

Complexes of *o*-Vanillin Oxime with La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III) & Yb(III)

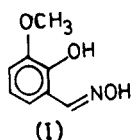
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Received 9 February 1987; revised 2 July 1987;
rerevised and accepted 18 January 1988

Ten complexes of lanthanides with *o*-vanillin oxime have been synthesised and characterised. The composition of the complexes as determined by elemental and thermal analyses infrared electronic spectral and magnetic moment studies is $[\text{Ln}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot \text{XH}_2\text{O}]$, where $X = 2$ when $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$ and $X = 3$ when $\text{Ln} = \text{Gd}, \text{Dy}, \text{Tb}, \text{Ho}, \text{Yb}$; $\text{C}_8\text{H}_8\text{NO}_3^-$ represents the the anion of the ligand.

o-Vanillin oxime has been reported to give colour reactions with a number of metal ions¹. We report here the results of our systematic study on the nature and compositions of some lanthanide complexes of *o*-vanillin oxime (I), isolated in the solid state.



o-Vanillin oxime was prepared by the known method² and recrystallized from water, m.p. 123° (lit. 123°). The Lanthanide (III) complexes were prepared by mixing the metal ion solution (in doubly distilled water) and ligand solution (in 95% ethanol) in the molar ratio of 1:10 (metal:ligand). The precipitated complexes were washed free of the excess of ligand by ethanol and dried *in vacuo* over anhydrous calcium chloride. Carbon, hydrogen and metal contents were estimated by standard methods while IR ($4000\text{-}200\text{ cm}^{-1}$), DRS ($50,000\text{-}10,000\text{ cm}^{-1}$) and thermal studies were carried out using Perkin-Elmer-377 grating IR spectrophotometer, VSU2P (Carl-Zeiss) spectrophotometer and Paulik-Paulik Erdy MOM derivatograph respectively. Magnetic measurements were done by the Gouy method.

The elemental analysis results (Table 1) for C, H and metal (M) suggest the composition of the metal complexes to be $[\text{Ln}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot \text{XH}_2\text{O}]$, where $X = 2$ when $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$ and $X = 3$ when $\text{Ln} = \text{Gd}, \text{Dy}, \text{Tb}, \text{Ho}, \text{Yb}$; $\text{C}_8\text{H}_8\text{NO}_3^-$ represents the anion of the ligand. This composition is further supported by the IR spectral studies of the ligand and the complexes. The ligand spectrum shows a band at 3350 cm^{-1} due to hydrogen bonded $\nu(\text{OH})$ mode. This band disappears in the spectra of complexes indicating coordination through hydroxyl oxygen

Table 1—Elemental Analysis (%) of the Complexes

Sl No.	Complexes	Colour	Found (Calc.), %			
			C	H	N	M
1	$[\text{La}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}]$	Grey	42.46 (42.79)	4.41 (4.16)	6.46 (6.24)	20.92 (20.64)
2	$[\text{Ce}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}]$	Dark grey	43.06 (42.72)	4.32 (4.15)	6.61 (6.23)	20.17 (20.73)
3	$[\text{Pr}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}]$	Light grey	42.45 (42.67)	4.38 (4.14)	6.59 (6.22)	21.10 (20.87)
4	$[\text{Nd}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}]$	Dark grey	42.79 (42.46)	4.40 (4.12)	6.38 (6.19)	21.52 (21.26)
5	$[\text{Sm}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}]$	Grey	42.45 (42.08)	4.38 (4.09)	6.27 (6.13)	22.25 (21.96)
6	$[\text{Gd}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$	Grey	40.95 (40.60)	4.55 (4.22)	6.20 (5.92)	22.44 (22.17)
7	$[\text{Tb}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$	Dark green	40.24 (40.51)	4.62 (4.21)	6.39 (5.90)	22.66 (23.35)
8	$[\text{Dy}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$	Grey	40.79 (40.30)	4.32 (4.19)	6.08 (5.87)	22.43 (22.74)
9	$[\text{Ho}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$	Dark grey	40.49 (40.17)	4.38 (4.18)	6.15 (5.85)	22.77 (23.00)
10	$[\text{Yb}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$	Grey	40.15 (39.72)	4.39 (4.13)	8.04 (5.79)	23.59 (23.86)

after deprotonation. This is corroborated by appearance of new bands in the spectra of complexes in the region $650\text{--}415\text{ cm}^{-1}$ due to $\nu(\text{M}-\text{O})$ mode. The ligand shows a band at 1625 cm^{-1} which has been assigned to $\nu(\text{C}=\text{N} + \text{C}=\text{C})$ mode. Its lowering by $10\text{--}45\text{ cm}^{-1}$ in the complexes shows coordination through oxime nitrogen. The complexes also

show bands in the region $3780\text{--}3700\text{ cm}^{-1}$ due to coordinated water molecules.

The magnetic susceptibility values and electronic absorption spectra (DRS) further corroborate the nature of the complexes. The La(III) complex is diamagnetic while the others are paramagnetic. The values are little different from those reported by

Table 2—Diffuse Reflectance Spectral and Magnetic Moment Data of the Complexes

Sl No.*	μ_{eff} (B.M.)	Observed bands (cm^{-1})	Probable assignment of some bands (cm^{-1})
1	0.00	40000, 29411, 25000, 22727, 17857	Intra-ligand charge transfer
2	0.42	40816, 31461, 31250, 28571, 19230	${}^2D_{5/2} \leftarrow {}^2F_{5/2}$ ${}^2D_{3/2} \leftarrow$
3	3.46	42553, 37735, 23809, 16666	${}^3P_2 \leftarrow {}^3H_4$ ${}^1D_2 \leftarrow$
4	3.54	38461, 28571, 22222, 18518	${}^2P_{1/2} \leftarrow {}^4I_{9/4}$ ${}^2G_{9/2} \leftarrow$ ${}^4G_{7/2} \leftarrow$
5	0.88	38461, 29411, 14705, 11111	${}^6D_{7/2} \leftarrow {}^6H_{5/2}$ ${}^6F_{3/2} \leftarrow$
6	7.83	39215, 26315, 21739, 16129	${}^6P_{7/2} \leftarrow {}^8S_{7/2}$
7	4.40	42553, 28571, 21739, 15262	${}^6H_{3/2} \leftarrow {}^6H_{5/2}$
8	10.40	40816, 26315, 23255, 15125	${}^5D_3 \leftarrow {}^7F_6$ ${}^5D_2 \leftarrow$
9	10.32	42553, 26315, 19230, 15625	${}^5G_4 \leftarrow {}^5I_8$ ${}^5F_3 \leftarrow$ ${}^5F_5 \leftarrow$
10	4.43	41666, 28571, 20833, 13513	$4f \leftarrow 5P$ ${}^2F_{5/2} \leftarrow$

*Numbers same as in Table 1.

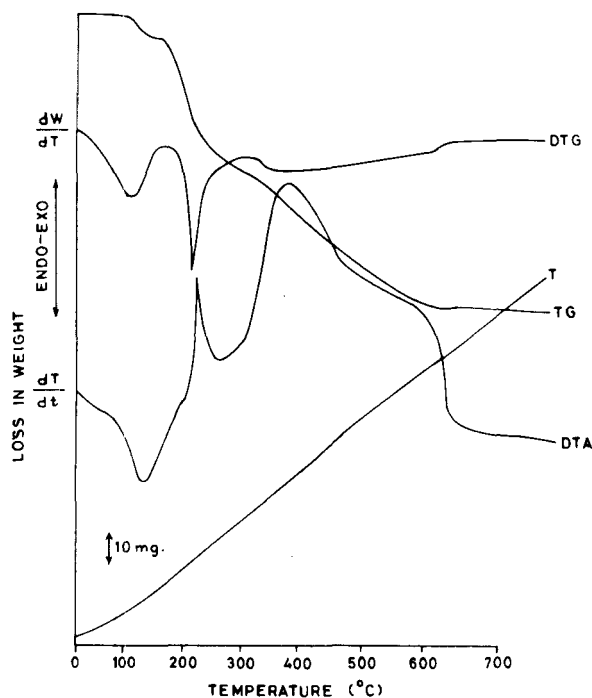


Fig. 1—Simultaneous DTG, DTA and TG curves of $[\text{La}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}]$

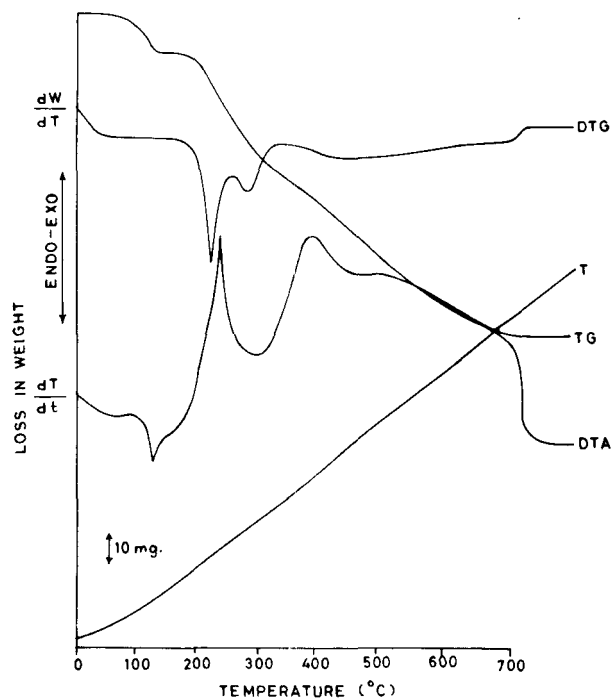


Fig. 2—Simultaneous DTG, DTA and TG curves of $[\text{Yb}(\text{C}_8\text{H}_8\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$

Hund and Van Vleck for free ions³. This behaviour is in agreement with similar literature reports^{4,5}. The electronic absorption spectra and the assignment of bands are based on the available data on the absorption spectra of free lanthanide ions, the hypersensitive transitions in lanthanides and the absorption spectra of lanthanide ions in crystals and in solutions. The qualitative assignments⁶⁻¹² of the bands are given in Table 2. The other unassigned bands are electron transfer bands of the $5d \leftarrow 4f$ type, charge transfer bands and intra-ligand transitions. Based on observed data, square antiprismatic geometries^{13,14} for La(III), Ce(III), Pr(III), Nd(III) and Sm(III) complexes and tricapped trigonalbipyramidal configurations^{15,16} for Gd(III), Dy(III), Tb(III), Ho(III) and Yb(III) complexes are suggested.

Figures 1 and 2 show the simultaneous DTA, DTG and TG curves of La(III) and Yb(III) complexes at the heating rate of 10° per minute. The DTA curve of La(III) complex shows one sharp endothermic peak at 140°C and one broad at 390°C, whereas the DTA curve of Yb(III) complex shows one sharp endotherm at 130°C and two exotherms (one sharp at 250°C and one broad at 390°). There are corresponding peaks in DTG curves, but at slightly lower temperatures. The first arrest in TG curves of these complexes shows mass loss of 5.73% for La(III) complex (calc. 5.43%) and 7.27% for Yb(III) complex (calc. 7.44%) corresponding to the elimination of water molecules. After complete decomposition, the mass loss shown by TG curves is

75.40% for La(III) complex (calc. 75.79%) and 72.72% for Yb(III) complex (calc. 72.82°). The oxides formed on the pyrolysis of these complexes are La_2O_3 and Yb_2O_3 , respectively. It is inferred from spectral, magnetic and thermal studies that water molecules are coordinated to the metal ions.

From the above discussion it is concluded that *o*-vanillin oxime behaves as a bidentate ligand coordinating through oxygen and nitrogen to the metal ions and forms 8 or 9 coordinated complexes.

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