Synthesis and characterization of some lanthanoid complexes of salicylaldehyde salicyloyl hydrazone

T R Rao*, Sabita Shrestha*, & K K Narang†
Department of Chemistry, Faculty of Science,
Banaras Hindu University, Varanasi 221 005, India

Received 25 November 1999; revised 28 February 2001

Some lanthanoid complexes of the types, [Ln(ssh)(H₂O)₃]H₂O and [Ln'(Hssh)(X)(H₂O)₂]H₂O, where Ln = Y, La, Nd, Gd, Tb and Dy; Ln' = Pr/Sm for X = NO₃/Cl and H₂ssh = salicylaldehyde salicyloyl hydrazone, have been synthesized and characterized by elemental analyses, molar conductance, magnetic susceptibility, infrared, electronic and ¹H NMR spectral data. Selected complexes have also been studied on the basis of their solid state electrical conductivity, band gap, and powder X-ray diffraction data. The complexes, except those of the Pr and Sm, are polymeric in nature showing high decomposition points. Dehydration study indicates the presence of water molecules both in the lattice and coordination sphere of the complex metal ions. IR and ¹H NMR spectral data suggest trinuclear tetradentate and dinuclear tridentate coordination of H₂ssh in the complexes. The chloro and nitrate groups are found to coordinate to the metal ion as monodentate and bidentate-chelating species respectively. Solid state electrical conductivity data at various frequencies show semi-conducting nature of the complexes. Optical band gap studies show the complex [Gd(ssh)(H₂O)₃]H₂O to be a direct band gap semi-conducting material with a band gap of 2.64 eV. Powder X-ray diffraction patterns show orthorhombic structure for most of the complexes. Various polyhedral geometries such as distorted octahedron, pentagonal bipyramid and distorted square antiprism are tentatively proposed for the complexes.

Co-ordination chemistry of Schiff bases in general and hydrazones in particular continues to attract the attention of several investigators due to their biological activity and variable bonding potentialities for complexation¹. Salicylaldehyde salicyloyl hydrazone (H₂ssh), C₆H₄(OH)CONHN=CH(C₆H₄)OH [I], is a potential Schiff base having two phenolic groups in addition to the amide and azomethine moieties.

The presence of several alternate bonding possibilities is likely to give additional stability to metal complexes and thus, H₂ssh may prove to be a versatile chelating ligand with the additional possibility of undergoing tautomerism as a function of pH.

In continuation of our studies on 3d and 4f metal complexes of aromatic/aliphatic Schiff base hydrazones³, the present paper deals with the synthesis of lanthanoid complexes of salicylaldehyde salicyloyl hydrazone (H₂ssh) and their structural characterization on the basis of magnetic, spectral (IR, electronic, ¹H NMR) and powder X-ray diffraction techniques. Studies on band gap measurement, solid-state conductivity and dielectric constant were also carried out for some of the complexes and the results are discussed.

Materials and Methods

Lanthanide carbonates (Ln = La, Nd, Gd, Tb, Dy) were purchased from Indian Rare Earths Ltd. Praseodymium nitrate, samarium chloride and yttrium carbonate were obtained from GSC Chemical Testing Lab and Allied Industries, Mumbai. The metal carbonates were converted into the corresponding acetates while the metal nitrate and chloride were used as such.

Salicylaldehyde salicyloyl hydrazone was prepared as reported in literature⁶ by reacting together ethanolic solutions of salicyloyl hydrazone (1.52 g; 10 mmol in 50 ml) and salicylaldehyde (1.22 g; 10 mmol in 50 ml). The crude product was recrystallized from hot ethanolic solution; [m.p., 277-278 °C; lit⁶, 277 °C].

Structure I

¹Department of Applied Chemistry, Institute of Technology,
Banaras Hindu University, Varanasi 221 005, India
[\text{Ln}((ssh)(H_2O)_n),H_2O (Ln = Y, La, Nd, Gd, Tb, Dy)]

Lanthanide acetates were prepared in situ by neutralizing the appropriate metal carbonate (~4 mmol) with a few drops of 8N warm acetic acid. The resultant clear solution in each case was reacted with ethanolic solution of salicylaldehyde salicyloyl hydrazone (1.04 g; 4 mmol in 50 ml). The reaction mixture, which instantaneously changed to yellow/yellowish green, was refluxed for 4-5 h; the solid crude product was filtered off, washed 4-5 times with 5 ml portions of ethanol and finally with ether and dried at room temperature. The reaction may be represented by the following equation:

$$
\text{Ln(OAc)}_3 + H_{ssh} \xrightarrow{\text{EtOH/H}_2\text{O}; \text{Reflux, 4-5 h}} \text{Ln(ssh).xH}_2\text{O} + 3\text{AcOH}
$$

[\text{Ln'}((Hssh)(X)(H_2O)_3),H_2O (Ln' = Pr and Sm; X = NO}_3\text{ and Cl)}]

Ethanolic solutions of lanthanide nitrate/chloride (4 mmol in ~40 ml) and salicylaldehyde salicyloyl hydrazone (1.04 g; 4 mmol in ~40 ml) were mixed together, the reaction mixture was refluxed for 6-7 h, and the volume reduced to ~20 ml. The metal complexes, which precipitated upon addition of 4-5 ml of diethyl ether, were filtered off, and washed twice with a mixture of ethanol and ether. The complexes were dried at room temperature. The reactions may be represented by the following equations:

$$
\text{Pr(NO}_3)\text{3} + H_{ssh} \xrightarrow{\text{EtOH/H}_2\text{O}; \text{Re flux, 6 h}} \text{Pr(Hssh)(NO}_3\text{).yH}_2\text{O} + 2\text{HNO}_3
$$

$$
\text{SmCl}_3 + H_{ssh} \xrightarrow{\text{EtOH/H}_2\text{O}; \text{Re flux, 6 h}} \text{Sm(Hssh)(Cl).yH}_2\text{O} + 2\text{HCl}
$$

The metal content was estimated gravimetrically as M_2O_3 and volumetrically by standard complexometric titration using xylene orange as indicator and hexamine as buffer. The ligand content was estimated by dissolving a weighed quantity of the complex in 10 ml of 50% HCl and titrating the solution against a standard solution (~0.1N) of KBRO_3 using methyl orange as indicator. The ligand content was adjudged from calibration curve, which was constructed by plotting the data of at least five sets of titrations, in each case an aqueous solution of the ligand (varying amounts dissolved in ~10 ml portions of 6N HCl) was titrated against a standard solution of KBrO_3. Hydrazine was estimated volumetrically (after hydrolyzing the complex with 6-8N HCl for ca. 2 h) by titrating against a standard solution of potassium bromate using methyl orange as indicator. Nitrogen was micro-analyzed.

Molar conductances of the complexes in 0.001M DMSO solution were measured at room temperature on a WTW conductivity meter using a commercial conductivity 'dip cell' of cell constant, 0.59. The room temperature magnetic susceptibility measurements were carried out on a Cahn Faraday electrobalance using Hg[Co(NCS)_4] as the calibrant. Solid-state conductivity of the complexes was recorded on Schlumberger, Impedance/Gain phase Analyzer, SI 1260 at room temperature.

Infrared spectra (4000-400 cm^-1) of the ligand and the complexes were obtained in KBr pellets on an FT-IR Jasco-5300 spectrophotometer. Electronic absorption spectra of the complexes [in solid state as nujol mull and DMSO solutions] were obtained on a Shimadzu UV-vis 160A spectrophotometer while the NMR spectra were recorded on a JEOL-FX90Q spectrometer. Thermal studies of the neodymium(III) complex were performed on a Lineis Tape L40/390 system in the 20-700°C temperature range with a heating rate of 10°C/min in an alumina crucible using alumina as a reference material. Powder XRD patterns were obtained on a Rigaku Rotaflex RTP 300Rc using CuKα radiation. Dehydration studies of all the complexes were done by subjecting them to two specific temperatures (viz., ~110°C and ~150°C).

**Results and Discussion**

The analytical data of the complexes are shown in Table 1. The absence of anions was indicated in all the complexes except those of the Pr and Sm, showing that the ligand was deprotonated to the extent of three protons. All the complexes are stable in air; non-hygroscopic and are soluble in dimethyl sulfoxide and dimethyl formamide. The insolvability of the complexes in common organic solvents and the high decomposition temperature, except those of the Pr and Sm, indicate their polymeric nature. The molar conductance values in DMSO solutions (Table 1) indicate non-electrolytic nature of the complexes.

The number of lattice-held and coordinated water molecules in the present complexes was determined...
by thermal study (Table 1). At 110 °C, all the complexes suffered weight-loss of about 4-5% which may be due to the elimination of one lattice water molecule. At ≈150 °C, additional weight-loss of about 8-11% in the Y(III) complex, 12-13% in the Pr(III), Sm(III), Gd(III), Tb(III) and Dy(III) complexes and 14-16% in the La(III) and Nd(III) complexes was registered corresponding to the loss of two, three and four coordinated water molecules respectively. The room temperature magnetic moments of all the paramagnetic complexes (Table 1) show very little deviation from the Van Vleck values suggesting feeble interaction of 4f electrons in metal-ligand bond formation. In the case of the samarium complex, the slightly higher value may be related to thermal population of the higher energy level next to the ground state owing to low J-J separation.

The conductivity values are known to depend on the nature and amount of imperfections present in a crystal and its packing arrangement. The room temperature a.c. conductivity values of H$_3$ssh and the La(III), Nd(III) and Dy(III) complexes (solid state) determined at different frequencies ($10^2$-$10^7$ Hz) lie in the range, $10^4$ to $10^8$ ohm$^{-1}$ cm$^{-1}$ [Fig. 1] which are in agreement with the prescribed range$^{11}$ for semiconductors ($10^2$-$10^9$ ohm$^{-1}$ cm$^{-1}$). Since there is no considerable difference in the conductivity values of the diamagnetic and the paramagnetic complexes, it may be presumed that the unpaired electrons in the

*Fig. 1—Plot of solid state conductance vs. frequency of H$_3$ssh and its La(III), Nd(III) and Dy(III) complexes.*

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>M.P.</th>
<th>Analysis, Found (Calcd) %</th>
<th>Wt. loss (%)</th>
<th>μ$_{eff}$ (B.M.)</th>
<th>$\Lambda_m$ $^a$ (Ω$^{-1}$ cm$^2$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Metal</td>
<td>N</td>
<td>N$_2$H$_4$</td>
<td>Ligand</td>
</tr>
<tr>
<td>[Y(ssh)(H$_2$O)$_2$]H$_2$O</td>
<td>280$^d$</td>
<td>22.08, 22.85</td>
<td>3.12</td>
<td>7.96</td>
<td>63.15</td>
</tr>
<tr>
<td>(Light yellow, 70, 396.0)</td>
<td></td>
<td>(22.47)</td>
<td>(3.78)</td>
<td>(8.08)</td>
<td>(63.88)</td>
</tr>
<tr>
<td>[La(ssh)(H$_2$O)$_2$]H$_2$O</td>
<td>300$^d$</td>
<td>28.80, 29.00</td>
<td>3.48</td>
<td>6.71</td>
<td>52.94</td>
</tr>
<tr>
<td>(Light yellow, 70, 481.9)</td>
<td></td>
<td>(28.83)</td>
<td>(3.94)</td>
<td>(6.63)</td>
<td>(52.48)</td>
</tr>
<tr>
<td>[Pr(ssh)(NO$_2$)(H$_2$O)$_2$]H$_2$O</td>
<td>148</td>
<td>27.00, 27.54</td>
<td>3.46</td>
<td>6.48</td>
<td>49.10</td>
</tr>
<tr>
<td>(Light green, 65, 528.9)</td>
<td></td>
<td>(26.86)</td>
<td>(3.94)</td>
<td>(6.04)</td>
<td>(48.10)</td>
</tr>
<tr>
<td>[Nd(ssh)(H$_2$O)$_4$]H$_2$O</td>
<td>310$^d$</td>
<td>28.54, 29.28</td>
<td>3.65</td>
<td>6.65</td>
<td>52.26</td>
</tr>
<tr>
<td>(Light green, 60, 487.0)</td>
<td></td>
<td>(29.56)</td>
<td>(3.90)</td>
<td>(6.57)</td>
<td>(51.95)</td>
</tr>
<tr>
<td>[Sm(ssh)(Cl)(H$_2$O)$_3$]H$_2$O$^b$</td>
<td>149</td>
<td>28.78, 28.10</td>
<td>3.09</td>
<td>6.38</td>
<td>50.04</td>
</tr>
<tr>
<td>(Yellowish brown, 70, 511)</td>
<td></td>
<td>(29.32)</td>
<td>(3.51)</td>
<td>(6.26)</td>
<td>(49.70)</td>
</tr>
<tr>
<td>[Gd(ssh)(H$_2$O)$_3$]H$_2$O</td>
<td>308$^d$</td>
<td>31.68, 32.06</td>
<td>3.27</td>
<td>6.58</td>
<td>52.16</td>
</tr>
<tr>
<td>(Yellow, 60, 482.0)</td>
<td></td>
<td>(32.57)</td>
<td>(3.52)</td>
<td>(6.63)</td>
<td>(52.48)</td>
</tr>
<tr>
<td>[Tb(ssh)(H$_2$O)$_3$]H$_2$O</td>
<td>305$^d$</td>
<td>31.75, 31.96</td>
<td>3.18</td>
<td>6.68</td>
<td>52.78</td>
</tr>
<tr>
<td>(Yellow, 55, 483.9)</td>
<td></td>
<td>(32.85)</td>
<td>(3.51)</td>
<td>(6.61)</td>
<td>(52.27)</td>
</tr>
<tr>
<td>[Dy(ssh)(H$_2$O)$_3$]H$_2$O</td>
<td>280$^d$</td>
<td>32.35, 32.95</td>
<td>3.02</td>
<td>6.72</td>
<td>52.15</td>
</tr>
<tr>
<td>(Greenish yellow, 70, 487.0)</td>
<td></td>
<td>(33.26)</td>
<td>(3.49)</td>
<td>(6.57)</td>
<td>(51.95)</td>
</tr>
</tbody>
</table>

$^a$Measured in $10^{-3}$ M DMSO solution; $^b$Cl, found, 7.38%; calcld. 6.84%; $^d$decomposition temperature
4f orbital do not play any important role in the electrical conductivity.

In the IR spectrum of the ligand the absorption bands at 3280, 1670, 1620, 1580, 1360 and 1000 cm\(^{-1}\) have been attributed to v(N-H), amide-I, v(C=N), amide-II, amide-III and v(N-N) respectively. All the amide and the v(N-H) bands seem to disappear in all the complexes except in those of the Pr and Sm, indicating destruction of the >C=O group and loss of NH proton via enolization. Further, some new peaks appeared in the complexes, viz., a sharp band at 1610 cm\(^{-1}\) due to >C=N-N=C< group and medium intensity bands at 1530 and 1400 cm\(^{-1}\) due to v(NCO\(^{-}\)) vibration.

There was no change in the position of the amide bands in the spectra of the Pr(III) and Sm(III) complexes owing to non-coordination of the amide group. The presence of bands at 1270 and 1460 cm\(^{-1}\) indicates coordination of the nitro group in a bidentate-chelating manner. The hypsochromic shift of the v(N-N) vibration in the complexes implies coordination through one of the nitrogen atoms. The earlier statement about the presence or coordinated water is substantiated by the new band appearing ~830 cm\(^{-1}\) which disappears upon dehydration of the Gd(III) complex, studied as a representative case.

The electronic spectral bands of the Nd(III) complex show considerable red shifts compared to the \(\lambda_{max}\) positions of the aqua ion due to Nephelauxetic effect. The oscillator strength \((P)\) for the transition, \(^4\)I\(_{15/2}\) \(\rightarrow\) \(^4\)F\(_{5/2},\ ^4\)F\(_{7/2}\), is nearly two-fold compared to that of the aqua ion, which suggests the hypersensitive nature of the transition. The increase in \(P\) may be due to the lowering of molecular symmetry around the Nd(III) ion. The calculated spectral parameters, \(\beta\), \(b^{1/2}\), \(\%\delta\) and \(\eta\), suggest a weak covalent nature of the metal-ligand bond.

The bonding sites of the ligand actually involved in coordination were determined by comparing the \(^1\)H NMR spectra of the ligand with those of the La(III) and Y(III) complexes. The -NH and the phenolic-OH proton signals of the ligand appearing at 11.7 and 12.1 \(\delta\) respectively, disappear in the complexes indicating protonation consequent upon coordination with the metal ion. All the ring proton signals of the ligand appearing in the region 7-8 \(\delta\) get slightly shifted to 6.5-7.9 \(\delta\) in the complexes. The aliphatic CH proton signal of the ligand (at 8.8 \(\delta\)) shifts to slightly higher magnetic field (to ~8.4 \(\delta\)) in the complexes. A broad peak appearing between 3-4 \(\delta\) in the complexes is assigned to the protons of water molecules.

The band gap of the complex, \([\text{Nd(ssh)}(\text{H}_2\text{O})_4]\).\text{H}_2\text{O}\) as a representative case, was determined from the optical absorption spectrum (nujol mull spectrum) recorded at room temperature. The optical absorption coefficient \((\alpha)\) is given by the equation:

\[
\alpha = A(h\nu - E_g)^n
\]

where \(A\) is a constant, \(h\) is Planck’s constant, \(\nu\) is the frequency of the incident photon, \(E_g\) is the band gap of the material and \(n\) is a constant equal to 1/2.

![Fig.2](image1.png)

Fig.2—Plot of \(\alpha^2\) vs. photon energy of \([\text{Gd(ssh)}(\text{H}_2\text{O})_3]\).\text{H}_2\text{O}

![Fig.3](image2.png)

Fig.3—Plots of dielectric constant vs. frequency of H\(_2\)ssh and its La(III), Nd(III), and Dy(III) complexes: (a) real part, \(\varepsilon'\) and (b) imaginary part, \(\varepsilon''\) of the dielectric constant.
and 2 for the allowed direct and the indirect transitions, respectively. From the figure of $\alpha^2$ vs. photon energy (Fig.2), it is clear that only one straight line can be drawn, which means that only one slope exists, thereby, indicating that the complex is a direct band gap material. The straight-line portion of the curve when extended makes an intercept on the x-axis corresponding to the energy, 2.64 eV, which is the band gap of the material.

Combined TG-DTA studies were made on ~15 mg amount of the Nd(III) complex. The TG thermogram shows a decrease in the weight by 18.66% (calc. 18.40%) in the 110-180°C temperature range, accompanied by an endothermic peak at 160°C. This may be due to the loss of lattice-held as well as coordinated water molecules. About 40% loss in the weight was observed over the temperature range, 375-615°C corresponding to the two exothermic peaks at 430 and 560°C; this may be due to the decomposition followed by the collapse of various groups, e.g., salicylaldehyde, amide, phenyl group etc. The weight of the complex was, however, constant above 615°C presumably owing to the formation of stable oxide and/or non-stoichiometric residues.

Measurement of dielectric constant

The real and imaginary parts of the dielectric constants ($\varepsilon'$ and $\varepsilon''$ respectively) of the ligand (H$_3$s$sh$) and the La(III), Nd(III) and Dy(III) complexes were measured; the imaginary part was recorded directly from the instrument while the real part was calculated by the equation:

$$\varepsilon' = \frac{C \times \delta}{\varepsilon_0}$$

where $C$ = capacitance (in Farad); $\delta$ = thickness of the pellet (in meter); $\varepsilon_0$ = dielectric constant of the vacuum ($8.854 \times 10^{-12}$ F/m).

The values of $\varepsilon'$ and $\varepsilon''$ were plotted (Fig.3 a & b) against frequency (>10 MHz) to understand the nature of dielectric relaxation, but no distinct peaks were observed in the curve. However, the nature of the curves implies that: (i) the dielectric constant of the ligand and the complexes gets dispersed in the frequency range, (ii) there is a slow decrease of the dielectric constant with increasing frequency in H$_3$s$sh$ and the Dy(III) complex, and (iii) there is a sharp decrease of the dielectric constant (both the real and imaginary parts) in the Nd(III) and La(III) complexes up to 400 Hz and 1000 Hz respectively.

X-ray diffraction studies

Powder XRD patterns of the La(III), Gd(III), Tb(III) and Dy(III) complexes were obtained and the peaks were indexed on the basis of orthorhombic unit cell. The observed $hkl$ and the calculated 20 values as well as the $d$ spacing for each reflection of the representative sample, [La(s$sh$)(H$_2$O)$_2$].H$_2$O, can be had from the authors on request. The lattice parameters of the unit cell were calculated by the least square refinement method and the values together with the unit cell volume are given in Table 2.

Based upon elemental analyses, various physicochemical and spectral data, the structures as shown in Fig. 4 have been tentatively proposed for the present lanthanoid complexes.

---

Table 2—Lattice parameters* (Å) and unit cell volume (Å$^3$) of Ln(III) complexes of H$_3$s$sh$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>Unit cell volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>[La(s$sh$)(H$_2$O)$_2$].H$_2$O</td>
<td>06.739±0.005</td>
<td>07.359±0.005</td>
<td>11.054±0.008</td>
<td>00546.3±001.2</td>
</tr>
<tr>
<td>[Gd(s$sh$)(H$_2$O)$_2$].H$_2$O</td>
<td>38.251±0.033</td>
<td>13.262±0.011</td>
<td>24.730±0.021</td>
<td>12546.3±032.8</td>
</tr>
<tr>
<td>[Tb(s$sh$)(H$_2$O)$_2$].H$_2$O</td>
<td>32.66±0.110</td>
<td>14.795±0.050</td>
<td>23.451±0.080</td>
<td>11195.8±115.0</td>
</tr>
<tr>
<td>[Dy(s$sh$)(H$_2$O)$_2$].H$_2$O</td>
<td>38.250±0.033</td>
<td>13.262±0.011</td>
<td>24.731±0.021</td>
<td>12546.1±033.1</td>
</tr>
</tbody>
</table>

* $\alpha = \beta = \gamma = 90^\circ$ for all the complexes.
Acknowledgement

The authors thank the Head, Department of Chemistry, Faculty of Science, BHU, Varanasi, for providing laboratory facilities, the Director, Royal Drug Research Laboratory, Kathmandu, Nepal for recording the electronic spectra and Prof. D. Pandey, School of Materials Science, Institute of Technology, BHU, for providing access to X-ray facility. One of the authors (TRR) thanks the CSIR, New Delhi, for providing financial assistance in the form of a project [No.01(1437)/97].

References

7 Geary W J, *Coord chem Rev*, 7 (1971) 81