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Synthesis, Characterization and Thermal Analysis of Lanthanide(III) Nitrates Complexes of Schiff Base Derived From *o*-Vanillin and *p*-Toluidine

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A series of 6 complexes were synthesized using lanthanide(III) nitrates with Schiff base (L) 2-[(4-methylphenylimino)methyl]-6-methoxyphenol from *o*-vanillin and *p*-toluidine and characterized by elemental analysis, molar conductance, infrared spectra, thermal analysis. Their chemical formula are $[LnL_2(NO_3)_3]$ (Ln = Dy, Ho, Er, Tm, Yb, Y). The central Ln(III) ion in the complexes coordinates with both two L *via* 4 oxygen atoms of the phenol hydroxy groups and methoxy groups and 3 bidentate nitrates *via* their 6 oxygen atoms. Their coordination numbers are 10. The thermal behaviour of these complexes has been studied by TG and DTG. These complexes show 4 steps weight loss and show almost similar mode of decomposition. The residues after heating correspond to metal oxide Ln_2O_3.

Key Words: Lanthanide(III) complexes, Schiff base, Thermal analysis.

INTRODUCTION

Various studies showed that Schiff bases derived from salicylaldehyde and its derivants have considerable biological importance because such ligands have many donor atoms (N, O) and biological environment. They were widely used in the fields of biology, pharmacology, catalysis, organic synthesis and chemical analysis[1-4]. Much attentions have been focused on these Schiff bases because of the stability of the ligands and various properties of their metal complexes[5-9]. Although lots of work has been done on lanthanide(III) complexes of Schiff base. For example, Datt and Nag[10] have reported a series of lanthanides(III) chelates with tetradentate Schiff bases obtained from salicylaldehyde and ethylenedimine and *o*-phenylenediamine. Ansari *et al.*[11] have studied on lanthanide complexes of *bis* vanillin-benzidine. But there are little work has been done on lanthanide(III) complexes of Schiff base about thermal analysis. In the view of this, 6 complexes of lanthanides(III) (Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Y(III)) nitrates with Schiff base derived from *o*-vanillin and *p*-toluidine were synthesized in absolute alcohol and characterized by elemental analysis, molar conductance, FT-IR, spectra and thermal analysis.

EXPERIMENTAL

Lanthanide oxide (99.95 %), other reagents were of AR Grade. $Ln(NO_3)_3 \cdot 6H_2O$ was prepared by dissolving lanthanide oxide in concentrated nitric acid and crystallising the salt by evaporating the solution on a steam bath. The metal contents were determined by EDTA complexometric titration after decomposition a known amount of the complexes with concentrated nitric acid. Elemental analyses for C, H and N were carried out on an Elementar Vario EL III elemental analyzer. IR spectra on KBr pellets were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer in the range of 4000-400 cm^{-1}. Molar conductivity of the complexes were measured with a Shanghai DDS-11A conductivity meter in DMF (1.0×10^{-3} mol L^{-1}). Thermal analyses was carried out using Mettler-Toludo TGA/SDTA851^e thermal analyzer in air atmosphere at a heating rate 10 ºC min^{-1}.

Synthesis of ligand: Schiff base ligand (L) was prepared by the direct reaction of equimolar quantities of the *o*-vanillin(3.46 g, 0.03 mol) and *p*-toluidine (3.21 g, 0.03 mol) in 50 mL absolut ethanol. The reaction mixture was stirred for 0.5 h at room temperature, then the orange solid ligand were isolated by filtration, washed with ethanol and dried in air, yield 5.20 g (86 %), m.p. 100 ºC.

Synthesis of solid complexes: A solution of 0.45 g $Ln(NO_3)_3 \cdot 6H_2O$ (1 mmol) in absolut ethanol (10 mL) was added dropwise with stirring to a solution of 0.48 g Schiff base ligand (2 mmol) in absolut ethanol (30 mL). The mixture was stirred at room temperature for *ca.* 2 h and the solid formed was separated by filteration, washed with absolut ethanol and dried in air. Yield 0.70 g, 85 %. The formulation of the complexes may be representedly the general equation:

$$Ln(NO_3)_3 \cdot 6H_2O + 2L \longrightarrow \underset{\text{(orange)}}{[LnL_2(NO_3)_3]\downarrow} + 6H_2O$$

RESULTS AND DISCUSSION

Lanthanides(III) complexes are stable in air and have no sharp melting point. They are soluble easy in polar organic solvents (methanol, ethanol, acetone, Py, DMF, DMSO) and a little soluble in non-polar solvents (benzene, cyclohexane). The composition of ligand and prepared complexes are summarized in Table-1. The C, H, N, Ln contents both theoretically calculated values and actual values are in accordance for their formula $[LnL_2(NO_3)_3]$ (Ln = Dy, Ho, Er, Tm, Yb, Y) of the complexes and it shows that the Schiff base ligand is neutral. Their molar conductance in DMF solvent lies in the range of 17-22 S cm^2 mol^{-1}. The conductance values in accordance with the non-electrolytic nature of complexes, which clearly indicates that anions are coordinated with the metal atom. suggesting that the complexes are all non-electrolytes[12].

Infrared spectra: The broad absorption band at 3451 cm^{-1} due to the hydroxy group in the IR spectra of the free ligand appears at lower frequency in the corresponding complex, *viz.*, 3427-3419 cm^{-1}, showing coordination of oxygen atom of the phenolic hydroxy with the central Ln(III) ion. The shift of the C-O stretching vibration of the phenolic part of *o*-vanillin from 1261 cm^{-1} (free ligand) to 1243-1240 cm^{-1} also supports the coordination of oxygen atoms. However, a strong band in the free Schiff base ligand occurring at 1617 cm^{-1} due to C=N stretching is found shifted to higher frequency, *viz.*, 1642-1641 cm^{-1}, but the nitrogen atom of azomethine was regarded as non-coordination with Ln(III)[13,14]. A new band at 492-488 cm^{-1} was present due to (Ln-O) stretching vibration[15]. Five absorbption peaks at 1505-1500 cm^{-1} (ν_1), 1298-1294 cm^{-1} (ν_4), 1029-1023 cm^{-1} (ν_2), 819-818 cm^{-1} (ν_3) and 743-742 cm^{-1} (ν_5), $\Delta\nu$ (ν_1-ν_4) = 205 cm^{-1} in the spectra of complexes are coordinated nitrates which behave as bidentate ligand[16,17].

TABLE-1
PHYSICAL AND ELEMETAL ANALYSIS DATA OF THE LIGAND AND ITS Ln(III) COMPLEXES

Compound	m.w.	Colour	Elemental analysis: Found (Calcd.) (%)				Λ_M S cm^2 mol^{-1}
			C	H	N	Ln	
L	241.280	Orange	74.66 (74.59)	6.27 (6.30)	5.81 (5.77)	–	–
1 [$DyL_2(NO_3)_3$]	831.111	Orange	43.38 (43.35)	3.69 (3.64)	8.47 (8.43)	19.45 (19.55)	17
2 [$HoL_2(NO_3)_3$]	833.538	Orange	43.21 (43.23)	3.68 (3.63)	8.45 (8.40)	19.85 (19.78)	19
3 [$ErL_2(NO_3)_3$]	835.871	Orange	43.15 (43.10)	3.60 (3.62)	8.44 (8.38)	19.90 (20.01)	18
4 [$TmL_2(NO_3)_3$]	837.542	Orange	43.00 (43.02)	3.58 (3.61)	8.44 (8.36)	20.07 (20.17)	19
5 [$YbL_2(NO_3)_3$]	841.651	Orange	42.72 (42.81)	3.54 (3.59)	8.39 (8.32)	20.47 (20.56)	21
6 [$YL_2(NO_3)_3$]	757.858	Orange	47.61 (47.56)	4.03 (3.99)	9.30 (9.25)	11.80 (11.74)	18

TABLE-2
IR SPECTRAL DATA OF THE LIGAND AND ITS Ln(III) COMPLEXES (cm^{-1})

Compound	ν(C=N)	ν(O-H)	$\nu(NO_3^-)$					ν(Ln-O)	ν(C-O)
L	1616s	3451m							1261s
$DyL_2(NO_3)_3$	1642s	3426m	1500s	1294s	1024m	819m	742m	489m	1240s
$HoL_2(NO_3)_3$	1642s	3427m	1502s	1296s	1023m	818m	742m	488m	1240s
$ErL_2(NO_3)_3$	1642s	3427m	1503s	1297s	1025m	819m	743m	489m	1241s
$TmL_2(NO_3)_3$	1642s	3427m	1503s	1297s	1026m	818m	743m	489m	1242s
$YbL_2(NO_3)_3$	1641s	3419m	1504s	1298s	1029m	818m	743m	492m	1243s
$YL_2(NO_3)_3$	1642s	3426m	1505s	1296s	1024m	819m	743m	489m	1240s

Thus Schiff base ligand behaves as bidentate ligand. Therefore, it is concluded that every central Ln(III) ion in the complexes coordinates with both two Schiff base ligands *via* four oxygen atoms of phenol hydroxy groups and methoxy groups and three nitrates *via* oxygen atoms. Their coordination numbers are 10. The structure of proposed complexes are shown in Fig. 1.

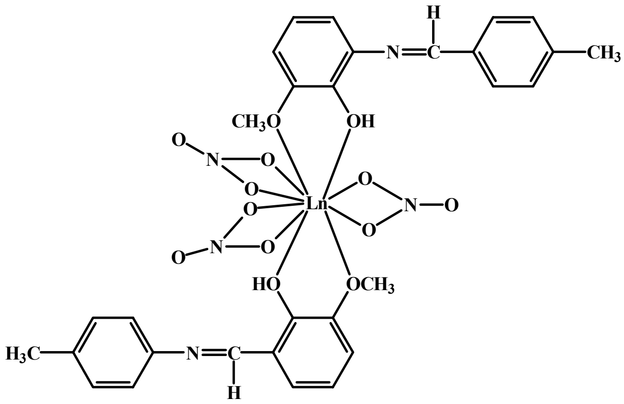

Fig. 1. Proposed structure of the complexes

Thermal analysis: Take complex $[DyL_2(NO_3)_2]$ as an example, its TG-DTG curves are shown in Fig. 2. The first step decomposition temperature is in the range of 213.1- 286.7 ºC with a mass loss 16.98 % which corresponds to the loss of $3NO_2$ (theoretical loss is 16.61 %). The second weight loss is 14.39 % (calcd. 14.22 %) at 286.7-343.9 ºC, corresponds to the decomposition of C_8H_8N of Schiff base ligand. The third step of decomposition from 343.9-438.7 ºC with a weight loss 28.71 % (calcd. 29.03 %), accompanied with the decomposition of another Schiff base ligand L. The forth step decomposition temperature is in the range of 438.7- 660.1 ºC with a mass loss 17.61 % which corresponds to the loss of another residue part of complex (theoretical loss is 17.69 %). The residue weights 22.31 % correspond to values calculated for Dy_2O_3 22.44 %. This result is in good accordance with the composition of the complex.

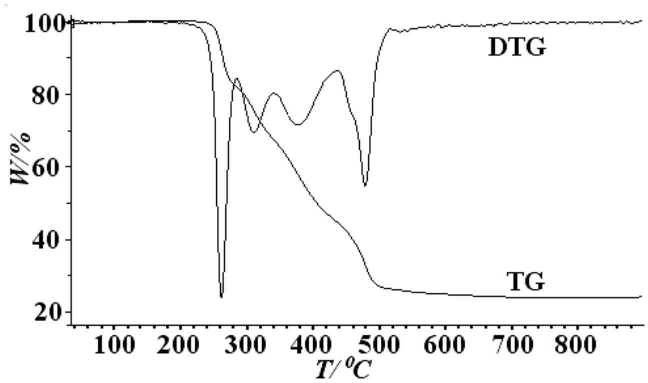

Fig. 2. The TG-DTG curves of complex **1**

The TG and DTG curves for the complexes show that the release of volatile species occur in 4-step process according to the following equation:

$$[LnL_2(NO_3)_3] \longrightarrow LnL_2O_3 + 3NO_2$$
$$LnL_2O_3 \longrightarrow LnC_{22}H_{22}NO_7 + C_8H_8N$$
$$LnC_{22}H_{22}NO_7 \longrightarrow LnC_7H_7O_5 + L$$
$$LnC_7H_7O_5 \longrightarrow C_7H_7O_{3.5} + \tfrac{1}{2}Ln_2O_3$$

The process of thermal decomposition of the present lanthanide(III) complexes are very similar and 4 stages of decomposition are observed (Figs. 3 and 4), the residues are lanthanide oxides Ln_2O_3. No weight loss was observed of complexes before 210 °C, indicating the absence of small molecular of solvent in the complexes.

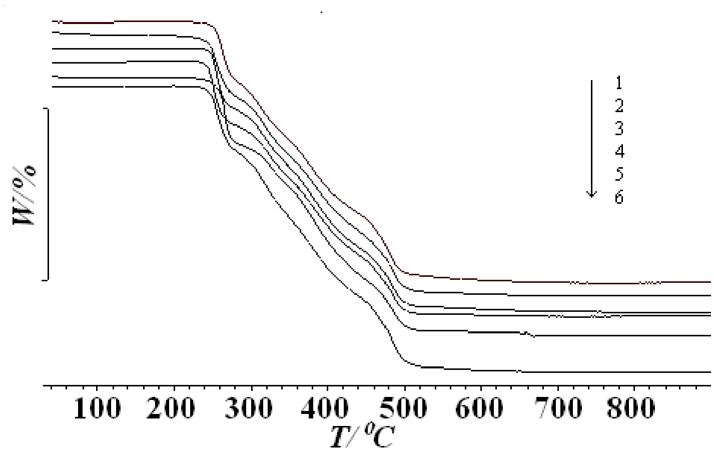

Fig. 3. TG curve of series complexes

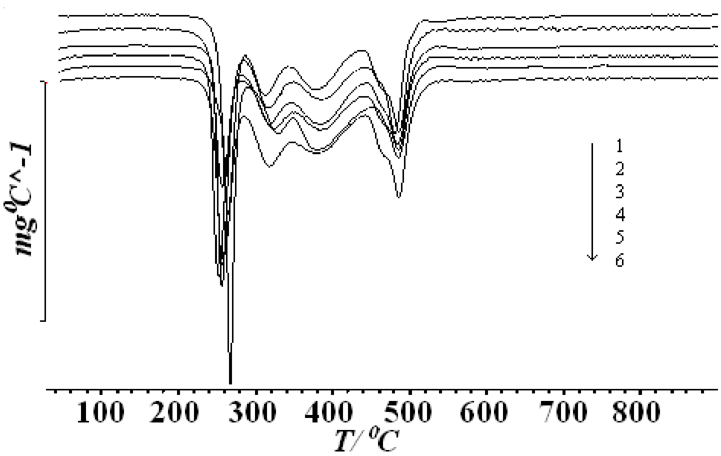

Fig. 4. DTG curve of series complexes

REFERENCES

1. K. Dey, *J. Scient. Ind. Res.*, **33**, 76 (1974).
2. D.N. Dhar, C.L. Taploo, *J. Scient. Ind. Res.*, **41**, 501 (1982).
3. X.L. Liu, Y.H. Liu, Y.C. Shi and P.M. Jian, *Chin. J. Org. Chem.*, **22**, 482 (2002).
4. E.M. Hodnett and W.J. Dunn, *J. Med. Chem.*, **13**, 768 (1970).
5. J.P. Costes, F. Dahan and F. Nicodene, *Inorg. Chem.*, **42**, 6556 (2003).
6. A. Golcu, M. Tumer, H. Demireli and R.A. Wheatley, *Inorg. Chim. Acta*, **358**, 1785 (2005).
7. P.A. Vigato and D.E. Fenton, *Inorg. Chim. Acta*, **139**, 39 (1987).
8. Z.S. Wu, *J. Central China Normal Univ. (Nat. Sci. Ed.)*, **17**, 61 (1983).
9. X.Y. Zhang, Y.J. Zhang and L.Yang, *Chem. Res. Appl.*, **14**, 9 (2002).
10. N.K. Duti and K. Nag, *Inorg. Chem.*, **7**, 30 (1968).
11. M.S. Ansari and N. Ahmad, *J. Inorg. Nucl. Chem.*, **38**, 1232 (1976).
12. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
13. K. Binnemans, Y.G. Galyametdinov, R. Van Deun, D.W. Bruce, S.R. Collinson, A.P. Polishchuk, I. Bikchantaev, W. Haase, A.V. Rakhmatullin, K. Uytterhoeven and L. Van Meervelt, *J. Am. Chem. Soc.*, **122**, 4335 (2000).
14. W.H. Xie, M.J. Heeg and P.G. Wang, *Inorg. Chem.*, **38**, 2541 (1999).
15. G.F. Liu, Y.N. Zhao and X.X. Liu, *Acta Chim. Sinica*, **50**, 473 (1992).
16. K. Nakamoto (D.R. Huang, R.Q. Wang translation), Infrared and Raman Spectra of Inorganic and Coordination Compounds, Chemical Industrial Press, Beijing, China, p. 251 (1986).
17. Y.Q. Liang, Y.N. Zhao, S.G. Zhang, F.L. Yu and J.Z. Ni, *Acta Chim. Sinica*, **41**, 199 (1983).

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