

Synthesis and Structural Studies of some Trivalent Lanthanide Metal Complexes of Salicylaldehyde (*N*-*o*-Hydroxybenzalidene)tyrosyl Hydrazone

T. R. RAO*, I. A. KHAN and R. C. AGGARWAL

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221 005

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Salicylaldehyde (*N*-*o*-hydroxybenzalidene)tyrosyl hydrazone (SalTH) has been found to form complexes of the types $[M(\text{SalTH})\text{Cl}_2(\text{H}_2\text{O})]2\text{H}_2\text{O}$ and $M(\text{SalTH} - 3\text{H}) \cdot (\text{H}_2\text{O})$, where $M = \text{La}^{\text{III}}, \text{Pr}^{\text{III}}, \text{Nd}^{\text{III}}, \text{Sm}^{\text{III}}, \text{Eu}^{\text{III}}, \text{Gd}^{\text{III}}$ and Dy^{III} . The complexes have been characterised by elemental analysis, molar conductance, magnetic susceptibility, infrared, electronic and pmr spectroscopy. The nephelauxetic ratio (β), covalency (δ) and the bonding parameter ($b^{1/2}$) have been calculated for the neodymium complexes. Infrared spectral studies show that the SalTH acts as a neutral bidentate ligand in the adduct complexes and as a tribasic pentadentate one in the neutral complexes. A coordination number six has been proposed around the metal ion in all the complexes.

RECENTLY a number of papers¹⁻⁴ have been published from our laboratories on 3d-metal complexes of isonicotinoylhydrazine, tyrosine hydrazide, *N*-benzoylglycyl hydrazide, and their Schiff bases. This work has been extended to the lanthanum(III) complexes of the above types of ligands. The synthesis and structural studies of lanthanum(III) complexes of isonicotinoyl hydrazine and *o*-hydroxyacetophenoneisonicotinoyl hydrazine have been published^{5,6} since then. The present paper describes the results of our similar investigations on the complexes of salicylaldehyde (*N*-*o*-hydroxybenzalidene)tyrosyl hydrazone with $\text{La}^{\text{III}}, \text{Pr}^{\text{III}}, \text{Nd}^{\text{III}}, \text{Sm}^{\text{III}}, \text{Eu}^{\text{III}}, \text{Gd}^{\text{III}}$ and Dy^{III} .

Experimental

Lanthanide trichlorides were obtained from Indian Rare Earths, and 1-tyrosine hydrazide from Sigma. All other chemicals used were of AnalaR grade.

Preparation of ligand: Salicylaldehyde (*N*-*o*-hydroxybenzalidene)tyrosyl hydrazone was prepared by refluxing tyrosine hydrazide (25 mmol in 50 ml of methanol) and salicylaldehyde (50 mmol in 50 ml of methanol) for ~6 h. The yellow amorphous solid obtained on slow cooling of the reaction mixture to room temperature was separated by filtration, washed repeatedly with cold methanol and the crude product was recrystallised from hot methanol, m.p. 215° (Found: C, 68.48; H, 5.21; N, 10.42; N_2H_4 , 7.94. $\text{C}_{23}\text{H}_{21}\text{N}_5\text{O}_4$ calcd. for: C, 68.32; H, 5.18; N, 10.33; N_2H_4 , 7.88%).

Preparation of complexes: The complexes, $[M(\text{SalTH})\text{Cl}_2(\text{H}_2\text{O})]2\text{H}_2\text{O}$, were prepared by mixing ethanolic solutions of SalTH (~2.5 mmol) and the appropriate metal chloride (~2.5 mmol). Addition

of a few drops of dilute HCl to the above solution resulted in the formation of a gummy solid, which, on maceration with acetonitrile yielded the microcrystalline complex. The complexes were filtered, washed successively with acetonitrile and ether and dried *in vacuo*.

The neutral complexes containing the deprotonated form of the ligand were prepared by mixing together aqueous ethanolic solutions of the ligand (1 mmol), KOH (3 mmol) and the appropriate metal chloride (1 mmol) and adjusting pH of the solution to 7.5 by the addition of a few drops of dilute HCl. The precipitated complexes were digested on a water-bath for ~30 min, filtered, washed successively with water and ethanol, and dried at room temperature.

Analysis: Lanthanides were gravimetrically estimated as oxides⁷ as well as oxalates after decomposing the organic matter with aqua regia and subsequently with concentrated H_2SO_4 . Hydrazine was estimated volumetrically after subjecting the complexes to acid hydrolysis. The C, H and N were analysed on Coleman analysers.

Physical measurements: The magnetic susceptibility measurements were carried out at room temperature on a Cahn-Faraday electrobalance and the molar conductance determined on a WTW conductivity meter. The infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer, while the electronic spectra were obtained on a Cary-14 spectrophotometer.

Results and Discussion

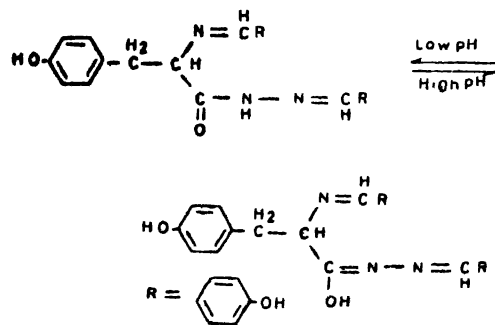
The analytical data (Table 1) show that the metal-ligand interaction gives rise to the formation

TABLE 1—ANALYTICAL AND PHYSICAL DATA OF Ln^{III} COMPLEXES OF SaI^{TH}

Compd.	Colour	M.p. °C	Analysis % : Found/(Calcd.)				Molar conductance $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	μ_{eff} B.M.
			Metal	Cl	N	N ₂ H ₄		
[La(SalTH)Cl ₂ (H ₂ O)]2H ₂ O	Light yellow	246	19.43 (19.77)	15.04 (15.14)	5.98 (5.89)	4.43 (4.55)	135.7	Diamag.
[Pr(SalTH)Cl ₂ (H ₂ O)]2H ₂ O	Yellow	228	19.12 (20.00)	14.98 (15.10)	5.96 (5.90)	4.27 (4.54)	129.8	3.30
[Nd(SalTH)Cl ₂ (H ₂ O)]2H ₂ O	Yellow	236	19.91 (20.38)	14.67 (15.03)	5.93 (5.86)	4.32 (4.52)	106.2	3.37
[Sm(SalTH)Cl ₂ (H ₂ O)]2H ₂ O	Light yellow	185d	20.91 (21.06)	14.65 (14.90)	5.88 (5.78)	4.15 (4.48)	118.0	2.04
[Eu(SalTH)Cl ₂ (H ₂ O)]2H ₂ O	Yellow	173d	20.59 (21.24)	14.26 (14.87)	5.87 (5.69)	—	129.8	3.22
[Gd(SalTH)Cl ₂ (H ₂ O)]2H ₂ O	Yellow	165d	21.40 (21.82)	14.30 (14.76)	5.82 (5.72)	4.35 (4.44)	141.6	7.38
[Dy(SalTH)Cl ₂ (H ₂ O)]2H ₂ O	Yellow	240	22.30 (22.38)	14.28 (14.65)	5.78 (5.70)	4.20 (4.40)	141.6	8.97
La(SalTH-3H)(H ₂ O)	Yellow	> 300	24.81 (24.94)	—	7.54 (7.34)	5.45 (5.74)	3.0	Diamag.
Pr(SalTH-3H)(H ₂ O)	Reddish yellow	> 300	24.92 (25.21)	—	7.51 (7.45)	5.62 (5.72)	2.95	3.61
Nd(SalTH-3H)(H ₂ O)	Reddish yellow	> 300	24.98 (25.65)	—	7.47 (7.31)	5.50 (5.69)	2.89	3.23
Sm(SalTH-3H)(H ₂ O)	Yellow	> 300	26.21 (26.45)	—	7.38 (7.28)	5.34 (5.63)	9.40	2.03
Eu(SalTH-3H)(H ₂ O)	Reddish yellow	> 300	26.30 (26.66)	—	7.36 (7.22)	—	10.62	3.88
Gd(SalTH-3H)(H ₂ O)	Yellow	> 300	27.12 (27.33)	—	7.30 (7.21)	5.40 (5.56)	3.54	7.67
Dy(SalTH-3H)(H ₂ O)	Yellow	> 300	27.35 (27.99)	—	7.24 (7.18)	5.42 (5.51)	3.83	9.22

d = Decomposes.

of two types of complexes, viz. the adduct complexes involving the non-deprotonated form of the ligand and the neutral complexes in which SalTH coordinates in its deprotonated form. The formation of the neutral complexes in slightly alkaline medium suggests the amide \rightleftharpoons imidol tautomerism of SalTH as a function of pH as shown below,



All the complexes are fairly stable under normal atmospheric conditions. The adduct complexes are soluble in water, methanol, DMF and DMSO but are insoluble in non-polar organic solvents like benzene and CCl_4 , while the neutral complexes are soluble only in hot DMF and DMSO. The molar conductance values of the adduct complexes in 0.001 *M* DMF solution show their 1 : 2 electrolytic behaviour⁸ presumably due to the solvolysis of two

of the three chloride groups. The neutral complexes, however, behave as non-electrolytes in 0.001 *M* DMF solutions⁸.

All the adduct complexes are found to melt/decompose at specific temperatures below 250° while the neutral complexes do not melt below 300° (Table 1). The thermolysis of the adduct complexes corresponds to the loss of two molecules of water in the temperature range 85-100° and to the loss of one more water molecule around 140°. The above observation suggests that two molecules of water are lattice-held while the third one is present within the coordination sphere resulting in its loss at a relatively high temperature.

The paramagnetic behaviour of the lanthanide(III) ions is consistent with the presence of unpaired electrons. Since these electrons are well shielded by the $5s^2p^6$ octet both in their spin and orbital motion, the magnetic moments show little deviation from the Van Vleck values⁶ indicating a very little participation of the 4f-electrons in bond formation in these complexes. The Sm^{III} and Eu^{III} complexes, however, show greater values than the calculated ones presumably on account of the low J-separation¹⁰.

Electronic spectra : The f-f transition bands show normally, unlike the d-d ones, weak perturbation due to complexation. Increase in the intensity, shift of the barycentre and splitting of certain bands due to the crystal field with respect to the aquo ions

TABLE 2—ELECTRONIC SPECTRAL DATA OF Nd^{III} COMPLEXES OF SalTH

	A		B		Assignment	Spectral parameter*
	λ_{\max} cm ⁻¹	ϵ	λ_{\max} cm ⁻¹	ϵ		
A[Nd(SalTH)Cl ₂ (H ₂ O)]2H ₂ O	11 455	6.5	11 428	3.0	⁴ I _{9/2} → ⁴ F _{5/2}	$A\bar{\beta} = 0.9833$ $b^{1/2} = 0.0763$
	11 585	5.0	—	—	→ ⁴ F _{5/2}	
	12 470	21.5	12 422	14.5	→ ² H _{9/2}	$\delta = 1.698$
	13 420	13.0	13 868	12.8	→ ⁴ F _{7/2}	
	13 615	13.0	13 468	13.0	—	
	13 605	12.0	—	—	—	
B[Nd(SalTH-3H)(H ₂ O)]	14 705	3.5	14 598	3.5	→ ⁴ F _{9/2}	$B\bar{\beta} = 0.9781$ $b^{1/2} = 0.1046$ $\delta = 2.239$
	17 095	35.0	17 005	33.5	→ ⁴ G _{5/2} , ² G _{7/2}	
	19 045	11.5	18 865	19.3	→ ⁴ G _{7/2}	
	19 495	8.5	19 415	17.5	→ ⁴ G _{9/2}	
	—	—	—	—	—	

* Calculated for the hypersensitive transition ⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2}

$$\bar{\beta} = \frac{1}{n} \sum_{n=1}^n \frac{\nu_{\text{complex}}}{\nu_{\text{quo}}}, b^{1/2} = [1/(1 - \bar{\beta})]^{1/2}, \% \delta = \left(\frac{1 - \bar{\beta}}{\bar{\beta}} \right) \times 100$$

spectral data are recorded in 0.02 M DMF solution.

are effects that can be observed on complex formation. The electronic spectra of the Nd^{III} complexes are recorded in 2×10^{-2} M DMF solutions. The spectra of the complexes show a shift of the spectral bands towards lower energy as compared to those of the aquo ions^{11,12} due to the nephelauxetic effect. The band shape of the hypersensitive transition (⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2}) is almost similar in both the adduct and the neutral complex, which indicates that the complexes maintain the same coordination number. The various parameters calculated from the hypersensitive bands are given in Table 2. The nephelauxetic parameter ($\bar{\beta}$) is less than unity while the bonding parameter ($b^{1/2}$) and the Sinha's parameter (δ) are positive for both the complexes indicating the presence of a moderate amount of covalency between the metal and the ligand^{13,14}. Further, the relative comparison of the above parameters reveals enhanced covalency in the neutral complex compared to the adduct complex of Nd^{III}.

Infrared spectra: The coordination sites of the ligand involved in bonding with the metal ion have been determined by a careful comparison of the ir spectra of the complexes with that of the parent ligand. Since the full spectrum of the ligand is highly complex, only those bands diagnostic of coordination with the metal ion have been taken for discussion. The 3 500-3 200 cm⁻¹ region of the spectra of particularly the adduct complexes, contains a broad band which may be due to the ν_{OH} and ν_{NH} bands arising from the ligand and the water molecules associated with the complexes. Hence, we have refrained from drawing any conclusion based on the bands appearing in the above region.

The salTH shows intense absorptions at 1 660, 1 615, 1 510 and 1 275 cm⁻¹ which may be respectively assigned to the amide I, $\nu_{\text{C=N}}$, amide II and amide III bands¹⁵; the corresponding bands are observed in the spectra of the adducts in 1 635-1 630,

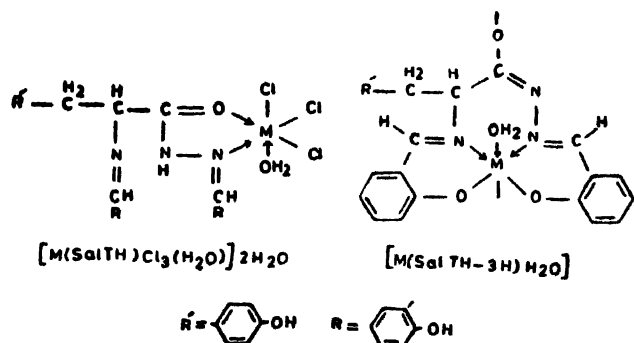
1 605-1 600, 1 500-1 495 and 1 285 cm⁻¹ regions, respectively. Thus, the observed negative shifts in the C=N, amide I and amide II bands and the positive shift in the amide III band suggest coordination through the azomethine group and the carbonyl group of the ligand in all the adduct complexes. The coordination through the azomethine nitrogen atom is further substantiated by the observed positive shift of the order of 40-55 cm⁻¹ in the $\nu_{\text{N-N}}$ mode of the adduct complexes compared to its position at 995 cm⁻¹ in the spectrum of the parent ligand. A monodentate coordination of the N-N moiety was reported¹⁶ to increase the $\nu_{\text{N-N}}$ mode by an order of 40-50 cm⁻¹. Further, the ν_{asym} (C-O, phenolic) band appearing at 1 235 cm⁻¹ in the spectrum of the parent ligand remains almost unaltered in the spectra of all the adduct complexes suggesting the absence of phenolic OH group coordination. Thus, in all the adduct complexes, the SalTH seems to behave as a bidentate ligand coordinating through the carbonyl oxygen and the azomethine nitrogen of the hydrazide moiety.

In the spectra of the neutral complexes, all the amide bands, however, disappear while the $\nu_{\text{C=N}}$ and the $\nu_{\text{N-N}}$ bands undergo negative (10-15 cm⁻¹) and positive (40-50 cm⁻¹) shifts, respectively suggesting the coordination of the C=N and N-N moieties and the destruction of the C=O group presumably via the amide-imidol tautomerism of the ligand. The coordination of the ligand in its imidol form in all the neutral complexes has been further suggested by the appearance of new peaks characteristic of ν_{NCO} in the 1 360 and 1 545 cm⁻¹ regions of the spectra¹⁷. The ν_{asym} (C-O, phenolic) band appearing at 1 235 cm⁻¹ in the spectrum of the parent ligand undergoes a positive shift of the order of 35-40 cm⁻¹ and a new band characteristic of ν_{asym} (C-O-M) appears at 1 535-1 525 cm⁻¹ region in the spectra of the neutral complexes indicating bonding through

the oxygen atoms of both the phenolic groups¹⁸. Thus, in all the deprotonated complexes the SalTH appears to behave as a trinegative pentadentate ligand coordinating through the imidol oxygen, the two azomethine groups and the two phenolate oxygen atoms. The non-ligand bands appearing in the 330-310 and 400-370 cm^{-1} regions in the spectra of all the complexes may tentatively be assigned to the $\nu_{\text{M-N}}$ and the $\nu_{\text{M-O}}$ modes, respectively^{19,20}.

Pmr spectra : In order to decide the bonding sites of the ligand involved in the complexes, the pmr spectra of a representative adduct complex, viz. $[\text{La}(\text{SalTH})\text{Cl}_3 \cdot \text{H}_2\text{O}]2\text{H}_2\text{O}$, and a representative neutral complex, viz. $[\text{La}(\text{SalTH-3H})\text{H}_2\text{O}]$ have been recorded in DMSO-d_6 and their spectral features compared with those of the parent ligand recorded in the same solvent. The pmr spectrum of SalTH exhibits signals at δ 6.48-7.50, 8.04-8.25, 11.40 and 12.73 assignable²¹ to the aromatic protons, methine protons of the azomethine moieties, imine proton of the hydrazone moiety and the phenolic hydroxyl protons, respectively. Of the two singlets observed for the methine protons, one undergoes a downfield shifting with a slight broadening while the other remains unchanged in the adduct complex. This clearly indicates the coordination of only one of the azomethine groups, viz. the azomethine group of the hydrazone moiety (based on the pmr and ir spectra taken together) in the adduct complexes. However, both the singlets due to the methine protons undergo a downfield shift with broadening in the neutral complex which seems to be due to the coordination of both the azomethine groups with the metal ion. The signals due to the phenolic hydroxyl protons and the imine proton of the hydrazone moiety could not, however, be located in the spectra of the complexes.

Based on the elemental analyses and the various physicochemical studies, the structures shown below have been proposed for the lanthanum(III) complexes.



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References

1. R. O. AGGARWAL and T. R. RAO, *Curr. Sci.*, 1977, **46**, 625.
2. T. R. RAO, M. SAHAY and R. O. AGGARWAL, *Indian J. Chem., Sect. A*, 1984, **23A**, 214.
3. T. R. RAO, M. SAHAY and R. O. AGGARWAL, *Synth. React. Inorg. Metal-Org. Chem.*, 1985, **15**, 175.
4. T. R. RAO, M. SAHAY and R. O. AGGARWAL, *Synth. React. Inorg. Metal-Org. Chem.*, 1985, **15**, 209.
5. T. R. RAO, I. A. KHAN and R. O. AGGARWAL, *Curr. Sci.*, 1985, **54**, 218.
6. T. R. RAO, I. A. KHAN and R. O. AGGARWAL, *J. Less-Common Met.*, 1986, **115**, 325.
7. I. M. KOLTHOFF, P. J. ELVING and E. B. SANDELL, "Treatise on Analytical Chemistry", Interscience, New York, 1963, Part II, 8, pp. 29.
8. W. J. GEARY, *Coord. Chem. Rev.*, 1971, **7**, 81.
9. J. H. VAN VLECK and A. FRANK, *Phys. Rev.*, 1929, **32**, 1494.
10. S. P. SINHA, "Complexes of Rare Earths", Pergamon, New York, 1966, p. 14.
11. G. R. CHOPPIN, D. E. HENRIE and K. BUIJS, *Inorg. Chem.*, 1966, **5**, 1743.
12. S. MISUMI, S. KIDA and M. AIHARA, *Coord. Chem. Rev.*, 1968, **3**, 193.
13. S. P. SINHA, *Spectrochim. Acta*, 1966, **22**, 57.
14. D. E. HENRIE and G. R. CHOPPIN, *J. Chem. Phys.*, 1968, **49**, 477.
15. K. NAGANO, H. KINOSHITA and A. HIRAKAWA, *Chem. Pharm. Bull.*, 1964, **12**, 1198.
16. A. BRAIBANTI, F. DALLAVALLI, M. A. PELLINGHELLI and E. LEPORATI, *Inorg. Chem.*, 1968, **7**, 1430.
17. C. N. R. RAO, "Chemical Applications of Infrared Spectroscopy", Academic, New York, 1964, pp. 758-765.
18. E. SINN and C. H. HARRIS, *Coord. Chem. Rev.*, 1969, **4**, 391.
19. J. L. CHARPANTIER and T. MOELLER, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3575.
20. N. NGSEE, H. W. LATZ and D. G. HENDRICKER, *J. Inorg. Nucl. Chem.*, 1977, **39**, 71.
21. R. L. DUTTA and B. R. DAS, *Indian J. Chem., Sect. A*, 1985, **24**, 493.