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Synthesis, Characterization, and Biological Activities of Lanthanide(III) Complexes of β-Diketone Hydrazone Derivatives

W. H. Hegazy[1,2] **and I. H. Al-Motawaa**[1]
[1]*Chemistry Department, College of Science, King Faisal University, Al-Ahsa, Saudi Arabia*
[2]*College of Science, Suez Canal University, Suez, Egypt*

A series of *β*-diketone hydrazone derivatives has been synthesized through condensation of *β*-diketone with aromatic aldehydes followed by reaction with phenylhydrazine. The structures of the ligands and intermediates are well defined through elemental and spectroscopic analyses. These hydrazones are potential ligands toward lanthanide metal ions. New complexes of trivalent scandium, yttrium, lanthanum, and cerium have been synthesized. The composition of these complexes is discussed on the basis of elemental analyses, infrared (IR) spectroscopy, magnetic moments and thermal analyses. The ligands are supposed to be bidentate with the two-sp2 nitrogen atoms. The prepared (1:1) metal:ligand complexes were screened for antibacterial and antifungal properties and have exhibited potential activity. Scandium(III) complexes are more active toward bacterium, yeast, and fungi.

Keywords biological activities, coordination chemistry, lanthanoids, phenylhydrazones, Schiff bases

INTRODUCTION

Metal complexes of Schiff bases occupy a central role in coordination chemistry for analytical, physical, and biochemical purposes.[1–19] Using many complexation processes with *β*-diketones Schiff bases, and/or hydrazones, lanthanide metal ions have been synthesized and characterized by elemental analysis, differential thermal analysis/thermogravimetry (DTA-TG), x-ray diffraction, infrared (IR) spectroscopy, fluorescence, ultraviolet (UV) spectra, and molar conductance.[20–31] Biochemical activities of some complexes were reported.[32]

Many studies were accomplished for the synthesis, characterization, properties, and biological activity for complexes of Schiff bases.[33–37]

The present investigation deals with the preparation of some new *β*-diketone dihydrazone derivatives (L_1–L_{12}) and their mononuclear Sc(III), Y(III), La(III), and Ce(III) complexes. The prepared ligands were characterized by elemental analysis and by IR, ^{1}H-nuclear magnetic resonance (NMR), and mass spectra. Elemental analysis, IR spectroscopy, magnetic susceptibility measurements, TG, and conductivity measurements characterize the prepared complexes. The antibacterial activities of the prepared complexes were assessed against gram-positive bacteria *Bacillus subtilis* and *Staphylococcus aureus* and gram-negative bacteria *Escherichia coli* and *Salmonella typhi*. Prepared complexes were also screened for their antifungal activities against two fungi (*Aspergillus niger* and *Candida albicans*).

EXPERIMENTAL

Chemicals and Equipment

The required 3-benzylidene-2,4-pentanedione, 3-benzylidene-1-phenyl-1,3-butandione, and 3-benzylidene-1,3-diphenyl-1,3-propanedione were synthesized as described previously.[38] The Schiff bases were prepared by condensation with phenylhydrazine (BDH, England) in dry absolute ethanol (Riedel-de Haën) in the presence of HCl (Riedel-de Haën) as a catalyst.[31] $Sc(NO_3)_3{\cdot}xH_2O$ 99%, $Y(NO_3)_3{\cdot}6H_2O$ 99%, $Ce(NO_3)_3{\cdot}6H_2O$ 99%, and $La(NO_3)_3{\cdot}6H_2O$ 97% were purchased from BDH. 4-Chloro-benzaldehyde 97% (Fluka), 4-fluorobenzaldehyde 98% (BDH), 4-nitrobenzaldehyde 98% (BDH), 4-bromobenzaldehyde 99% (BDH), 1,3-diphenyl-1,3-propandione 98% (BDH), phenyl-1,3-butanedione 99% (BDH), and acetylacetone 99% (WINLAB) were also used. All other solvents used were of the ANALAR grade. Elemental analyses were performed using combustion analysis. Melting points were recorded on a Gallenkamp melting point apparatus. Infrared (IR) spectra were recorded on Perkin Elmer (Spectrum 1000) Fourier-transform infrared (FTIR) spectrometer using KBr pellets. Proton nuclear magnetic resonance (NMR) spectra were recorded using JEOL EX-270 MHz (DMSO-d_6) with trimethylsilane (TMS) as an internal reference. Mass spectra

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Address correspondence to W. H. Hegazy, Chemistry Department, College of Science, King Faisal University, Al-Ahsa, Saudi Arabia. E-mail: whegazy@kfu.edu.sa

were recorded with the aid of a GCMS-QP 1000 EX Shimadzu spectrophotometer at 70 eV using a direct insertion probe at 25–300°C. Thermogravimetric analyses were measured under a nitrogen flow rate of 30 cm^3 min^{-1} using a Shimadzu TGA-60H thermo balance from room temperature up to 1000°C. The magnetic susceptibilities were measured using a Sherwood Scientific Ltd. magnetic susceptibility balance.

Preparation of the Ligands

Condensation of substituted {*p*-F(1), *p*-Cl(2), *p*-Br(3) and *p*-NO_2(4)} 3-benzylidene-2,4-pentanedione (I), 3-benzylidene-1-phenyl-1,3-butandione (II), and 3-benzyllidene-1,3-diphenyl-1,3-propanedione (III) with phenylhydrazine (see equation later) was performed by refluxing 20 mmol solution of the carbonyl compounds ($I_1 = 4.124$, $I_2 = 4.453$, $I_3 = 5.342$, $I_4 = 4.662$ g), ($II_1 = 5.363$, $II_2 = 5.690$, $II_3 = 6.581$, $II_4 = 5.903$ g) and ($III_1 = 6.604$, $III_2 = 6.932$, $III_3 = 7.822$, $III_4 = 7.140$ g) with 40 mmol phenylhydrazine (3.93 cm^3) in 30 cm^3 ethanol absolute in the presence of 5 cm^3 concentrated HCl as a catalyst for 18–24 h. The solution was then cooled to room temperature and added in portions with continuous stirring to crushed ice prepared from bidistilled water. The resulting yield was filtered, washed with

TABLE 1
Physical properties and elemental analyses of the ligands

				Elemental analyses found (calc.)		
Ligand	Color	Yield %	Melting point (°C)	% C	% H	% N
$L_1 \cdot 4H_2O$ $C_{24}H_{23}N_4F$ 460.46	Yellow	81	213	62.88 (61.65)	6.95 (6.75)	12.23 (12.36)
$L_2 \cdot 7H_2O$ $C_{24}H_{23}N_4Cl$ 530.8	Yellow	83	238	54.49 (54.40)	7.00 (6.74)	10.60 (11.36)
L_3 $C_{24}H_{23}N_4Br$ 447.36	Yellow	80	188	64.43 (63.69)	5.14 (5.00)	12.51 (11.37)
L_4 $C_{24}H_{23}N_5O$ 397.41	Orange-Red	79	163	69.60 (69.73)	5.30 (5.57)	16.50 (16.95)
$L_5 \cdot 3H_2O$ $C_{29}H_{23}N_4F$ 502	Dark Green	88	225	69.31 (68.87)	6.17 (6.17)	11.15 (10.67)
$L_6 \cdot 3H_2O$ $C_{29}H_{25}N_4Cl$ 518.88	Light Pink	74	216	67.18 (66.64)	5.97 (5.22)	10.81 (10.41)
L_7 $C_{29}H_{25}N_4Br$ 509.43	Light Pink	74	20	68.42 (69.13)	4.95 (5.26)	10.99 (10.17)
$L_8.3H_2O$ $C_{29}H_{25}N_5O_2$ 530	Orange	67	231	65.78 (65.05)	5.86 (5.25)	13.23 (13.31)
L_9 $C_{34}H_{27}N_4F$ 510.59	Pale Beige	70	138	80.00 (80.90)	5.32 (5.32)	10.97 (10.95)
L_{10} $C_{34}H_{27}N_4Cl$ 527.04	Beige	88	143	77.48 (76.61)	5.15 (4.82)	10.63 (9.99)
L_{11} $C_{34}H_{27}N_4Br$ 571.47	Beige	65	173	71.46 (71.46)	4.75 (5.31)	9.80 (9.72)
L_{12} $C_{34}H_{27}N_5O_2$ 537.58	Orange	70	190	75.00 (74.25)	5.03 (5.22)	13.03 (12.65)

TABLE 2
Selected infrared data (cm^{-1})

	υ (N-H)	υ (C = N)	υ (C-N) δ (N-H)	υ (N = N)	δ (N-H)	υ (N-N)
L_1	3431.36	1600.92	1456.26	1373.32	1222.87	1072.42
L_2	3430.62	1598.83	1443.86	1376.13	1249.30	1071.15
L_3	3421.72	1598.99	1487.12	1375.94	1247.94	1072.42
L_4	3433.11	1601.2	1442.31	1375.87	1192.64	1080.48
L_5	3447.22	1598.59	1502.21	1365.53	1226.99	1098.20
L_6	3429.18	1596.65	1497.26	1364.57	1221.00	1070.68
L_7	3449.46	1594.04	1454.83	1359.54	1211.50	1066.40
L_8	3346.50	1597.06	1444.68	1346.31	1240.23	1060.85
L_9	3430.00	1595.46	1446.91	1346.74	1182.83	1109.24
L_{10}	3448.03	1594.03	1445.73	1320.88	1260.61	1089.81
L_{11}	3441.01	1595.13	1446.41	1359.82	1251.80	1072.42
L_{12}	3408.93	1594.14	1451.70	1360.34	1281.66	1067.78

water, and recrystallized from ethanol until constant melting point. Color, melting point, yield, and elemental analyses are given in Table 1.

General Procedure for Preparation of the Complexes

A solution containing 5 mmol of ligand in 40 cm^3 ethanol was refluxed with a solution of 7 mmol of Sc(III), Y(III), La(III), and Ce(III) nitrates for about 12 h after adjusting the pH (6.5–7.8) using ammonia (1:1) or Theil buffer (oxalic acid, boric acid, succinic acid, sodium tetraborate, and sodium sulfate solution).[39] Gradually, changes in color and formation of precipitates were observed. After cooling at room temperature, the complexes were filtered, washed with excess ethanol and water, recrystallized from ethanol, and dried in desiccators. The physical properties of the prepared complexes were very stable under ordinary conditions.

Antimicrobial Studies

Preparation of the Discs

The complex (60 μg) in DMF (0.01 cm^3) was mounted on a paper disc (prepared from blotting paper, 5 mm diameter) with the help of a micropipette. The discs were left at room temperature until dryness and then applied on the microorganism-grown agar plates.

Preparation of Agar Plates

Minimal agar was used for the growth of specific microbial species. The preparation of agar plates for *B. subtilis*, *S. aureus*, *E. coli,* and *S. typhi* (bacteria) utilized nutrient agar (2.30 g; obtained from Panreac Quimica SA, Spain) suspended in freshly distilled water (100 cm^3), and potato dextrose agar medium (3.9 g/100 cm^3; obtained from Merck) was used for *A. niger* and *C. albicans* (fungi). This was allowed to soak for 15 min

TABLE 3
^{1}HNMR spectroscopic data (δ, ppm)

	2CH$_3$ groups of azo form (d, 3H)	2CH$_3$ groups of hydrazo form (d, 3H)	2CH groups of azo form (d, 2H)	NH groups of hydrazo form (D$_2$O exchangeable; s, 1H)	Aromatic + methylenic protons (m)
L_1	1.588	2.50	3.41	Broad	7.12–7.50
L_2	1.61	2.50	3.36	Broad	6.85–7.75
L_3	1.60	2.495	3.39	Broad	6.70–7.60
L_4	2.00	2.44	3.52	Broad	6.71–7.54
L_5	2.24	2.49	3.85	Broad	6.56–7.63
L_6	1.37	2.50	4.00	4.80, 7.77	6.91–7.25
L_7	1.436	2.50	3.34	4.83, 7.98	6.83–7.68
L_8	1.45	2.50	3.34	4.79, 8.21	7.06–7.77
L_9	—	—	3.45	—	6.42–7.97
L_{10}	—	—	3.40	—	6.62–7.95
L_{11}	—	—	3.50	—	6.50–7.12
L_{12}	—	—	3.38	—	7.39–8.23

and then boiled on a water bath until the agar was completely dissolved. The mixture was autoclaved for 15 min at 120°C, then poured into previously washed and sterilized petri dishes, and stored at 30°C for inoculation.

Procedure of Inoculation

Inoculation was done with the help of platinum wire loop, which was heated to red-hot in a flame, cooled, and then used for the application of the microbial strains.

Application of the Discs

Sterilized forceps were used for the application of the paper disc on previously inoculated agar plates. When the discs were applied, they were incubated at 37°C for 24 h for bacteria and yeast, and at 28°C for 48 h for fungi. The zone of inhibition around the disc was then measured in millimeters.[40]

RESULTS AND DISCUSSION

The synthesized ligands L^1–L^{12} were characterized by their physical properties elemental analyses, IR spectra, ^{1}H-NMR, and mass spectra. The data are given in Tables 1–4, respectively.

The elemental analyses of the ligands (Table 1) were found in good agreement with the calculated data (±0.9%).

The infrared spectra of the ligands show broad bands in the region 3449.46–3208.93 cm^{-1} assigned to N–H stretching vibrations, strong intensity bands in the region 1601.2–1594.04 cm^{-1} assigned to C = N stretching vibrations, strong intensity bands in the region 1502.21–1442.31 cm^{-1} assigned to interaction (coupling) between C–N stretching and N–H bending vibrations of the C–H–N group, medium intensity bands in the region 1376.13–1320.88 cm^{-1} assigned to N = N asymmetric stretching vibrations of the azo form of the ligands, which formed as a result of the azo-hydrazo tautomerism.[21] Substitutions at the *ortho* and *para* positions enhance the mesomeric effect, which activate azo–hydrazo tautomerism. Weak intensity bands in the region 1281.66–1182.83 cm^{-1} are assigned to N–H in-plane bending vibrations. Medium intensity bands in the region 1109.24–1060.85 cm^{-1} are assigned to N–N stretching vibrations. It is notable that no bands around 1700 cm^{-1} are observed, which confirms the condensation of C = O groups of the Knövenagel condensates with phenylhydrazine.[31,41] Two medium intensity bands corresponding to C = C stretching vibrations of the aromatic rings are shown around 1600 and 1500 cm^{-1}. Selected infrared data of the new ligands are listed in Table 2.

TABLE 4

m/z Values (relative intensities) of the main fragments of the ligands

	[M]$^+$	[A]$^+$	[B]$^+$	[C]$^+$	[D]$^+$	[E]$^+$	[F]$^+$	[G]$^+$
L_1	386	281	263	173	131	118	92	77
	(11)	(20)	(19.0)	(18.1)	(10.40)	(31)	(12.6)	(100)
L_2	402	297	263	173	131	118	92	77
	(0.28)	(4.12)	(1.01)	(6.07)	(3.74)	(40)	(15.54)	(100)
L_3	447	342	263	173	131	118	92	77
	(0.12)	(1.34)	(0.79)	(8.90)	(2.61)	(29.64)	(23.06)	(100)
L_4	413	308	263	173	131	118	92	77
	(8)	(12.7)	(41.1)	(11.3)	(12.7)	(28)	(53)	(100)
L_5	448	343	325	234	131	118	92	77
	(1.11)	(6.1)	(13.1)	(16.2)	(4.4)	(13.5)	(7.7)	(97)
L_6	464	359	324	233	131	118	92	77
	(26.0)	(22.27)	(0.19)	(4.64)	(0.82)	(2.57)	(3.67)	(100)
L_7	509	404	325	234	131	118	92	77
	18.9	—	13.1	12.5	1.0	13.5	7.7	97.3
L_8	475	370	324	233	131	118	92	77
	(8.6)	(2.4)	(25.9)	(4.4)	(1.3)	(1.0)	—	(62)
L_9	510	405	386	295	193	180	154	77
	(8)	—	—	(40.2)	(11.6)	(4.2)	(1.1)	(72.6)
L_{10}	527	422	387	296	194	181	155	78
	(3.24)	—	(2.8)	—	(12.3)	—	(2.03)	(84)
L_{11}	571	466	386	295	193	180	154	77
	(7.11)	—	—	32.9	8.6	25.7	—	81.4
L_{12}	537	432	386	297	193	180	154	77
	[M+1]$^+$	(8)	—	(90)	(28)	(4)	(29)	(31)
	(10)							

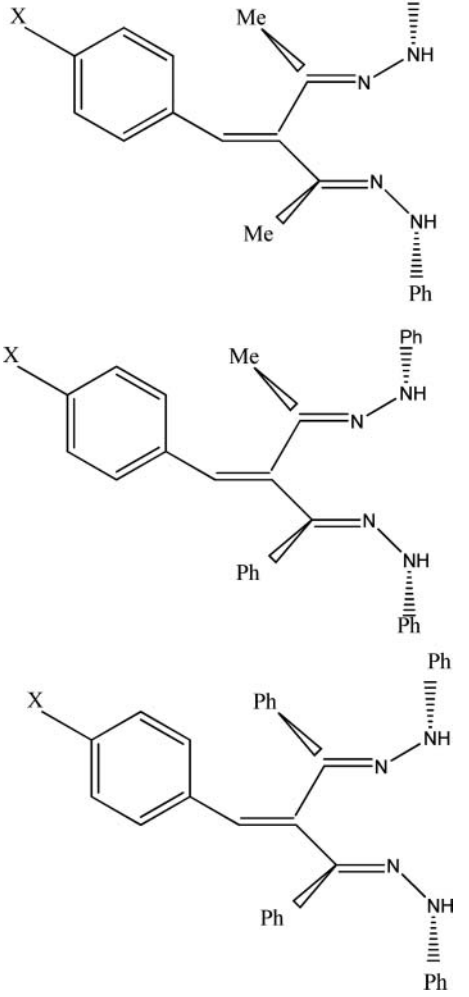


FIG. 1. Representative structural formulas of the ligands; X = F (L_1, L_5, L_9), Cl (L_2, L_6, L_{10}), Br (L_3, L_7, L_{11}) or NO_2 (L_4, L_8, L_{12}).

The ^{1}H-NMR chemical shifts and coupling constants of dimethyl sulfoxide (DMSO)-d_6 are given in Table 3, suggesting the existence of two tautomeric forms except for ligands L_9–L_{12}. Two sets of signals are observed for the methyl group for ligands L_1–L_8. The resonance of the CH groups of the azo form is readily detectable for all ligands, whereas the peaks of the two NH groups of the hydrazo form (L_1–L_8) are broad in the case of (L_1–L_5). These IR and NMR spectroscopic features point to an azo–hydrazo tautomerism for ligands L_1–L_8 as shown later. Steric hindrance and electron donating properties of the two phenyl groups prevent the hydrazo form.

Representative structural formulas of the ligands are given in Figure 1, where X is F, Cl, Br, or NO_2.

The mass spectroscopic fragmentation pathway of the ligands is shown in Scheme 1. The molecular ions in the mass spectra and their relative abundances are given in Table 4.

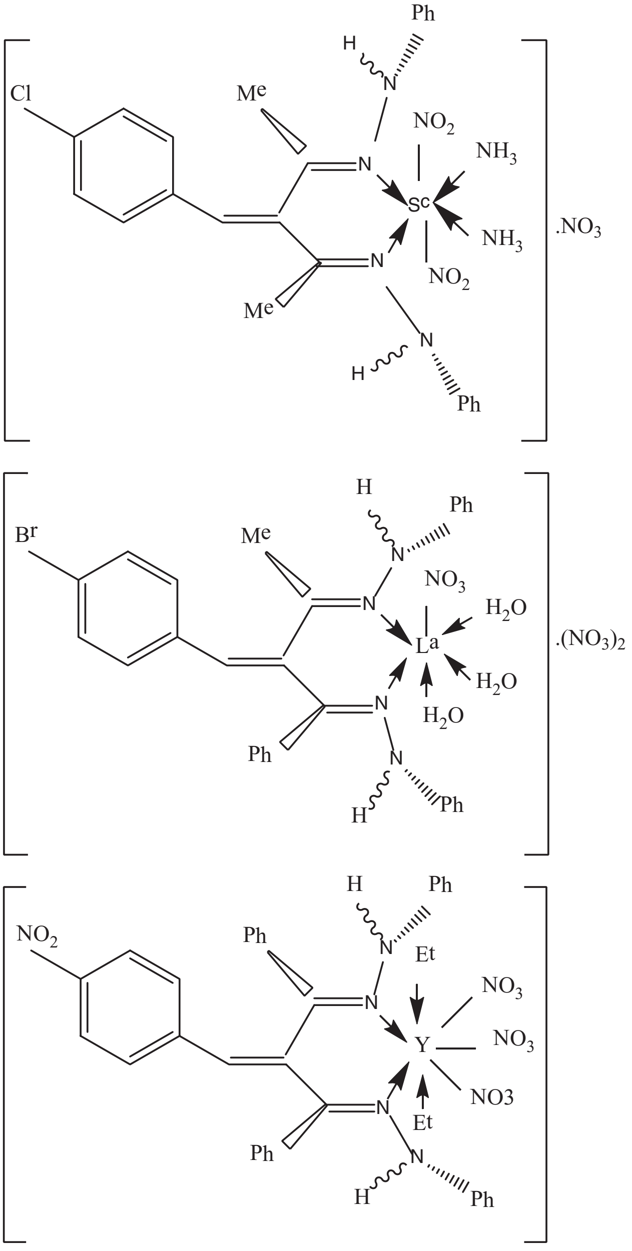


FIG. 2. Structure formulas of some complexes.

Reaction of the ligands $L_{1\text{-}2}$, $L_{4\text{-}5}$, $L_{7\text{-}9}$, and L_{12} with $Sc(NO_3)_3{\cdot}XH_2O$, $Y(NO_3)_3{\cdot}6H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, and $La(NO_3)_3{\cdot}6H_2O$ were performed in ethanol. The complexes show 1:1 metal-to-ligand ratio as indicated by their elemental analyses. Their physical properties, magnetic moments, and elemental analyses are listed in Table 5. The results are in agreement with the postulated formulas (±1%). Complexes of ligands 3, 6, 10, and 11 cannot be separated in the solid state.

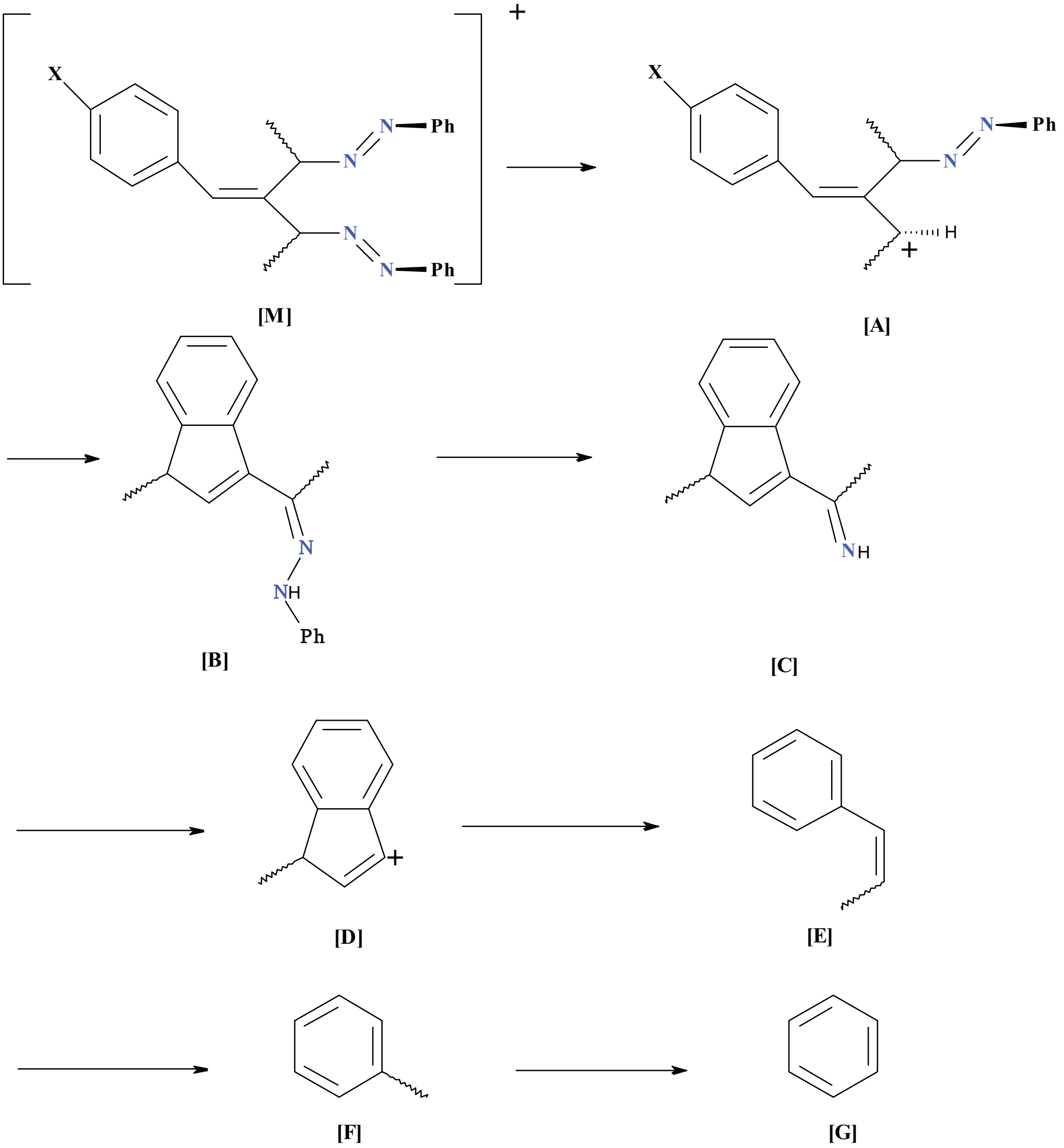
To achieve an idea about the groups involved in complex formation as well as the influence of the electrical field of the central metal ion on the change distribution within the ligand, the spectra of the complexes were carefully compared with those of the ligands.

TABLE 5
Physical properties, magnetic moments, and elemental analyses of complexes

Complex (formula weight)	Color	Melting point (°C)	Yield(%)	μ eff., B.M., found (calc.)	Elemental analyses found (calc.) % C	 % H	 % N
Sc[$C_{24}H_{25}N_7O_{10}F$](635.51)	White	255	60	—	46.27(45.35)	3.70(3.93)	15.14(15.43)
Ce[$C_{24}H_{27}N_7O_{11}F$](747.9)	Yellow	302	64	2.31(2.54)	36.81(35.50)	3.95(3.61)	13.11(13.10)
Sc[$C_{24}H_{29}N_8O_6Cl$]NO_3(667.54)	White	308	72	—	44.06(43.14)	5.13(4.34)	18.26(18.87)
Y[$C_{24}H_{33}N_5O_7$]$(NO_3)_3$.3H_2O(831.86)	Yellow-orange	288	78	—	35.81(34.62)	3.87(4.69)	14.07(13.46)
Ce[$C_{24}H_{33}N_5O_7$]$(NO_3)_3$·4H_2O(901.12)	Gray	294	77	2.26(2.54)	30.81(31.90)	4.35(4.55)	12.45(12.43)
Y[$C_{29}H_{29}N_7O_{11}F$](757.01)	White	313	62	—	45.22(45.97)	3.74(3.83)	13.22(12.95)
Sc[$C_{29}H_{31}N_5O_6Br$]NO_3(731.95)	Yellow	289	54	—	46.92(44.54)	4.74(4.23)	11.35(12.48)
La[$C_{29}H_{31}N_5O_6Br$]$(NO_3)_2$(887.91)	White	301	81	—	37.92(39.19)	3.74(3.49)	10.46(11.04)
Y[$C_{29}H_{28}N_9O_{11}$] ·0.5H_2O(775.95)	Yellow	296	58	—	45.88(44.85)	4.21(3.74)	15.99(16.24)
La[$C_{29}H_{35}N_5O_7$]$(NO_3)_3$(889.98)	Yellow-white	293	87	—	40.15(39.10)	4.21(3.93)	13.42(12.58)
Sc[$C_{34}H_{35}N_4O_4F$]$(NO_3)_3$·5H_2O(902.83)	White	314	60	—	42.15(45.09)	5.31(4.99)	10.70(10.86)
Y[$C_{38}H_{39}N_7O_{11}F$](877)	White	287	65	—	52.15(52.00)	4.85(4.47)	10.90(11.18)
La[$C_{34}H_{33}N_6O_9F$](NO_3) ·4H_2O(960.85)	Black	299	76	—	43.55(42.42)	4.99(4.27)	11.11(10.20)
Ce[$C_{34}H_{37}N_4O_5F$]$(NO_3)_3$·H_2O(944)	Yellow-white	301	66	2.42(2.54)	43.31(43.22)	4.58(3.91)	12.21(10.38)
Sc[$C_{34}H_{35}N_5O_6$]$(NO_3)_3$·H_2O(857.79)	White	305	79	—	48.22(47.57)	3.86(4.38)	(13.05)14.31
Y[$C_{38}H_{39}N_8O_{13}$](903.69)	White	317	79	—	51.60(50.44)	4.27(4.31)	14.04(12.39)
La[$C_{34}H_{37}N_5O_7$]$(NO_3)_3$·3H_2O(1011.91)	White	306	63	—	42.20(43.83)	3.99(3.22)	10.16(11.85)
Ce[$C_{34}H_{33}N_6O_{11}$](NO_3) ·H_2O(935.0)	Brown	288	72	2.37(2.54)	45.27(43.63)	4.38(3.52)	10.44(11.90)

TABLE 6
Selected infrared data of complexes (cm^{-1})

Complexes	υ (O-H)	υ (N-H)	υ (C = N)	δ (N = O)	υ (C-N) + δ (N-H)	υ (N = N)	υ (N = O)	δ (N-H)	υ (N-N)	υ (C-O)
Sc-L_1	3425.79	overlap	1598.55	1528.36	1503.77	1365.29	1302.57	1225.13	1079.61	—
Ce-L_1	3427.25	overlap	1596.33	1479.72	1499.92	1397.93	1318.22	1248.61	1069.54	—
Sc-L_2	3445.75	3208.93	1613.89	1451.67	1493.14	1360.34	1281.55	1281.66	1067.78	—
Y-L_4	3445.63	3300.00	1610.60	—	1503.87	1381.31	—	1227.46	1097.53	—
Ce-L_4	3611.37	overlap	1648.13	—	1457.00	1372.12	—	1228.04	1157.08	—
Y-L_5	3748.80	overlap	1609.78	1540.21	1505.50	1382.05	1300.17	1235.68	1156.53	—
Sc-L_7	3450.00	3331.63	1596.43	1510.20	1490.03	1382.85	1330.62	1235.21	1072.56	—
La-L_7	3423.94	overlap	1606.81	1511.00	1499.18	1379.53	1312.48	1253.20	1089.99	—
Y-L_8	3455.00	3395.66	1597.83	1520.31	1512.53	1345.75	overlap	1224.45	1062.36	—
La-L_8	3538.06	3342.70	1594.46	—	1511.13	1382.86	—	1246.12	1105.74	—
Sc-L_9	3500.00	3448.32	1617.82	—	1492.65	1365.47	—	1242.13	1113.28	—
Y-L_9	3540.67	3116.40	1592.61	1521.44	1444.42	1361.50	1345.23	1210.11	1168.65	1016.39
La-L_9	3523.94	overlap	1609.13	1456.13	1494.21	1383.65	1360.87	1211.45	1020.35	—
Ce-L_9	3413.39	3115.44	1591.95	—	1489.74	1356.68	—	1208.18	1168.65	—
Sc-L_{12}	3435.00	overlap	1594.08	—	1491.44	1360.78	—	1290.54	1067.71	—
Y-L_{12}	3427.25	overlap	1596.33	1480.34	1499.92	1379.93	1290.27	1248.61	1069.54	1008.31
La-L_{12}	3430.19	3430.17	1603.24	—	1496.53	1383.86	—	1347.92	1106.70	—
Ce-L_{12}	3500.73	3412.73	1653.92	1456.88	1492.15	1383.59	overlap	1299.11	1087.64	—



SCH. 1. The general route of fragmentation of ligands (color figure available online).

The IR spectra of all complexes exhibit broad bands around 3748.80–3413.39 cm^{-1}, which are attributed to O–H stretching vibrations of the associated water molecules that may be water of hydration or coordinated molecules. N–H and O–H stretching vibrations of complexes are overlapped for eight complexes. The N–H stretching vibrations of the other 10 complexes show shifts to wave numbers differ from those of the free ligand (~315–45 cm^{-1}). Red chemical shifts are observed (~7–60 cm^{-1}) that are attributed to C = N stretching vibrations. Positive chemical shifts (~10–75 cm^{-1}) are also detected for the C = N stretching vibrations and N–H in-plane bending vibrations. Red shifts for complexes compared with ligands (~6–35 cm^{-1}, ~5—91 cm^{-1}, and ~7–50 cm^{-1}) are seen for N = N stretching vibrations, N–H in-plane bending vibrations, and N–N stretching vibrations, respectively. All these shifts in infrared spectra of the complexes compared with those of the ligands suggest coordination through the two lone pair of electrons of the two-sp^2 nitrogen atoms of the hydrazo form as a bidentate ligand forming two stable six-membered rings. The infrared spectral data of the complexes are listed in Table 6.

TABLE 7
Thermogravimetric results

	Hygroscopic water				Coordinated water			
		Percent weight loss				Percent weight loss		
Complexes	T (°C)	Found	Calc.	Number of water molecules	T (°C)	Found	Calc.	Number of water molecules
$Sc[L_1 (NO_3)_3 (H_2O)]$	—	—	—	—	130-235	2.62	2.78	1
$Ce[L_1 (NO_3)_3 (H_2O)_2]$	—	—	—	—	Up to 220	4.89	4.72	2
$Sc[L_2 (NO_3)_2 (NH_3)_2]NO_3$	—	—	—	—	—	—	—	—
$Y[L_4 (H_2O)_5](NO_3)_3.3H_2O$	92	6.18	6.49	3	130-210	9.20	10.82	5
$Ce[L_4 (H_2O)_5](NO_3)_3.4H_2O$	90	7.31	7.99	8	130-210	10.20	9.25	5
$Y[L_5 (NO_3)_3 (H_2O)_2]$	—	—	—	—	160-210	3.99	4.78	2
$Sc[L_7 (NO_3) (H_2O)_3](NO_3)_2$	—	—	—	—	170-220	6.42	7.38	3
$La[L_7 (NO_3) (H_2O)_3](NO_3)_2$	—	—	—	—	180-240	6.49	6.08	3
$Y[L_8 (NO_3)_3(NH_3)]\cdot 0.5H_2O$	98	1.13	1.16	0.5	—	—	—	—
$La[L_8 (H_2O)_5](NO_3)_3$	—	—	—	—	190-250	11.63	10.11	5
$Sc[L_9 (H_2O)_4](NO_3)_3\cdot 5H_2O$	90	11.12	9.97	7	140-210	6.22	7.67	4
$Y[L_9 (NO_3)_3 (C_2H_5OH)_2]$	—	—	—	—	—	—	—	—
$La[L_9 (NO_3)_2 (H_2O)_3](NO_3)\cdot 4H_2O$	85	7.00	7.49	4	130-160	5.58	5.62	3
$Ce[L_9 (H_2O)_5](NO_3)_3\cdot H_2O$	105	2.47	1.95	1	160-220	8.95	9.73	5
$Sc[L_{12} (H_2O)_4](NO_3)_3\cdot H_2O$	100	2.05	2.10	1	160-260	9.19	8.39	4
$Y[L_{12} (NO_3)_3 (C_2H_5OH)_2]$	—	—	—	—	—	—	—	—
$La[L_{12} (H_2O)_5](NO_3)_3\cdot 3H_2O$	95	4.00	5.37	3	130-160	11.70	10.95	5
$Ce[L_{12} (NO_3)_2 (H_2O)_3](NO_3)\cdot H_2O$	100	2.17	1.95	1	130-220	5.20	5.86	3

Complexes that complete their coordination sphere with nitrato ligands show two stretching bands related to N = O, whereas the complexes that complete their coordination sphere with ethanol ligands show bands at 1008.31 and 1016.39 cm^{-1} related to C–O stretching.

The thermograms of the complexes show a loss of hygroscopic water molecules from 85 to 105°C. The anhydrous complexes show thermal stability up to 130°C. Removal of coordinated water molecules takes place at 130–260°C.

The magnetic moments of complexes given in Table 5 indicate diamagnetic characters for Sc(III), Y(III), and La(III) complexes, whereas Ce(III) complexes have paramagnetic characters ranging from 2.42 to 2.26 J T^{-1}.[42]

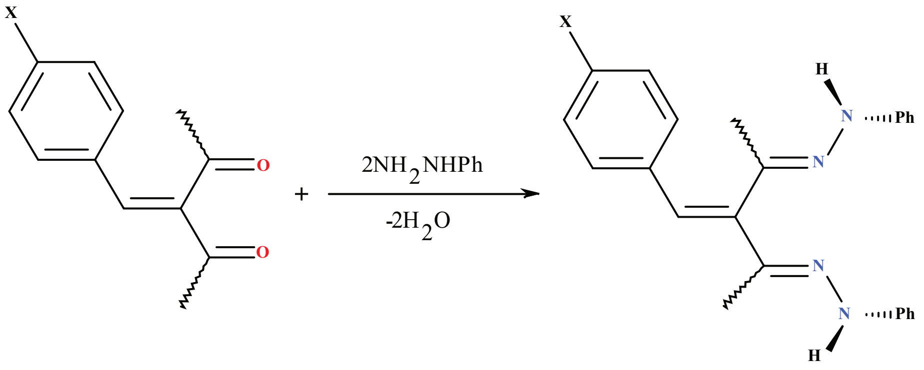


FIG. 3. Preparation of ligands (color figure available online).

TABLE 8
Antimicrobial activity data for the complexes*

Complex	*B. subtilis*	*S. aureus*	*E. coli*	*S. typhi*	*A. niger*	*C. albicans*
Sc-L_1	15	7	10	6	+	++
Ce-L_1	9	—	7	—	+	+
Sc-L_2	10	6	6	11	++	++
Y-L_4	7	7	7	7	+	+
Ce-L_4	6	—	7	6	+	++
Y-L_5	10	7	6	8	—	+
Sc-L_7	11	10	10	12	+	+
La-L_7	6	—	—	6	—	—
Y-L_8	6	8	8	8	+	+
La-L_8	6	7	6	6	+	—
Sc-L_9	12	11	12	12	+	+
Y-L_9	14	9	13	9	+	+
La-L_9	6	—	—	—	+	+
Ce-L_9	7	6	6	6	+	+
Sc-L_{12}	17	10	10	15	++	+++
Y-L_{12}	11	11	10	8	+	++
La-L_{12}	11	7	7	—	—	++
Ce-L_{12}	12	9	10	7	++	+++
Ampicillin	18	16	15	14	—	—
Tetracycline	16	15	17	17	—	—
Salicylic acid	—	—	—	—	++++	++++

*Inhibition zone diameter (% inhibition): +, 6–9 mm (33–50%); ++, 10–12 mm (55–67%); +++, 13–15 mm (72–83%); ++++, 16–18 mm (89–100%). Percentage inhibition values were relative to inhibition zone (18 mm) with 100% inhibition.

The thermogravimetric results given in Table 7 and the elemental analyses suggest that Sc-L_2 and Y-L_8 complexes complete their geometry by ammonia molecules, Y-L_9 completes its geometry by ethanol molecules, and Sc-L_1, Ce-L_1, Sc-L_2, Y-L_5, Sc-L_7, La-L_7, Y-L_8, Y-L_9, La-L_9,, and Ce-L_{12} complexes complete their geometry by ethanol molecules. Y-L_{12} complex completes its geometry by ammonia and ethanol molecules.

Conductivity measurements for mmol concentrations of complex solutions at 25°C show that Sc-L_1, Ce-L_1, Y-L_5, Y-L_8, Y-L_9, and Y-L_{12} are neutral, whereas other complexes appear at ~213.42–197.63 cm^3 ohm^{-1} mol^{-1}, suggesting the presence of free nitrate anions.

Elemental analyses, conductivity measurements, magnetic susceptibility measurements, and thermogravimetry of the complexes reinforce each other, suggesting octahedral geometry with coordination number 6 for the complexes Sc-L_1, Sc-L_2, Sc-L_7, La-L_7, Y-L_8, Sc-L_9, and Sc-L_{12}. For complexes of coordination number 7, Cotton and Willkinson[43] suggest a distorted pentagonal bipyramid structure.

In the light of the preceding discussion, representative structures of the complexes may be as shown in Figure 2.

The metal complexes and standard drugs (ampicillin, tetracycline, and salicylic acid) were tested for their antimicrobial activity at a concentration of 60 μg ml^{-1} in dimethylformamide (DMF) using the paper disc diffusion method.[40,44] The diameter of the susceptibility zones was measured and the results are given in Table 8. The susceptibility zones measured were the clear zones around the discs inhibiting the microbial growth. It is clear that scandium(III) complexes are more active toward bacteria, yeast, and fungi. Because of the relatively large positive charge density on a scandium atom, it is partially shared with the donor nitrogen atoms of the ligands and there is π-electron delocalization over the whole chelate ring.[37,41] This, in turn, increases its permeation through the lipoid layers of the microorganism membranes. Other factors such as solubility, conductivity, and dipole moment may also increase activity.[37,38,40–44]

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