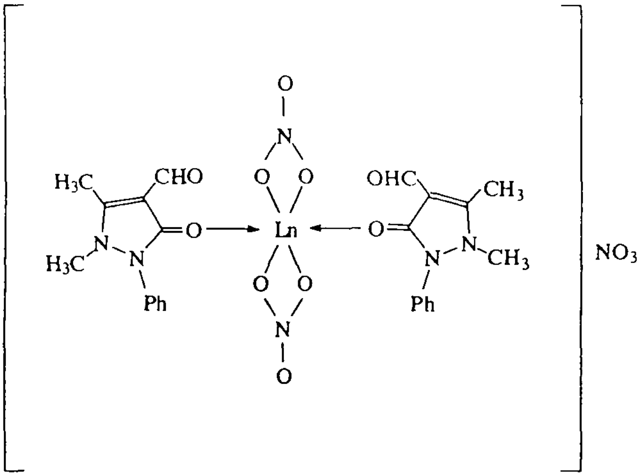
Compound	Abs. Max. (kK)	Tentative assignments	Covalency parameters calculated
Pr	16.83	${}^{3}H_4 \rightarrow {}^{1}D_2$	$\beta = 0.9972$
	21.23	" $\rightarrow {}^{3}P_1$	$\delta = 0.2808$
	22.42	" $\rightarrow {}^{3}P_2$	$b^{1/2} = 0.0264$
			$\eta = 0.0014$
Nd	11.50	${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$	$\beta = 0.9937$
	12.53	" $\rightarrow {}^{2}H_{9/2}$	$\delta = 0.6340$
	13.53	" $\rightarrow {}^{4}S_{3/2}$	$b^{1/2} = 0.0397$
	17.18	" $\rightarrow {}^{4}G_{5/2}, {}^{2}G_{7/2}$	$\eta = 0.0032$
	19.08	" $\rightarrow {}^{4}G_{7/2}$	
Sm	21.05	${}^{6}H_{5/2} \rightarrow {}^{4}I_{11/2}$	$\beta = 0.9923$
	24.50	" $\rightarrow {}^{4}L_{13/2}$	$\delta = 0.7760$
			$b^{1/2} = 0.0439$
			$\eta = 0.0039$
Ho	15.48	${}^{5}I_8 \rightarrow {}^{5}F_5$	$\beta = 0.9982$
	18.48	" $\rightarrow {}^{5}F_4, {}^{5}S_2$	$\delta = 0.1803$
	20.57	" $\rightarrow {}^{5}F_3$	$b^{1/2} = 0.0212$
	22.02	" $\rightarrow {}^{5}G_6$	$\eta = 0.0009$
	23.92	" $\rightarrow {}^{5}G_5, {}^{3}G_5$	
Er	12.37	${}^{4}I_{15/2} \rightarrow {}^{4}I_{9/2}$	$\beta = 0.9977$
	15.24	" $\rightarrow {}^{4}F_{9/2}$	$\delta = 0.2305$
	19.02	" $\rightarrow {}^{2}H_{11/2}$	$b^{1/2} = 0.0240$
			$\eta = 0.0011$

of β were found to be less than unity and those of $b^{1/2}$ and η are positive. These observations together with the values of δ, which are less than 1.5, suggest weak covalent character of the metal–ligand bond.[5] The hypersensitive bands observed in the spectra of the Nd, Ho and Er complexes closely resemble that of the six-coordinated complexes reported earlier.[18] Since Nd, Ho and Er nitrate complexes of FDPP are isomorphous with the remaining nitrate complexes of FDPP, the same coordination number of six also may be proposed to other metal ions in these complexes. Besides, the spectra of the complexes, both in solid and solution states, are identical in nature, suggesting that these complexes maintain the same structure in both of these media.

Thermal Behaviour

The thermograms of the lanthanide nitrate complexes of FDPP do not show any appreciable mass loss up to 170° C indicating the absence of water or solvent molecules. The complexes undergo a two-stage decomposition process. The first stage starts in the range 170–223° C and ends in the range 345–367° C accompanied with a mass loss in the range 27.10–27.90%. This is attributed to the loss of one ligand molecule. The respective DTG peaks are obtained in the range 334–354° C where the rate of mass loss is maximum. The second stage starts in the range 345–367° C and ends in the range 650–708° C which may be due to the loss of the second ligand molecule and the complete decomposition of all nitrate groups. The observed mass loss is in the range 46.80–48.60% and the corresponding DTG peaks are obtained in the range 495–534° C. The final product of decomposition in all the complexes is found to be the respective anhydrous lanthanide oxide.

The tentative structure of the complexes is given in Fig. 2.



where, Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er; Ph = $-C_6H_5$

Fig. 2. Tentative structure of the complexes

EXPERIMENTAL

Materials

The metal nitrates were prepared by dissolving the respective oxides (99.99%) in 60% nitric acid and then crystallising out the salt by evaporating the solution on a steam bath.

Preparation of the Complexes

A solution of 1 mmol (0.4 g) of the metal nitrate in ethyl acetate (10 mL) was added drop-wise to the solution of 2.2 mmol (0.45 g) of the ligand dissolved in ethyl acetate (30 mL) kept under reflux. The mixture was then refluxed for about 10 min. The resulting solution was cooled to room temperature when solid complex was precipitated. It was filtered, washed several times with hot ethyl acetate and finally with hot benzene to remove any ligand present in excess. It was then recrystallised from acetonitrile and dried under vacuum over phosphorus(V) oxide.

Analytical Methods

All the complexes were analysed for the metal content by the method reported[19] earlier. Molar conductances in nitrobenzene, acetonitrile and DMF (10^{-3} M solutions) were measured at room temperature using a Toshniwal conductivity bridge with a dip-type cell of platinum electrodes (cell constant: 0.1098). The infrared spectra of the ligand and the complexes were recorded in the range 4000-400 cm^{-1} on a Shimadzu IR 470 spectrophotometer and in the range 400-100 cm^{-1} on a Bruker IFS 66v FT-IR spectrophotometer. Electronic spectra were recorded in CH_3CN (10^{-4} M solutions) and in the solid state (using a paste with Nujol) on a Shimadzu UV 160 A spectrophotometer in the range 200–900 nm. The C, H and N analyses were carried out using a Heraeus CHNO rapid analyser. The ^1H NMR spectra were recorded using DMSO-d_6 as the solvent on a JEOL GSX 400 instrument. Thermogravimetric analyses were conducted on a Delta Series TGA7 thermal analyser in nitrogen atmosphere (sample mass: 2 mg, heating rate: 10° C/minute).

Conclusion

FDPP acts as a neutral monodentate ligand coordinating through the ring carbonyl oxygen in these complexes. Two of the nitrate groups are coordinated to the metal ion in a bidentate manner. Hence, a coordination number of six may be assigned to the metal ion in these complexes.

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