

Lanthanide(III) Nitrate Complexes of the Schiff Base Vanillideneanthranilic Acid

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Received 2 July 1986; revised 10 March 1987;
revised and accepted 12 May 1987

The complexes formed by the lanthanide(III) nitrates with the schiff base vanillideneanthranilic acid (H_2L) have been isolated and characterised. These compounds have the formula $[Ln(HL)_2(NO_3)(H_2O)]$ where $Ln = La, Ce, Pr, Nd, Sm, Eu$ and Gd . The structures of the complexes have been established on the basis of IR, PMR and electronic spectroscopy and thermal analysis. The IR spectral data reveal that the ligand acts in a monovalent bidentate manner in the chelates.

Coordination compounds formed by schiff bases with d -transition elements have been extensively studied¹. A survey of literature shows that corresponding compounds of lanthanide elements have been much less studied²⁻⁸. No systematic studies have been carried out on the reactions of the schiff base vanillideneanthranilic acid with lanthanides. In continuation of our earlier work⁹⁻¹² on vanillideneanthranilic acid complexes of d -transition metal ions, we report here the results of our studies on some new lanthanide(III) complexes of this schiff base.

Vanillideneanthranilic acid was prepared as reported earlier⁹ (M.P., 173°C). $La(III)$, $Ce(III)$, $Pr(III)$, $Nd(III)$, $Sm(III)$, $Eu(III)$ and $Gd(III)$ nitrates, supplied by BDH, were used as such. All the other chemicals were of reagent quality.

An ethanolic solution (0.01 mol) of vanillideneanthranilic acid was mixed with an ethanolic solution of lanthanide(III) nitrate (0.01 mol) and the mixture was stirred magnetically. After 5 min, dilute ammonia (1:20) was added till the solution became turbid. Soon a flocculent mass was obtained, which was stirred for 5-6 h. The precipitate was filtered, washed with hot ethanol and dried *in vacuo* over P_2O_5 .

The lanthanides were determined by conversion into the corresponding oxides. Microanalyses for carbon, hydrogen and nitrogen were performed at the Central Drug Research Institute, Lucknow.

Conductance measurements were made with a Toshniwal conductivity bridge. Infrared spectra were recorded in nujol and KBr in the region 4000-200 cm^{-1} on a Perkin Elmer 257 spectrophotometer. Electronic spectra of the complexes were recorded in ethanol on a Carl Zeiss DMR-21 UV-Vis spectrophotometer; NMR spectra were obtained in $DMSO-d_6$

Table 1—Analytical Data of Complexes

Complexes	Found (Calc.) %			
	C	H	N	M
$La(LH)_2(NO_3)(H_2O)$	47.62 (47.44)	3.52 (3.45)	5.64 (5.53)	18.33 (18.29)
$Ce(LH)_2(NO_3)(H_2O)$	47.56 (47.37)	3.62 (3.45)	5.71 (5.52)	18.32 (18.42)
$Pr(LH)_2(NO_3)(H_2O)$	47.42 (47.32)	3.58 (3.44)	5.67 (5.52)	18.41 (18.51)
$Nd(LH)_2(NO_3)(H_2O)$	46.96 (47.11)	3.49 (3.43)	5.52 (5.49)	18.71 (18.86)
$Sm(LH)_2(NO_3)(H_2O)$	46.68 (46.74)	3.35 (3.40)	5.49 (5.45)	19.31 (19.50)
$Eu(LH)_2(NO_3)(H_2O)$	46.55 (46.64)	3.32 (3.39)	5.35 (5.44)	19.58 (19.67)
$Gd(LH)_2(NO_3)(H_2O)$	46.25 (46.33)	3.31 (3.37)	5.36 (5.40)	20.18 (20.22)

with TMS as an internal standard, using a Varian EM-390 NMR spectrometer. Thermal analyses were conducted on a Stanton recording thermobalance Model TR-1, in an atmosphere of static air. The heating rate was $4K\ min^{-1}$ and chart speed was $6\ in\ h^{-1}$.

All the complexes are solid reddish-yellow compounds. These compounds are finely divided powders which decompose above $120^\circ C$ without melting. The compounds could not be recrystallised due to their insolubility in common solvents. The results of the analyses of these compounds are presented in Table 1. The analytical data are in good accord with their formulation as $[Ln(HL)_2(NO_3)(H_2O)]$ where H_2L is the schiff base vanillideneanthranilic acid.

All the chelates are non-conducting ($\Lambda M = 0.5-4.8\ ohm^{-1}cm^2mol^{-1}$) in nitrobenzene at $28 \pm 2^\circ$ which indicates their non-electrolytic nature.

The medium intensity band at $2700\ cm^{-1}$ in the IR spectrum of the ligand may be due to intramolecularly H-bonded νOH ; this band remains largely unaffected in the chelates providing evidence for the uninegative bidentate nature of the ligand in these complexes. The band appearing in the region $3300-3100\ cm^{-1}$ is assigned to $\nu(-OH)$ of coordinated water. The free ligand band at $1620\ cm^{-1}$, assignable to $\nu C=N$, undergoes shift to lower wavenumbers ($1570-1590\ cm^{-1}$) in the complexes indicating participation of the nitrogen atom of the azomethine group in coordination¹³⁻¹⁶.

The asymmetric and symmetric stretching vibrations of the carboxylate group occur at $1590-1630$ and $1440-1450\ cm^{-1}$, respectively, showing a $\Delta\nu$ value of $140-190\ cm^{-1}$. these observations suggest that

the present compounds contain monodentate carboxylate group^{15,17,18}. The IR spectrum shows bands around 1290, 1030 and 745 cm^{-1} corresponding to the ν_1 , ν_2 and ν_3 vibrations of unidentate nitrate group¹⁹. The formation of M—N and M—O bonds is further supported by the appearance of $\nu(\text{M—N})$ and $\nu(\text{M—O})$ in the regions 400-600 and 350-440 cm^{-1} respectively in the spectra of the chelates²⁰.

The NMR spectrum of vanillideneanthranilic acid in DMSO- d_6 is characterised by four signals at δ 9.5, 8.7, 7.2 and 3.8 and they have been attributed to the various proton resonances due to —OH, —HC=N, phenyl and methoxy groups respectively. In the spectra of the complexes, the resonance due to the —OH group does not disappear but the resonance due to the azomethine proton shifts to upfield due to shielding effect and merges with proton signal at 7.3 δ . These observations suggest that the azomethine nitrogen coordinates with Ln(III).

The electronic spectrum of the ligand shows one absorption maximum due to $n \rightarrow \pi^*$ transition at \approx 330 nm. The spectrum below 300 nm ($\pi \rightarrow \pi^*$) region has not been investigated. The very broad band observed in the visible region with absorption maximum around \approx 380 nm in all the complexes may be assigned to the very strong ligand to metal charge-transfer transition.

The thermogravimetric studies of lanthanide(III) chelates show mass loss corresponding to one water molecule around 160°C. Above this temperature, the

complexes undergo continuous decomposition and oxidation to give the stable oxides.

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