Lanthanide Complexes of Substituted \(\beta\)-Diketone Hydrazone Derivatives: Synthesis, Characterization, and Biological Activities

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A series of \(\beta\)-diketone hydrazone derivatives have been synthesized through condensation of \(\beta\)-diketone with aromatic aldehydes followed by reaction with phenylhydrazine. The structure 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, IR, magnetic moments, and thermal analyses. The prepared complexes were screened for antibacterial and antifungal properties and have exhibited potential activity.

1. Introduction

Metal complexes of Schiff bases occupy a central role in coordination chemistry for analytical, physical, and biochemical purposes [1–19]. Many complexation process of \(\beta\)-diketones Schiff bases and/or hydrazones with lanthanide metal ions have been synthesized and characterized by elemental analysis, DTA-TG, X-ray, IR, fluorescence, UV spectra, and molar conductance [20–31]. Biochemical activities of some complexes were reported [15].

The present investigation deals with the preparation of some new \(\beta\)-diketone dihydrazone derivatives (\(L_1^{–12}\)) and their mononuclear Sc(III), Y(III), La(III), and Ce(III) complexes. The prepared ligands were characterized by elemental analysis, \(^1\)H NMR, and mass spectra. Elemental analysis, IR, magnetic susceptibility measurements, TG, and conductivity measurements characterize the prepared complexes. The antibacterial activities of the prepared complexes were assessed against Gram-positive bacteria \(B. subtilis\) and \(S. aureus\) and Gram-negative bacteria \(E. coli\) and \(S. typhi\). Prepared complexes were also screened for their antifungal activities against two fungi (\(A. niger\) and \(C. albicans\)).

2. Results and Discussion

The synthesized ligands \(L_1^{–12}\) 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. Figure 1 represents tautomerization of the ligands.

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=\(\equiv\)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, and medium-intensity bands in the region 1376.13–1320.88 cm\(^{-1}\) assigned to N=\(\equiv\)N asymmetric stretching vibrations of the azoform 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 inplane bending.
### Table 1: Physical properties and elemental analyses of the ligands.

| Color          | Yield% | MP/°C | %C   | %H   | %N   | Elemental analyses found (calc.) |
|----------------|--------|-------|------|------|------|---------------------------------|
| **L₁·4H₂O**   | Yellow | 81    | 213  | 62.88| 6.95 | 12.23                          |
| C₂₄H₂₃N₄F    |        |       |      | 61.65| 6.75 | 12.36                          |
| **L₂·7H₂O**   | Yellow | 83    | 238  | 54.49| 7.00 | 10.60                          |
| C₂₄H₂₃N₄Cl   |        |       |      | 54.40| 6.74 | 11.36                          |
| **L₃**        | Yellow | 80    | 188  | 64.43| 5.14 | 12.51                          |
| C₂₄H₂₃N₄Br   |        |       |      | 63.69| 5.00 | 11.37                          |
| **L₄**        | Orange-red | 79  | 163  | 69.60| 5.30 | 16.50                          |
| C₂₄H₂₃N₄O    |        |       |      | 69.73| 5.57 | 16.95                          |
| **L₅·3H₂O**   | Dark-green | 88  | 225  | 69.31| 6.17 | 11.15                          |
| C₂₄H₂₃N₄F    |        |       |      | 68.87| 6.17 | 10.67                          |
| **L₆·3H₂O**   | Light-pink | 74  | 216  | 67.18| 5.97 | 10.81                          |
| C₂₉H₂₅N₄Cl   |        |       |      | 66.64| 5.22 | 10.41                          |
| **L₇**        | Light-pink | 74  | 20   | 68.42| 4.95 | 10.99                          |
| C₂₉H₂₅N₄Br   |        |       |      | 69.13| 5.26 | 10.17                          |
| **L₈·3H₂O**   | Orange | 67    | 231  | 65.78| 5.86 | 13.23                          |
| C₂₉H₂₅N₅O₂   |        |       |      | 65.05| 5.25 | 13.31                          |
| **L₉**        | Pale-beige | 70  | 138  | 80.00| 5.32 | 10.97                          |
| C₃₄H₂₇N₄F    |        |       |      | 80.90| 5.32 | 10.95                          |
| **L₁₀**       | Beige  | 88    | 143  | 77.48| 5.15 | 10.63                          |
| C₃₄H₂₇N₄Cl   |        |       |      | 76.61| 4.82 | 9.99                           |
| **L₁₁**       | Beige  | 65    | 173  | 71.46| 4.75 | 9.80                           |
| C₃₄H₂₇N₄Br   |        |       |      | 71.46| 5.31 | 9.72                           |
| **L₁₂**       | Orange | 70    | 190  | 75.00| 5.03 | 13.03                          |
| C₃₄H₂₇N₅O₂   |        |       |      | 74.25| 5.22 | 12.65                          |

### Table 2: Selected infrared data of the ligands (cm⁻¹).

| ν(N–H) | ν(C=N) | ν(C–N) | δ(N–H) | ν(N=N) | δ(N–N) |
|--------|--------|--------|--------|--------|--------|
| L₁     | 3431   | 1600   | 1456   | 1373   | 1222   | 1072   |
| L₂     | 3430   | 1598   | 1443   | 1376   | 1249   | 1071   |
| L₃     | 3421   | 1598   | 1487   | 1375   | 1247   | 1072   |
| L₄     | 3433   | 1601   | 1442   | 1375   | 1192   | 1080   |
| L₅     | 3447   | 1598   | 1502   | 1365   | 1226   | 1098   |
| L₆     | 3429   | 1596   | 1497   | 1364   | 1221   | 1070   |
| L₇     | 3449   | 1594   | 1454   | 1359   | 1211   | 1066   |
| L₈     | 3446   | 1597   | 1444   | 1346   | 1240   | 1060   |
| L₉     | 3430   | 1595   | 1446   | 1346   | 1182   | 1109   |
| L₁₀    | 3448   | 1594   | 1445   | 1320   | 1260   | 1089   |
| L₁₁    | 3441   | 1595   | 1446   | 1359   | 1251   | 1072   |
| L₁₂    | 3408   | 1594   | 1451   | 1360   | 1281   | 1067   |
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 condensation with phenylhydrazine [31, 32]. 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. The \(^1\)H NMR chemical shifts and coupling constants of 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 azoform is readily detectable for all ligands, whereas the peaks of the two NH groups of the hydrazoform (\(L_1–L_5\)) are broad in the case of \(L_1–L_5\). The above IR and NMR spectroscopic features

### Table 3: \(^1\)HNMR spectroscopic data of the ligands (\(\delta/\text{ppm}\)).

| \(L_i\) | 2 CH\(_3\) groups of azoform (d, 3H) | 2 CH\(_3\) groups of hydrazoform (d, 3H) | 2 CH\(_2\) groups of azoform (d, 2H) | NH groups of hydrazoform (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 |

### 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 (11) | 281 (20) | 263 (19.0) | 173 (18.1) | 131 (10.40) | 118 (31) | 92 (77) |
| \(L_2\)  | 402 (0.28) | 297 (4.12) | 263 (1.01) | 173 (6.07) | 131 (3.74) | 118 (40) | 92 (77) |
| \(L_3\)  | 447 (0.12) | 342 (1.34) | 263 (0.79) | 173 (8.90) | 131 (29.64) | 118 (23.06) | 92 (77) |
| \(L_4\)  | 413 (8) | 308 (12.7) | 263 (41.1) | 173 (11.3) | 131 (12.7) | 118 (29.64) | 92 (77) |
| \(L_5\)  | 448 (1.11) | 343 (6.1) | 325 (13.1) | 234 (16.2) | 131 (4.4) | 118 (7.7) | 92 (77) |
| \(L_6\)  | 464 (26.0) | 359 (22.27) | 324 (0.19) | 233 (4.64) | 131 (0.82) | 118 (2.57) | 92 (77) |
| \(L_7\)  | 409 (5.0) | 404 (41.1) | 325 (13.1) | 234 (16.2) | 131 (4.4) | 118 (7.7) | 92 (77) |
| \(L_8\)  | 18.9 | 13.1 | 12.5 | 1.0 | 13.5 | 7.7 | 97.3 |
| \(L_9\)  | 475 (8.6) | 370 (2.4) | 324 (25.9) | 233 (4.4) | 131 (1.3) | 118 (1.0) | 92 (77) |
| \(L_{10}\) | 510 (8) | 405 (40.2) | 386 (11.6) | 295 (4.2) | 193 (1.1) | 180 (72.6) |
| \(L_{11}\) | 537 (3.24) | 422 (2.8) | 387 (12.3) | 296 (2.03) | 194 (84) |
| \(L_{12}\) | 571 (7.11) | 466 (2.8) | 386 (12.3) | 295 (2.03) | 193 (84) |
| \(L_{13}\) | 537 (10) | 432 (8) | 386 (28) | 297 (4) | 193 (29) | 180 (31) |

The \(L_1–L_5\) are broad in the case of \(L_{11–L_{12}}\). Two sets of signals are observed for the methyl group for ligands \(L_1–L_8\). The resonance of the CH groups of the azoform is readily detectable for all ligands, whereas the peaks of the two NH groups of the hydrazoform (\(L_1–L_5\)) are broad in the case of \(L_{11–L_{12}}\). The above IR and NMR spectroscopic features
point to an azo-hydrazo tautomerism for ligands $L_1$–$L_8$ as shown below. Steric hindrance as well as electron-donating properties of the two phenyl groups prevent hydrazoform.

The mass spectrometric 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.

Reaction of the ligands $L_{1,2}$, $L_{4,5}$, $L_{7,9}$, and $L_{12}$ with Sc(NO$_3$)$_3$·$x$H$_2$O, Y(NO$_3$)$_3$·6H$_2$O, Ce(NO$_3$)$_3$·6H$_2$O, and La(NO$_3$)$_3$·6H$_2$O 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 formulae (±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.

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 ten complexes show shifts to wave numbers differing from those of the free ligand (∼315–45 cm$^{-1}$). Red chemical shifts are observed (∼7–60 cm$^{-1}$) which are attributed to C=N stretching vibrations. Positive chemical shifts (∼10–75 cm$^{-1}$) is also detected for the C=N stretching vibrations and N–H inplane 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 inplane 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 pairs of electrons of the two sp$^2$ nitrogen atoms of the hydrazoform as a bidentate ligand forming two stable six-membered rings. The infrared spectral data of the complexes are listed in Table 6.

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 coordinated water molecules are found to be one for complexes Sc–$L_1$, two for complexes Ce–$L_1$, Y–$L_5$, three for complexes Sc–$L_7$, La–$L_7$, La–$L_9$, and Ce–$L_{12}$, four for complexes Sc–$L_9$ and Sc–$L_{12}$, and five for complexes Y–$L_4$, Ce–$L_4$, Y–$L_4$, Ce–$L_9$, and La–$L_{12}$; TG shows no coordinated water molecules in the complexes Sc–$L_2$, Y–$L_8$, Y–$L_9$, and Y–$L_{12}$.

The magnetic moments of complexes given in Table 7 suggest diamagnetic characters for Sc(III), Y(III), and La(III) complexes whereas Ce(III) complexes have paramagnetic characters ranging from 2.42–2.26 J·T$^{-1}$ [33] being consistent with mononuclear complexes and free from antiferromagnetism. The deviation of the values from the theoretical value suggests that the 4f electron participate in the bond formation of the metal to the ligand.

The thermogravimetric results given in Table 7 and the elemental analyses suggest that Sc–$L_2$ and Y–$L_8$ complexes complete their coordination sphere by ammonia molecules, Y–$L_9$ complete its coordination sphere by ethanol molecules and Sc–$L_1$, Ce–$L_1$, Y–$L_4$, Ce–$L_4$, Y–$L_5$, Sc–$L_7$, La–$L_7$, La–$L_8$, Sc–$L_9$, Ce–$L_9$, La–$L_9$, Sc–$L_{12}$, La–$L_{12}$, and Ce–$L_{12}$ complexes complete their coordination sphere by water molecules. Y–$L_{12}$ complex complete its coordination sphere by ammonia and ethanol molecules.

Conductivity measurements using conductivity meter of platinum electrodes for mmol concentrations of complex solutions in DMF 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 measure ∼213.42–197.63 cm$^{-1}$·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-L1, Sc-L2, Sc-L7, La-L7, Y-L8, Sc-L9, and Sc-L12, whereas they suggest distorted pentagonal bipyramid structure with coordination number 7 for other complexes [34].

In the light of the above discussion, representative structures of the complexes may be as follow:

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 DMF using the paper disc diffusion method [35, 36]. 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 towards bacterium, yeast, and fungi. Because of the relatively large positive charge density on 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 [36, 37]. This in turn, increases its permeation through the lipid layers of the microorganism membranes. Other factors such as solubility, conductivity, and dipole moment may also increasing activity [36, 37]. Representative structures of the complexes are given in Figure 2.

3. Methodology

3.1. Chemicals and Equipments. The required 3-benzylidene-2,4-pentanedione, 3-benzylidene-1-phenyl-1,3-butadiene, and 3-benzylidene-1,3-diphenyl-1,3-propanedione were...
Table 5: Physical properties, magnetic moments, and elemental analyses of complexes.

| Complex (formula weight) | Color       | MP/°C | Yield% | μ eff | BM found (calc.) | Elemental analyses found (calc.) |
|-------------------------|-------------|-------|--------|------|-----------------|---------------------------------|
|                         |             |       |        |      |                 | %C    | %H    | %N     |
| Sc[C_{24}H_{25}N_{7}O_{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_{7}O_{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_{8}O_{6}Cl]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_{9}O_{7}](NO_{3})_{3}·3H_{2}O (831.86) | Yellow-orange | 288   | 78     | —    | 35.81 (34.62)   | 3.87 (4.69)  | 14.07 (13.46) |
| Ce[C_{24}H_{33}N_{7}O_{11}F](NO_{3})_{3}·8H_{2}O (973.12) | Gray | 294   | 77     | 2.26 (2.54) | 30.81 (29.60) | 4.35 (5.04)  | 12.45 (11.51) |
| Y[C_{29}H_{29}N_{7}O_{11}]·0.5H_{2}O (775.01) | Yellow     | 301   | 81     | —    | 37.92 (39.19)   | 3.74 (3.49)  | 11.04 (10.04) |
| La[C_{29}H_{31}N_{5}O_{6}Br](NO_{3})_{2}·3H_{2}O (887.91) | White      | 296   | 58     | —    | 45.88 (44.85)   | 4.21 (3.74)  | 15.99 (11.24) |
| Y[C_{34}H_{31}N_{5}O_{6}Br](NO_{3})_{3}·H_{2}O (938.83) | Yellow-white | 293   | 87     | —    | 40.15 (39.10)   | 4.21 (3.93)  | 13.42 (12.58) |
| Y[C_{38}H_{39}N_{7}O_{11}]·0.5H_{2}O (877) | White      | 287   | 65     | —    | 52.15 (52.00)   | 4.85 (4.47)  | 10.90 (11.18) |
| La[C_{34}H_{35}N_{6}O_{9}F](NO_{3})_{3}·4H_{2}O (960.85) | Black      | 299   | 76     | —    | 43.55 (42.42)   | 4.99 (4.27)  | 11.11 (10.20) |
| Ce[C_{34}H_{37}N_{4}O_{5}F](NO_{3})_{3}·H_{2}O (944) | Yellow-white | 301   | 66     | 2.42 (2.54) | 43.31 (43.22) | 4.58 (3.91)  | 12.21 (10.38) |
| Y[C_{38}H_{39}N_{8}O_{13}] (903.69) | White      | 317   | 79     | —    | 48.22 (47.57)   | 3.86 (4.38)  | 14.31 (13.05) |
| La[C_{34}H_{37}N_{5}O_{11}](NO_{3})_{3}·3H_{2}O (1011.91) | White      | 306   | 63     | —    | 51.60 (50.44)   | 4.27 (4.31)  | 14.04 (12.39) |
| Ce[C_{34}H_{35}N_{6}O_{11}](NO_{3})_{3}·H_{2}O (935.0) | Brown      | 288   | 72     | 2.37 (2.54) | 45.27 (43.63) | 4.38 (3.52)  | 10.44 (11.90) |

Synthesized as described previously [32]. The Schiff bases were prepared by condensation with phenylhydrazine (BDH, England) in dry absolute ethanol (Riedel-de Haen) in presence of HCl (Riedel-de Haen) as a catalyst [31]. Sc(NO_3)_3·xH_2O 99%, Y(NO_3)_3·6H_2O 99%, Ce(NO_3)_3·6H_2O 99%, and La(NO_3)_3·6H_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-propandion 98% (BDH), phenyl-1,3-butanedion 99% (BDH), and acetylacetone 99% (WINLAB) were also used. All other solvents used were of the ANALAR grade. Elemental analyses were performed at King Saud University, Saudi Arabia. Melting points were recorded on a Gallenkamp melting point apparatus. IR spectra were recorded on Perkin-Elmer (spectrum 1000) FT-IR spectrometer using KBr pellets at the chemistry department, College of Science, King Fahd University for Petroleum and Minerals Saudi Arabia. Proton NMR spectra were recorded using JEOL EX-270 MHz (DMSO-d_6) with TMS as an internal reference. Mass spectra were recorded with the aid of GCMS-QP 1000 EX Shimadzu spectrophotometer at 70 eV using a direct insertion probe at 25–300°C at the Microanalytical Centre, Cairo University, Egypt. Thermogravimetric analyses were measured under nitrogen flow rate: 30 cm^3 min^(-1) using a Shimadzu TGA-60H thermobalance from room temperature up to 1000°C at the chemistry department, college of Science, King Faisal University Saudi Arabia. The magnetic susceptibilities were measured using a Sherwood Scientific Ltd. Magnetic susceptibility balance (England).
Table 6: Selected infrared data of complexes (cm$^{-1}$).

| Complexes | $\nu$(O–H) | $\nu$(N–H) | $\nu$(C=N) | $\nu$(C–N) + $\delta$(N–H) | $\nu$(N=N) | $\delta$(N–H) | $\nu$(N–N) |
|-----------|------------|------------|-------------|-----------------------------|------------|--------------|------------|
| Sc-L$_1$  | 3425       | overlap    | 1598        | 1503                        | 1365       | 1225         | 1079       |
| Ce-L$_1$  | 3427       | overlap    | 1596        | 1499                        | 1397       | 1248         | 1069       |
| Sc-L$_2$  | 3445       | 3208       | 1613        | 1493                        | 1360       | 1281         | 1067       |
| Y-L$_4$   | 3445       | 3300       | 1610        | 1503                        | 1381       | 1227         | 1097       |
| Ce-L$_4$  | 3611       | overlap    | 1648        | 1457                        | 1372       | 1228         | 1157       |
| Y-L$_5$   | 3748       | overlap    | 1609        | 1505                        | 1382       | 1235         | 1156       |
| Sc-L$_7$  | 3500       | 3448       | 1617        | 1492                        | 1365       | 1242         | 1113       |
| La-L$_9$  | 3500       | 3448       | 1617        | 1492                        | 1365       | 1242         | 1113       |
| Ce-L$_9$  | 3538       | 3342       | 1594        | 1511                        | 1382       | 1246         | 1105       |
| Sc-L$_7$  | 3538       | 3342       | 1594        | 1511                        | 1382       | 1246         | 1105       |
| Y-L$_9$   | 3538       | 3342       | 1594        | 1511                        | 1382       | 1246         | 1105       |

**Table 7: Thermogravimetric results of the complexes.**

| Complexes | T/°C | % Weight loss found | No. of water molecule | T/°C | % Weight loss found | No. of water molecule |
|-----------|------|---------------------|-----------------------|------|---------------------|-----------------------|
| Sc[L$_8$(NO$_3$)$_3$(H$_2$O)] | — | — | — | — | — | — |
| Ce[L$_8$(NO$_3$)$_3$(H$_2$O)$_2$] | — | — | — | — | — | — |
| Sc[L$_2$(NO$_3$)$_2$(NH$_2$)$_2$]NO$_3$ | — | — | — | — | — | — |
| Ce[L$_4$(H$_2$O)$_2$](NO$_3$)$_3$(H$_2$O)$_2$ | 90 | 12.80 | 8 | 130–210 | 10.20 | 12.86 | 5 |
| Y[L$_5$(NO$_3$)$_3$(H$_2$O)$_2$] | — | — | — | — | — | — |
| Sc[L$_2$(NO$_3$)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ | — | — | — | — | — | — |
| Ce[L$_4$(H$_2$O)$_2$](NO$_3$)$_3$(H$_2$O)$_2$ | 90 | 12.80 | 8 | 130–210 | 10.20 | 12.86 | 5 |
| Sc[L$_7$(NO$_3$)$_3$(H$_2$O)$_2$](NO$_3$)$_2$ | — | — | — | — | — | — |
| Ce[L$_8$(NO$_3$)$_3$(H$_2$O)$_2$](NO$_3$)$_2$ | — | — | — | — | — | — |
| Sc[L$_9$(NO$_3$)$_3$(H$_2$O)$_2$](NO$_3$)$_2$ | — | — | — | — | — | — |

3.2. 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-pentanediene (I), 3-benzylidene-1-phenyl-1,3-butadiene (II), and 3-benzylidene-1,3-diphenyl-1,3-propanedione (III) with phenylhydrazine (see equation below) 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$^3$ absolute ethanol in presence of 5 cm$^3$ concentrated HCl as a catalyst for 18–24 h. The solution was then cooled to room temperature.
Table 8: Antimicrobial activity data for the complexes*.

| Complex | B. subtilis | S. aureus | E. coli | S. typhi | A. niger | C. albicans |
|---------|------------|-----------|---------|----------|----------|-------------|
| Sc-L1   | 15         | 7         | 10      | 6        | +        | ++          |
| Ce-L1   | 9          | —         | 7       | —        | +        | +           |
| Sc-L2   | 10         | 6         | 6       | 11       | ++       | ++          |
| Y-L4    | 7          | 7         | 7       | 7        | +        | +           |
| Ce-L4   | 6          | —         | 7       | 6        | +        | ++          |
| Y-L5    | 10         | 7         | 6       | 8        | —        | +           |
| Sc-L7   | 11         | 10        | 10      | 12       | +        | +           |
| La-L7   | 6          | —         | —       | 6        | —        | —           |
| Y-L8    | 6          | 8         | 8       | 8        | +        | +           |
| La-L8   | 6          | 7         | 6       | 6        | +        | —           |
| Sc-L9   | 12         | 11        | 12      | 12       | +        | +           |
| Y-L9    | 14         | 9         | 13      | 9        | +        | +           |
| La-L9   | 6          | —         | —       | —        | +        | +           |
| Ce-L9   | 7          | 6         | 6       | 6        | +        | +           |
| Sc-L12  | 17         | 10        | 10      | 15       | +        | +++         |
| Y-L12   | 11         | 11        | 10      | 8        | +        | ++          |
| La-L12  | 11         | 7         | 7       | —        | —        | ++          |
| Ce-L12  | 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.

and added in portions with continuous stirring to crushed ice prepared from bidistilled water. The resulting yield was filtered, washed with water, and recrystallized from ethanol until constant melting point. Color, MP., yield, and elemental analyses are given in Table 1.

3.3. General Procedure for 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 using ammonia (1:1) or Thiel Buffer [38] solution, cooled to room temperature, filtered, washed with ethanol and water, recrystallized from ethanol, and dried on air. The physical properties of the prepared complexes were very stable under ordinary conditions.

3.4. Antimicrobial Studies

3.4.1. 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 micropipette. The discs were left at room temperature till dryness and then applied on the microorganism-grown agar plates.

3.4.2. 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) for A. niger and C. albicans (fungi). This was allowed to soak for 15 min 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.

3.4.3. 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.

3.4.4. 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 [35].
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Figure 2: Representative structures of the complexes.
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