Research Article

Synthesis, Characterization of La(III), Nd(III), and Er(III) Complexes with Schiff Bases Derived from Benzopyran-4-one and Thier Fluorescence Study

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The Schiff bases, L^1 , L^2 , and L^3 , are synthesized from the condensation of 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one (L) with 2-aminopyridine (1), p-phenylenediamine (2), and o-phenylenediamine (3). The prepared Schiff bases react with lanthanum (III), neodymium (III), and erbium (III) nitrate to give complexes with stoichiometric ratio (1 : 1) (ligand : metal). The binuclear complexes of Er(III) with L^3 and the three metal ions with L^2 are separated. The complexes have been characterized by elemental analysis, molar conductance, electronic absorption, and infrared, ^1H -NMR spectral studies. The presence of hydrated and coordinated water molecules is inferred from thermogravimetric analysis. Thermal degradation studies show that the final product is the metal oxide. The luminescence properties of the Nd(III) and Er(III) complexes in dimethylformamide (DMF) solutions were investigated.

1. Introduction

The coordination chemistry of lanthanide (III) ions is rapidly increasing, owing to the relevance of these compounds in basic and applied research in different scientific areas ranging from chemistry to material science to the life science [1–8]. Lanthanide coordination compounds are the subject of intense research efforts owing to their unique structures and their potential applications in advanced materials such as Ln-doped semiconductors [9], magnetic [10, 11], catalytic [12], fluorescent [13, 14], and nonlinear optical materials [15, 16]. It has been shown that ligands containing both nitrogen and oxygen donor atoms are good building blocks for the formation of various lanthanide coordination compounds [17–24]. Schiff bases continue to occupy an important position as ligands in metal coordination chemistry [25], even almost a century since their discovery. Schiff base metal complexes have played a key role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to modern

physicochemical and biochemically relevant studies of metal complexes [26]. The lanthanide cations can promote Schiff base condensation and can give access to complexes of otherwise inaccessible ligands.

It is essential to design appropriate ligands to optimize the luminescence properties of lanthanide ions by facilitating the well-known light conversion process, which show to be efficient ligand-to-metal energy transfer process [27]. In view of this, we have designed a series of Schiff bases, which can enhance the luminescence properties of lanthanide ions. In the present work, the complexes of rare earth (La(III), Nd(III), and Er(III)) nitrate with the Schiff bases derived from the condensation of aromatic amine (2-aminopyridine (1)), aromatic diamines (p-phenylenediamine (2)), and o-phenylenediamine (3)) with 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one (L) were synthesized. Their structures were characterized by elemental analysis, molar conductance, IR, UV-Vis, ^1H NMR, and thermal analysis. The luminescence properties of the Nd(III) and Er(III) complexes in dimethylformamide (DMF) solutions were investigated.

2. Experimental

2.1. Materials and Reagents. All materials and solvents employed in this study were chemically pure grade. They included 2-aminopyridine, p-phenylenediamine, o-phenylenediamine, 5-methoxy-2-methyl-furanobenzopyran-4-one, potassium dichromate, sulphuric acid, hydrochloric acid, dimethylformamide (DMF), and dimethylsulfoxide (DMSO). The rare earth (III) nitrates were prepared by dissolving La_2O_3 , Nd_2O_3 , Er_2O_3 (99.95%, Aldrich) in concentrated nitric acid and crystallizing the salts by evaporating the solution on a steam bath.

2.2. Analysis and Physical Measurements. Carbon, hydrogen, and nitrogen were analyzed by standard microanalysis methods at microanalytical center, Cairo University, Giza, Egypt. UV-Vis spectra of the metal complexes in DMF were recorded on UV/Vis-NIR 3101 PC Shimadzu spectrophotometer. IR spectra of the ligands and their metal complexes, as KBr discs, were recorded on a Shimadzu FTIR spectrometer. ^1H -NMR spectra of the ligands and their La(III) complexes, in DMSO-d_6 , were recorded on Varian 300 MHz NMR spectrometer at room temperature using TMS as an internal standard. Molar conductivity of $10^{-3} \text{ mol L}^{-1}$ solutions of the complexes in DMF was measured on the conductivity meter ORION model 150 of 0.6 cell constant. Thermal analyses have been carried out using Shimadzu-50 thermal analyzer from room temperature to 800°C under heating rate of $10^\circ\text{C min}^{-1}$. Analysis of the metal ions was carried out by dissolving the complexes in concentrated nitric acid followed by hydrogen peroxide, neutralizing the diluted aqueous solutions with sodium hydroxide to pH 5.5, and the metal content was determined by recommended method [28] or was determined by the weight of the complex residue after thermal decomposition. The fluorescence property of all Schiff bases and their neodymium (III) and erbium (III) complexes in dimethylformamide (DMF) was studied. 0.25 mL from $10^{-4} \text{ mol L}^{-1}$ stock solution is diluted to 50 mL by DMF to prepare $5 \times 10^{-7} \text{ mol L}^{-1}$. The measurements were made on a T80t PG spectrofluorophotometer equipped with quartz cuvettes of 1 cm path length. The excitation and emission slit widths were 7.5 nm and scan speed 500 nm/min.

2.3. Synthesis

2.3.1. Synthesis of the Schiff-Bases. 6-Formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one was synthesized as previously discussed [29] by oxidation of two grams of 5-methoxy-2-methyl-furanobenzopyran-4-one with chromic acid [60 mL of 10% H_2SO_4 and 40 mL of 10% $\text{K}_2\text{Cr}_2\text{O}_7$] at $70\text{--}80^\circ\text{C}$ with constant stirring, and then hydrolyzed by refluxing one gram with 25 mL 1:1 hydrochloric acid for about one hour. The yellow orange product of 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one (L) was filtered, dried, and recrystallized from toluene till constant melting point (195°C) [lit. m.p. 195] [30]. The Schiff bases were prepared by the addition of p-phenylenediamine, o-phenylenediamine (5 mMole), or 2-aminopyridine (10 mMole) in 20 mL ethanol dropwise with continuous stirring to a solution of

(L) in ethanol (20 mL, 10 mMole), Figure 1. The mixture was stirred at room temperature for at least 30 min, and the solids obtained were filtered off, washed with ethanol, and recrystallized from dimethylformamide.

2.3.2. Synthesis of the Metal Complexes. All the complexes were prepared by mixing requisite amount of the ligand and the $\text{Ln}(\text{NO}_3)_3$ (Ln: La(III), Nd(III), or Er(III)) sufficient to form 1:1, 1:2, and 2:1 (M:L) chelates as follows: an ethanolic solution (10 mL) of $\text{Ln}(\text{NO}_3)_3$ was added dropwise to ethanolic solution of Schiff base (L^1 , L^2 or L^3) (30 mL). The mixtures were heated under reflux for 4–6 hours, and then the solutions were reduced to 15 mL. The resulting solid complexes were filtered out, washed thoroughly with successive portions of hot ethanol, followed by petroleum ether until the filtrate becomes colorless. The obtained complexes were kept in a vacuum desiccator over anhydrous calcium chloride. The complexes are air stable in the solid state and soluble in DMF or DMSO.

3. Results and Discussion

The present study aims to investigate the structure of lanthanide ion complexes with the prepared ligands. These ligands have many centers of chelation; thus, making the elucidation and assignment of the chelation centers a challenge, the solving of this problem is tried through the investigation of the separated complexes using elemental analyses, molar conductance, electronic absorption and infrared, ^1H -NMR and thermogravimetric analysis. The complexes are stable in air, nonhygroscopic, and have high melting point $>350^\circ\text{C}$, and they are easy soluble in DMF and DMSO and slightly soluble in nonpolar solvents. The C, H, N, Ln contents of both theoretically calculated, and measured values are in accordance with the tentative formula of the complexes. The analytical and physical data of the metal complexes of L^1 , L^2 , and L^3 are shown in Table 1. The molar conductivities of $10^{-3} \text{ mol L}^{-1}$ solutions in dimethylformamide (DMF) of the given complexes were measured, Table 1. The molar conductance of the solutions of L^1 complexes, Nd- L^3 and (2:1) (M:L) complexes of L^2 are in the range of $108\text{--}124 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, showing that complexes are 1:1 electrolytes [31]. On the other hand, the value of $157.80 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for $\text{Er}_2\text{-L}^3$ is higher than the expected value for a 1:1 electrolyte which suggests that this complex is 1:2 electrolyte [32]. The molar conductance of the solution of La- L^3 complex and 1:1 (M:L) complexes of Schiff base L^2 are in the range of $22.5\text{--}38.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. These low values may be attributed to the coordination of anion in these complexes rather than the ionic association to the lanthanide (III) cations during complex formation. This directly supports the nonelectrolytic character of these complexes [31]. Unfortunately, attempts to prepare single crystals for X-ray diffraction studies were unsuccessful.

3.1. Characterization of the Complexes

3.1.1. IR Spectra of the Ligands and Their Complexes. The infrared spectra of the prepared complexes are compared with

FIGURE 1: Preparation of the Schiff bases.

those of the free ligands in order to determine the site of coordination that may be involved in chelation (Table 2). There are some guide peaks in the spectra of the ligands which are of good help for achieving this goal. These peaks are expected to be involved in chelation. The presence of the broad band at $3430\text{--}3364\text{ cm}^{-1}$ of the stretching vibrations of phenolic OH groups in the IR spectra of the ligands indicate that the OH groups of these Schiff bases are involved in intramolecular hydrogen bonds [33]. On the other hand, the broadbands around $3425\text{--}3417\text{ cm}^{-1}$ in the IR spectra of the

complexes are due to $\nu(\text{OH})$ of water molecules in the prepared complexes; this finding is also confirmed by elemental and thermal analyses.

The presence of bands with different intensities in the IR spectra of the Schiff bases at $1167\text{--}1228\text{ cm}^{-1}$ and $1109\text{--}1119\text{ cm}^{-1}$ are due to C–OH stretching and deformation of OH, respectively [33]. Coordination, through the phenolic oxygen after deprotonation, causes the shift of this band to higher frequency in all the complexes compared to that of the free ligands, suggesting that hydroxyl groups of the Schiff

TABLE 1: Analytical and physical data of the metal complexes of Schiff bases.

Ligand or complexes	Symbol	Formula	M.W.	M:L	C% Calc. (found)	H% Calc. (found)	N% Calc. (found)	M% Calc. (found)	Molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
L^1	L^1	$\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4$	296.28	—	64.86 (65.00)	4.08 (3.99)	9.46 (9.60)	—	—
$[\text{La L}^1 \cdot \text{OH} \cdot 4\text{H}_2\text{O}] \cdot \text{NO}_3 \cdot 2\text{H}_2\text{O}$	La-L^1	$\text{C}_{16}\text{H}_{24}\text{LaN}_3\text{O}_{14}$	621.28	1:1	30.93 (30.89)	3.89 (3.87)	6.76 (6.70)	22.36 (22.26)	108
$[\text{Nd L}^1 \cdot \text{OH} \cdot 4\text{H}_2\text{O}] \cdot \text{NO}_3 \cdot 4\text{H}_2\text{O}$	Nd-L^1	$\text{C}_{16}\text{H}_{28}\text{NdN}_3\text{O}_{16}$	662.64	1:1	29.00 (29.03)	4.26 (4.27)	6.34 (6.31)	21.77 (21.67)	109
$[\text{Er L}^1 \cdot \text{OH} \cdot 4\text{H}_2\text{O}] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$	Er-L^1	$\text{C}_{16}\text{H}_{22}\text{ErN}_3\text{O}_{13}$	631.62	1:1	30.42 (30.40)	3.51 (3.49)	6.65 (6.68)	26.48 (26.50)	111
L^2	L^2	$\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_8$	512.47	—	65.62 (65.69)	3.93 (3.79)	5.47 (5.37)	—	—
$[\text{La L}^2 \cdot \text{NO}_3 \cdot \text{OH} \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}] \cdot \text{H}_2\text{O}$	La-L^2	$\text{C}_{30}\text{H}_{30}\text{LaN}_3\text{O}_{15}$	811.48	1:1	44.37 (44.40)	3.73 (3.73)	5.18 (5.18)	17.11 (17.12)	32
$[\text{Nd L}^2 \cdot \text{NO}_3 \cdot \text{OH} \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}]$	Nd-L^2	$\text{C}_{30}\text{H}_{28}\text{NdN}_3\text{O}_{14}$	844.86	1:1	45.45 (45.49)	4.07 (4.06)	4.79 (4.97)	17.10 (17.07)	38
$[\text{Er L}^2 \cdot \text{NO}_3 \cdot \text{OH} \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}]$	Er-L^2	$\text{C}_{30}\text{H}_{28}\text{ErN}_3\text{O}_{14}$	821.82	1:1	44.00 (43.85)	3.42 (3.43)	5.12 (5.11)	20.30 (20.35)	35
$[\text{La}_2 \text{L}^2 \cdot 2\text{NO}_3 \cdot \text{OH} \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 3\text{H}_2\text{O}] \cdot \text{NO}_3$	$\text{La}_2\text{-L}^2$	$\text{C}_{32}\text{H}_{39}\text{La}_2\text{N}_5\text{O}_{23}$	1137.47	2:1	33.58 (33.79)	3.24 (3.28)	6.09 (6.16)	24.35 (24.42)	124
$[\text{Nd}_2 \text{L}^2 \cdot 2\text{NO}_3 \cdot \text{OH} \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 3\text{H}_2\text{O}] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$	$\text{Nd}_2\text{-L}^2$	$\text{C}_{32}\text{H}_{39}\text{Nd}_2\text{N}_5\text{O}_{24}$	1166.15	2:1	32.87 (32.96)	3.36 (3.37)	5.89 (6.01)	24.56 (24.74)	122
$[\text{Er}_2 \text{L}^2 \cdot 2\text{NO}_3 \cdot \text{OH} \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 3\text{H}_2\text{O}] \cdot \text{NO}_3 \cdot 3\text{H}_2\text{O}$	$\text{Er}_2\text{-L}^2$	$\text{C}_{32}\text{H}_{43}\text{Er}_2\text{N}_5\text{O}_{26}$	1248.22	2:1	30.86 (30.79)	3.43 (3.47)	5.72 (5.61)	26.72 (26.80)	124
L^3	L^3	$\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_8$	512.47	—	65.62 (65.89)	3.93 (3.84)	5.47 (5.29)	—	—
$[\text{La L}^3 \cdot \text{NO}_3 \cdot \text{C}_2\text{H}_5\text{OH}] \cdot 2\text{H}_2\text{O}$	La-L^3	$\text{C}_{30}\text{H}_{28}\text{LaN}_3\text{O}_{14}$	793.46	1:1	45.46 (45.41)	3.58 (3.56)	5.60 (5.29)	17.87 (17.51)	22
$[\text{Nd L}^3 \cdot \text{NO}_3 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}] \cdot \text{OH}$	Nd-L^3	$\text{C}_{30}\text{H}_{27}\text{NdN}_3\text{O}_{14}$	797.79	1:1	45.67 (45.17)	3.40 (3.41)	5.72 (5.27)	18.10 (18.08)	120
$[\text{Er}_2 \text{L}^3 \cdot 2\text{NO}_3 \cdot 4\text{H}_2\text{O}] \cdot 2\text{OH} \cdot \text{H}_2\text{O}$	$\text{Er}_2\text{-L}^3$	$\text{C}_{28}\text{H}_{30}\text{Er}_2\text{N}_4\text{O}_{21}$	1093.07	2:1	31.00 (30.77)	2.75 (2.77)	5.22 (5.12)	30.70 (30.60)	157

TABLE 2: Assignment of IR-bands of metal chelates of Schiff bas.

Compound	M:L	$\nu_{C=O}$	$\nu_{C=N}$	ν_{C-O}	$\nu_1(NO_3)$	$\nu_2(NO_3)$	$\nu_3(NO_3)$	$\nu_4(NO_3)$	Free NO_3	ν_{Ln-N}	ν_{Ln-O}
L^1	—	1659	1625	1170	—	—	—	—	—	—	—
$[La L^1 \cdot OH \cdot 4H_2O] \cdot NO_3 \cdot 2H_2O$	1:1	1650	1625	1185	—	—	—	—	1387	—	584
$[Nd L^1 \cdot OH \cdot 4H_2O] \cdot NO_3 \cdot 4H_2O$	1:1	1650	1625	1185	—	—	—	—	1385	—	588
$[Er L^1 \cdot OH \cdot 4H_2O] \cdot NO_3 \cdot H_2O$	1:1	1650	1625	1186	—	—	—	—	1385	—	588
L^2	—	1655	1617	1170	—	—	—	—	—	—	—
$[La L^2 \cdot NO_3 \cdot OH \cdot C_2H_5OH \cdot H_2O] \cdot H_2O$	1:1	1654	1626	1178	1453	1033	832	1334	—	451	554
$[Nd L^2 \cdot NO_3 \cdot OH \cdot C_2H_5OH \cdot H_2O]$	1:1	1654	1626	1179	1470	1033	832	1340	—	459	554
$[Er L^2 \cdot NO_3 \cdot OH \cdot C_2H_5OH \cdot H_2O]$	1:1	1654	1626	1179	1474	1033	832	1340	—	471	554
$[La_2 L^2 \cdot 2NO_3 \cdot OH \cdot 2C_2H_5OH \cdot 3H_2O] \cdot NO_3$	2:1	1651	1627	1179	1454	1033	833	1334	1384	451	551
$[Nd_2 L^2 \cdot 2NO_3 \cdot OH \cdot 2C_2H_5OH \cdot 3H_2O] \cdot NO_3 \cdot H_2O$	2:1	1651	1628	1179	1454	1033	833	1334	1384	451	555
$[Er_2 L^2 \cdot 2NO_3 \cdot OH \cdot 2C_2H_5OH \cdot 3H_2O] \cdot NO_3 \cdot 3H_2O$	2:1	1651	1628	1179	1454	1033	833	1334	1384	459	555
L^3	—	1656	1632	1171	—	—	—	—	—	—	—
$[La L^3 \cdot NO_3 \cdot C_2H_5OH] \cdot 2H_2O$	1:1	1653	1557	1183	1474	1043	846	1324	—	423	551
$[Nd L^3 \cdot NO_3 \cdot C_2H_5OH \cdot H_2O] \cdot OH$	1:1	1647	1632	1180	1477	1032	845	1324	—	—	536
$[Er_2 L^3 \cdot 2NO_3 \cdot 4H_2O] \cdot 2OH \cdot H_2O$	2:1	1645	1632	1186	1482	1030	847	1323	—	—	538

bases coordinate with Ln in C–O–Ln bond [34, 35]. The IR spectra of the Schiff bases L^1 , L^2 , and L^3 show strong C=O stretching band at 1658, 1655, and 1656 cm^{-1} , respectively [36], and the IR spectra of the three Schiff bases show the stretching vibration of azomethine group at 1625, 1617, and 1632 cm^{-1} [36], respectively. The shift of the characteristic band of the carbonyl group to lower wave number (Table 2) in the infrared spectra of all L^1 complexes, Nd(III), and Er(III) complexes of L^3 indicates that the involvement of the carbonyl group in position four in the interaction with the metal ion and the OH group in position five of benzopyran-4-one (C_5 –OH) is deprotonated. Mean while, the IR spectra of L^2 and La- L^3 complexes show a shift in the $\nu_{C=N}$ (azomethine group) band towards higher or lower wave number, Table 2, indicating that the chelation occurs in these complexes through the azomethine group [37, 38] and deprotonated hydroxyl group in position seven of the benzopyran-4-one moiety (C_7 –OH). This is confirmed by appearance of new weak bands in the range of 471–423 cm^{-1} in the IR spectra of L^2 , and La- L^3 complexes are tentatively assigned to ν_{Ln-N} [27, 39–41].

The appearance of the new bands in the spectra of the isolated solid complexes in the range 588–563 cm^{-1} with different intensities is characteristic for the stretching vibration of Ln–O [42–44]. These bands are not present in the IR spectra of the ligands.

A nitrate ligand can coordinate to the metal ion in three types, as monodentate, bidentate ligand, or uncoordinated ion [45–51]. The IR spectra of 1:1 (M:L) complexes of Schiff base L^2 give a $|\nu_4 - \nu_1|$ separation in the range 119–134 cm^{-1} suggesting monodentate bonding for the nitrate group [48]. For L^3 complexes, the separation $|\nu_4 - \nu_1|$ is approximately 150–165 cm^{-1} so in these complexes the nitrate group coordinated as bidentate ligand [49–51]. The presence of nitrate as counter ion was indicated from the IR spectra of L^1 and 2:1 (M:L) complexes of L^2 . These complexes show a band at 1384–1387 cm^{-1} [45–47].

3.1.2. ^1H -NMR Spectra of the Ligands and Their Complexes.

The stoichiometry of the complexes is determined by recording the chemical shifts of the hydroxyl protons and the HC=N protons of the produced complexes. The ^1H NMR spectral data are listed in Table 3. The two types of hydroxyl groups are unequivalent in the present ligands and their complexes. The resonance at $\delta = 14.45$ (1H), 16.10 (2H) and 15.20 (1H), 14.84 (1H) ppm in the spectra of free ligands are due to C_5 –OH of L^1 , L^2 , and L^3 , respectively. The downfield shift of these protons may be due to the decrease of electron density by hydrogen bond formation with carbonyl group in position four of benzopyran-4-one [52]. This signal cannot be seen in the spectra of the L^1 -Ln and L^3 -Er₂ complexes suggesting deprotonation of the C_5 –OH when the ligand coordinates to the metal ion. The signals of the azomethine (HC=N) groups show no significant shift in the ^1H -NMR spectra of these complexes.

The upfield shift (13.00–13.10 ppm, 1H) of C_7 –OH signal in the spectra of L^2 (1:1) (M:L) complexes is due to deprotonation of one C_7 hydroxyl groups. On the other

TABLE 3: The most important data of proton NMR spectra of the Schiff and their complexes.

Symbol	C_5 –OH	C_7 –OH	CH=N
L^1	14.45 s, 1H	13.63 s, 1H	10.21 s, 1H
La- L^1	—	13.63 s, 1H	10.21 s, 1H
Nd- L^1	—	13.63 s, 1H	10.22 s, 1H
Er- L^1	—	13.63 s, 1H	10.23 s, 1H
L^2	16.10 s, 2H	14.30 s, 2H	10.24 s, 2H
La- L^2	16.10 s, 2H	13.00 s, 1H	10.12, 10.24 d, 1H
Nd- L^2	16.10 s, 2H	13.05 s, 1H	10.12, 10.24 d, 1H
Er- L^2	16.10 s, 2H	13.10 s, 1H	10.12, 10.24 d, 1H
La ₂ - L^2	16.10 s, 2H	—	10.00 s, 2H
Nd ₂ - L^2	16.10 s, 2H	—	10.00 s, 2H
Er ₂ - L^2	16.10 s, 2H	—	10.00 s, 2H
L^3	15.20, 14.84 s, 1H	14.26, 13.04 s, 1H	10.23 s, 2H
La- L^3	15.20, 14.84 s, 1H	—	10.00 s, 2H
Nd- L^3	14.00 s, 1H	14.26, 13.04 s, 1H	10.21 s, 2H
Er ₂ - L^3	—	14.26, 13.04 s, 1H	10.22 s, 2H

hand, the azomethine resonance is splitted to doublet at 10.12 (1H) and 10.24 (1H) ppm as a result of the involvement of one of HC=N in the chelation. For L^2 binuclear complexes (2:1) (M:L), the signals due to two C_7 –OH are not observed and the upfield shift of HC=N (~ 0.2) confirming the complexation of the metal ion through the deprotonated C_7 hydroxyl groups and the azomethine nitrogen.

The magnetic environment of the hydroxyl protons is not equivalent for L^3 ligand, and this behavior shows a different complex formation with the three metal ions. For the mono nuclear 1:1 La- L^3 complex, the two signals at 14.26 and 13.04 ppm disappeared completely confirming the deprotonation of the two C_7 –OH groups in position seven when the ligand coordinates to the metal ion. The signal of the azomethine protons is shifted to 10.00 ppm, and this shift can be attributed to the effect of the metal ion on the HC=N electron clouds upon its coordination with the nitrogen lone pair. The signals due to C_5 –OH protons disappeared completely in the ^1H -NMR spectra of Er₂- L^3 complex confirming their involvement in the formation of this binuclear complex. On other hand, only one of these signals disappeared in the ^1H -NMR spectra of mononuclear Nd- L^3 complex, and this is due to the deprotonation and participation in the chelation. There are significant changes in the azomethine protons, (Table 3).

3.1.3. Electronic Spectra. The electronic absorption spectra of free Schiff bases L^1 , L^2 , and L^3 exhibit bands at 349, 392, and 400 nm, respectively, due to an intramolecular charge transfer (CT transition) involving the whole molecule [53]. The

spectra of L^2 and L^3 show also shoulders at 325 and 346 nm, respectively, assigned to the π - π^* transition within the azomethine ($\text{CH}=\text{N}$) group [54]. The complexes of L^1 , L^3 , and (1:1) complexes of L^2 show band in the range of 320–380 nm. On the other hand, the electronic spectra of (2:1) (M:L) La_2 - L^2 and Er_2 - L^2 complexes show a band at 360 nm and shoulder at 420 nm but that of Nd_2 - L^2 complex shows band at 420 nm and shoulder at 362 nm. The disappearance and the shifting which occurs in the bands of the ligands can be taken as evidence for the complex formation. The absorption bands due to the f - f transitions of neodymium and erbium ions could not be identified. This may be probably attributed to the fact that the f - f transitions are very weak [55].

3.1.4. Thermogravimetric Analysis. In the present study, the heating rate was suitably controlled at $10^\circ\text{C min}^{-1}$, and the weight loss was measured from the ambient temperature up to 1000°C . The residues are rare earth oxides. The weight loss for each chelate was calculated within the temperature range at which the hydrated water molecules were expelled. The experimentally found and calculated weight losses are listed in Table 4. The obtained weight loss calculations were based on thermogravimetric analysis and the calculated weight losses were calculated using the tentative formulae present in Table 1. The initial weight loss occurring in the temperature range 30 – 140°C is interpreted as loss of two (5.78%) and four (10.79%) crystal water molecules for La-L^1 and Nd-L^1 complexes (theoretical loss is 5.80% and 10.87%), respectively, whereas, that at 140 – 250°C is due to the loss of four coordinated water molecules (experimental loss is 11.56% and 10.82%, and theoretical loss is 11.60% and 10.87% for La-L^1 and Nd-L^1 , resp.). The TG curves show decomposition of the other anions and molecules [bound to the metal ion to satisfy its charge and/or its coordination number] followed by decomposition of the organic part of the chelates till a constant weight, in which the metal oxide residue is formed as final product, is obtained. In The TGA curve of Er_2 - L^2 complex (Figure 2), the first weight loss of 4.52% corresponding to the elimination of the three crystal water molecules (calculated 4.33%) occurred in the stage beginning at 50°C and ending at 110°C . The second weight loss that occurs in the temperature range of 110 – 175°C is due to loss of two ethanol molecules which are coordinated to the metal ion to fulfill its coordination center [56]. After that, the complex shows the weight loss of 4.20% (calculated 4.33%) around 175 – 250°C corresponding to three coordinated water molecules. Degradation of ligand was observed in the range of 250 – 550°C . At 550°C , the complex completely converts into Er_2O_3 , and the weight becomes stable. The experimental weight value of Er_2O_3 (30.76%) is in good agreement with the calculated one (30.64%). The TGA curve of Er_2 - L^3 shows the initial weight loss of 1.66% in the temperature range 36 – 61°C interpreted as a loss of moisture and hygroscopic water molecule (calculated 1.65%) during the drying of the complexes, whereas, the observed loss (6.38%) at 61 – 267°C is due to the loss of four coordinated water molecules (calculated 6.59%). On further heating, the TGA curve shows decomposition of the organic part of the complexes till a

FIGURE 2: Thermogravimetric curve of Er_2 - L^2 complex.

constant weight where the Er_2O_3 residue is formed as a final product. The residue weight 34.38% corresponds to Er_2O_3 (calculated 34.99%).

3.2. Emission Spectra of Schiff Bases and Their Complexes. At room temperature, complexes of the three Schiff bases (L^1 , L^2 , and L^3) with Nd(III) and Er(III) metal ions exhibited emission spectra in the UV-Vis region. These photophysical properties are summarized in Table 5. It is important to mention that the lanthanum complexes of all Schiff bases are nonfluorescent. The steady-state UV-Vis emission spectra of the free Schiff bases and their complexes in DMF solutions at a concentration of $5 \times 10^{-7} \text{ mol L}^{-1}$ were carried out. The photoluminescence excitation (PLE) spectrum reflects where the maximum contribution of the photoluminescence (PL) comes from. Under steady-state conditions, excited electrons relax from the highest excited states to the lowest excited states before they recombine radiatively or nonradiatively. It can be seen from Table 5 that the Er(III) and Nd(III) complexes of Schiff bases show strong emission when excited with 335 nm (L^1 and L^3) and 330 nm (L^2). Excited wavelength varied for different complexes due to the different maximum of absorption. An excitation wavelength of 335 nm was utilized as it corresponds to selective irradiation of the Schiff base L^1 and its complexes. The ligand emission dominating at 363 nm is assigned to intraligand transitions.

The emissions of the two complexes are shifted slightly to longer wavelength. Nd-L^1 and Er-L^1 complexes show broad emission bands at 375 and 373 nm, respectively, indicating charge-transfer [57] nature of the transitions. The emission intensities of Nd-L^1 and Er-L^1 complexes are stronger than that of the ligand. Significant difference from those of the ligand establishes the complexation process. At room temperature, complexes of L^2 with Nd(III) and Er(III) metal ions exhibited similar emission spectra in the UV-Vis region. The ligand exhibits emission at 363 nm with intensity of 95 which is assigned to intraligand transitions when excited with 330 nm. The emission spectra of Nd-L^2 and Er-L^2 complexes are slightly shifted to longer wavelength and appear at 412 nm with intensities of 719 and 666, respectively, as

TABLE 4: Thermogravimetric analysis data of some metal complexes.

Complexes	M:L	Dehydration stage			Decoordination stage			Metal oxide (Ln ₂ O ₃) residue %	
		Temp. range	% Calc.	Weight loss Found	Temp. range	% Calc.	Weight loss Found	Temp. °C	Calc. Found
[La L ¹ .OH.4H ₂ O].NO ₃ .2H ₂ O	1:1	50–120	5.80	5.78	120–250	11.60	11.56	700	26.22 26.00
[Nd L ¹ .OH.4H ₂ O].NO ₃ .4H ₂ O	1:1	30–140	10.87	10.79	140–250	10.87	10.82	700	25.38 25.40
[Er ₂ L ² .2NO ₃ .OH.2C ₂ H ₅ OH.3H ₂ O].NO ₃ .3H ₂ O	2:1	50–110	4.33	4.52	175–250	4.33	4.20	550	30.64 30.76
[Er ₂ L ³ .2NO ₃ .4H ₂ O].2OH.H ₂ O	2:1	36–61	1.65	1.66	61–267	6.59	6.38	900	34.99 34.38

TABLE 5: Fluorescence data of ligands and their neodymium and erbium complexes in DMF.

Symbol	$\lambda_{\text{exc.}}$ (nm)	λ_{em} (nm)	F. I.*
L ¹	335	363	75
Nd-L ¹	335	375	498
Er-L ¹	335	373	203
L ²	330	363	95
Nd-L ²	340	412	719
Er-L ²	340	412	666
L ³	330	363	88
Nd-L ³	325	421,448	104,105
Er ₂ -L ³	335	372,392	111,122

* F. I. is fluorescence intensity.

compared to the corresponding ligand. The difference in position of emission maximum and fluorescence from those of the ligand establishes the complexation process. It can be also seen that the emission intensities of Nd-L² and Er-L² complexes are stronger than that of the ligand when excited with 340 nm. The two complexes show broad emission bands indicating charge-transfer [57] nature of the transitions. The luminescence of Nd(III) and Er(III) complexes of Schiff base L³ (Figure 4) is related to the efficiency of the intramolecular energy transfer [57] between the triplet levels of the ligand and the emitting level of the ions, which depends on the energy gap between the two levels (Figure 3). In organic solvents, the energy gap between the ligand triplet level and the emitting level of the neodymium ion may be in favor of the energy transfer process than erbium. This makes the Nd(III) complexes show the blue emission, and the maximum emission peak of Nd-L³ complex was shifted to longer wavelength. It can be also seen that the emission intensities of Er(III) and Nd(III) complexes are stronger than that of the ligands.

4. Structural Interpretation

From the previous studies, the structures of the isolated complexes can be summarized as follow.

Schiff base L¹ forms mononuclear complexes, and the ligand behaves as mono-negative (OO) bidentate ligand and the chelation occurs via the oxygen of carbonyl group in position four and the deprotonated phenolic oxygen atom in position five of benzopyrone, Scheme 1, the formula of complexes is suggested to be $[\text{Ln L}^1 \cdot \text{OH} \cdot 4\text{H}_2\text{O}] \cdot \text{NO}_3 \cdot n\text{H}_2\text{O}$, where Ln = La(III), Nd(III), or Er(III) and $n = 2, 4$, or 1.

Moreover, the Schiff base L² forms both mononuclear and binuclear complexes. The chelation occurs through the nitrogen atom of azomethine group and the deprotonated phenolic oxygen in position seven of the benzopyrone moiety, Schemes 2 and 3. The formula of the mononuclear complexes is suggested to be $[\text{Ln L}^2 \cdot \text{NO}_3 \cdot \text{OH} \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}] \cdot n\text{H}_2\text{O}$, Ln = La(III), Nd(III), or Er(III) and $n = 1, 0$ or 0 and that for binuclear complexes

FIGURE 3: A schematic energy level diagram showing the origins of lanthanide luminescence through indirect excitation.

FIGURE 4: Emission spectra of L³ and its neodymium and erbium complexes in DMF (5×10^{-7} mol L⁻¹) SCHEME 1: The center of chelation in L¹ Schiff base.

SCHEME 2: The center of chelation in L^2 Schiff base in mononuclear complexes. SCHEME 3: The center of chelation in L^2 Schiff base in binuclear complexes. SCHEME 4: The center of chelation in L^3 Schiff base in $La-L^3$ complex. SCHEME 5: The center of chelation in L^3 Schiff base in $Nd-L^3$ complex.

is $[Ln_2L^2 \cdot 2NO_3 \cdot OH \cdot 2C_2H_5OH \cdot 3H_2O] \cdot NO_3 \cdot nH_2O$, $Ln = La(III)$, $Nd(III)$, or $Er(III)$ and $n = 0, 1$, or 3 .

In L^3 Schiff base the structure of separated complexes depends on the type of metal ion, lanthanum complex was separated as $(1:1)$ ($M:L$), and the chelation occurs via the

deprotonated OH protons in position seven of the two benzopyran-4-one moieties and the two nitrogen of azomethine group, and the Schiff base acts as dibasic tetradentate ligand, Scheme 4, and the formula of this complex is $[La L^3 \cdot NO_3 \cdot C_2H_5OH] \cdot 2H_2O$.

SCHEME 6: The center of chelation in L^3 Schiff base in Er_2-L^3 complex.

Neodymium forms with L^3 mononuclear complex in which the Schiff base acts as a bidentate ligand (OO), and the chelation occurs via the oxygen of carbonyl group in position four and the deprotonated phenolic oxygen atom in position five of benzopyrone, Scheme 5. The formula of this complex is $[Nd L^3 \cdot NO_3 \cdot C_2H_5OH \cdot H_2O] \cdot OH$.

While erbium forms with L^3 binuclear complex with formula of $[Er_2 L_3 \cdot 2NO_3 \cdot 4H_2O] \cdot 2OH \cdot H_2O$, and the chelation occurs through the two carbonyl groups in position four and two deprotonated OH groups in position five of the two benzopyran-4-one moieties, Scheme 6.

5. Conclusion

In this paper, we report the preparation, elemental analyses, IR, 1H -NMR, UV-vis spectra and thermal analysis to elucidate the structure of the solid complexes of lanthanide nitrates with a new Schiff bases of 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one and aromatic amines, which can form stable solid complexes. The following conclusions can be drawn concerning the ligating properties of the Schiff bases. The data elucidate three different modes of chelation of the Schiff bases. In the metal complexes, the Schiff bases behave as mono-negative (OO) bidentate ligand, and the chelation occurs via the oxygen of carbonyl group in position four, and the deprotonated phenolic oxygen atom in position five of benzopyrone (Schiff base L^1 with three metal ions and L^3 with $Er(III)$ and $Nd(III)$ ions) acts as monobasic (NO) bidentate ligand through the nitrogen atom of one of the two azomethine groups and one of the deprotonated phenolic oxygen atoms in position seven of the benzopyrone moiety (Schiff base L^2) or behaves as dinegative N_2O_2 tetradentate ligands as in $La-L^3$ complex, coordination occurring via the two azomethine nitrogen and the two deprotonated phenolic oxygen atoms in position seven of the benzopyrone moiety. All separated complexes are (1 : 1) (M : L). The binuclear complexes of $Er(III)$ ion with L^3 and the three metal ions with L^2 are only separated under the experimental conditions. The emission spectra of the free ligands and their neodymium and erbium complexes in DMF solutions at a concentration of 5×10^{-7} M were studied. Under the excitation, the neodymium and erbium complexes exhibited characteristic fluorescence. Based on those results, a series of new ligands could be designed and synthesized

to optimize the luminescent properties of these lanthanide ions.

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