Synthesis and Characterization of Cobalt(II), Cerium(III), and Dioxouranium(VI) Complexes of 2,3-Dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one Mixed Ligand Complexes, Pyrolytic Products, and Biological Activities

Z. H. ABD EL-WAHAB*, M. M. MASHALY, and A. A. FAHEIM

*Department of Chemistry, Faculty of Science, Al-Azhar University for Girls, Nasr-City, Cairo, Egypt
e-mail: zhabdelwahab@hotmail.com

bDepartment of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt

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New series of Co(II), Ce(III), and UO_2(VI) Schiff base complexes were prepared. The reactions of the Schiff base ligand 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one (HL) with the above metals in the presence of LiOH as a deprotonating agent yielded different types of mononuclear complexes. Also, the mixed ligand complexes of 2-aminopyridine, 8-hydroxy-quinoline, and oxalic acid were isolated. All the binary and mixed ligand complexes of Co(II) and Ce(III) have octahedral configuration, while the UO_2(VI) complexes have distorted dodecahedral geometries. HL is coordinated to the central metal atom as monoanionic tridentate ONO and/or monoanionic tetradentate ONON ligand. Binuclear Ce(III) complex was prepared pyrolytically through the thermal transformation of the mononuclear complex. All the complexes and the corresponding thermal products were isolated and their structures were elucidated by elemental analyses, conductance, IR and electronic absorption spectra, magnetic moments, ^1H NMR and TG-DSC measurements. HL and some of its metal complexes show higher antibacterial effects than those of some of the investigated antibiotics.

Antipyrine derivatives are reported to exhibit analgesic and anti-inflammatory effects [1—4], antiviral [5], antibacterial [6] activities and have also been used as hair colour additives [7] and to potentiate the local anesthetic effect of lidocaine [8]. These compounds have been widely used in spectrophotometric determination of metal ions. Many of these reagents give intense colours with transition metal ions, providing sensitive probes [9] and some of them can also coordinate to rare earth ions to form metal complexes with interesting structures [10].

Antipyrine Schiff base derivatives can serve as antiparasitic agents and their complexes with platinum(II) and cobalt(II) ions have been shown to act as antitumour substances [11].

The condensation between 4-aminooantipyrine and salicylaldehyde yields 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one (HL) which reacts alone or mixed with 2-aminopyridine (2-Ampy), 8-hydroxyquinoline (8-OHqu), and oxalic acid (Ox) with the metal ions Co^{2+}, Ce^{3+}, and UO_2^{5+} to give different structures of complexes. The binary complexes were tested for antifungal and antibacterial activities.

Thermal investigation explored the possibility of obtaining new complexes pyrolytically in the solid state, they cannot be synthesized from solutions.

EXPERIMENTAL

All reagents and solvents used were BDH, Analara or Merck products. The organic Schiff base ligand, 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one (HL) was prepared as reported earlier [12, 13].

Microanalyses of carbon, hydrogen, and nitrogen were carried out at the Microanalytical Centre,
Cairo University, Giza, Egypt. Metal contents were determined volumetrically by titration against standard EDTA solution after complete decomposition of their complexes with concentrated nitric acid in a Kjehldal flask, while the chlorine content was determined gravimetrically [14]. IR spectra were recorded on a Perkin—Elmer 437 ER spectrometer using KBr discs; polyethylene was used as a calibrant. Far IR spectra were measured with Nicolet 20F-FTIR spectrometer using polyethylene discs. $^1$H NMR spectra (DMSO-d$_6$) were recorded at room temperature on a Varian FT-290.90 MHz spectrometer, using TMS as an internal standard.

TG—DSC measurements were carried out on a Shimadzu thermogravimetric analyzer using the TA-50 WSI program. Mass spectra were recorded at 70 eV and 300 °C on an MS 5988 Hewlett—Packard mass spectrometer. Melting or decomposition points were measured on a melting point apparatus, Gallenkamp, England. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey (Alpha products), England. Magnetic susceptibilities of the complexes were measured on a Shimadzu thermogravimetric analyzer using the TA-50 WSI program. Mass spectra were recorded at 70 eV and 300 °C on an MS 5988 Hewlett—Packard mass spectrometer. Melting or decomposition points were measured on a melting point apparatus, Gallenkamp, England. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey (Alpha products), England. Magnetic susceptibilities of the complexes were measured on a Shimadzu thermogravimetric analyzer using the TA-50 WSI program. Mass spectra were recorded at 70 eV and 300 °C on an MS 5988 Hewlett—Packard mass spectrometer. Melting or decomposition points were measured on a melting point apparatus, Gallenkamp, England. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey (Alpha products), England.

**RESULTS AND DISCUSSION**

The analytical and physicochemical data of the ligand and its metal complexes, binary or mixed with (2-Ampy), (8-OHqu), and (Ox) are represented in Table 1, and from them the proposed formulae were derived.

The reactions of HL with transition metal ion, Co(III), lanthanide ion, Ce(III) or actinide ion, UO$_2$(VI) in the presence of LiOH as a deprotonating agent, yielded different products of the binary mononuclear complexes (Formula 1, structures I, IV, and VII).

The binary complexes are active towards the mixed ligands, 2-Ampy, 8-OHqu, and Ox to form the mixed ligand complexes. The addition of metal salt to a mixture of Schiff base, secondary ligands, and LiOH (1 : 1 : 1 : 1) yielded different products of mononuclear mixed.
MIXED LIGAND COMPLEXES

Table 1. Analytical and Physical Data of the Compounds Studied

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>( M_r )</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cl</th>
<th>Metal</th>
<th>%</th>
<th>Yield</th>
<th>M.p.</th>
<th>Colour</th>
</tr>
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<tbody>
<tr>
<td>HL</td>
<td>C(<em>{18})H(</em>{27})N(<em>{3})O(</em>{2})</td>
<td>307.35</td>
<td>70.30</td>
<td>5.50</td>
<td>13.90</td>
<td>–</td>
<td>–</td>
<td>85</td>
<td>199</td>
<td>Bright yellow</td>
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</tr>
<tr>
<td>Cobalt complexes</td>
<td></td>
<td></td>
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<tr>
<td>I [CoL(OH)(_2)]Cl</td>
<td>C(<em>{18})H(</em>{28})N(<em>{3})O(</em>{2})CoCl</td>
<td>436.76</td>
<td>49.21</td>
<td>4.40</td>
<td>9.33</td>
<td>8.15</td>
<td>13.15</td>
<td>90</td>
<td>&gt; 300</td>
<td>Deep brown</td>
<td></td>
</tr>
<tr>
<td>II [CoL(2-Ampy)(OH)(_2)]Cl</td>
<td>C(<em>{23})H(</em>{24})N(<em>{5})O(</em>{3})CoCl</td>
<td>512.86</td>
<td>53.90</td>
<td>4.91</td>
<td>13.70</td>
<td>6.71</td>
<td>11.60</td>
<td>83</td>
<td>&gt; 300</td>
<td>Orange</td>
<td></td>
</tr>
<tr>
<td>III [CoL(8-OHqu)(Cl)(<em>{-})(</em>{1/2})]H(_{2})O</td>
<td>C(<em>{27})H(</em>{26})N(<em>{5})O(</em>{3})Cl</td>
<td>554.90</td>
<td>58.51</td>
<td>4.66</td>
<td>9.22</td>
<td>6.11</td>
<td>10.32</td>
<td>81</td>
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<td>Brown</td>
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<tr>
<td>Uranyl complexes</td>
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<tr>
<td>IV [UO(_2)L(8-OH(_2))NO(_3)]</td>
<td>C(<em>{16})H(</em>{29})N(<em>{2})O(</em>{4})U</td>
<td>674.40</td>
<td>32.10</td>
<td>3.11</td>
<td>8.10</td>
<td>–</td>
<td>35.10</td>
<td>85</td>
<td>&gt; 300</td>
<td>Orange</td>
<td></td>
</tr>
<tr>
<td>V [UO(_2)L(2-Ampy)(OH)(_2)NO(<em>3)]·3/2H(</em>{2})O</td>
<td>C(<em>{23})H(</em>{27})N(<em>{6})O(</em>{9})(_{1/2})U</td>
<td>977.53</td>
<td>35.15</td>
<td>3.25</td>
<td>10.67</td>
<td>–</td>
<td>30.30</td>
<td>82</td>
<td>&gt; 300</td>
<td>Orange</td>
<td></td>
</tr>
<tr>
<td>VI [UO(<em>2)L(8-OHqu)NO(<em>3)]·(</em>{1/2})H(</em>{2})O</td>
<td>C(<em>{27})H(</em>{26})N(<em>{5})O(</em>{3})(_{1/2})U</td>
<td>792.54</td>
<td>40.63</td>
<td>2.92</td>
<td>8.61</td>
<td>–</td>
<td>30.20</td>
<td>86</td>
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<tr>
<td>VII [CeL(OH)(_2)]NO(_3)]NO(_3)</td>
<td>C(<em>{18})H(</em>{29})N(<em>{3})O(</em>{10})Ce</td>
<td>606.50</td>
<td>35.41</td>
<td>3.25</td>
<td>11.20</td>
<td>–</td>
<td>22.81</td>
<td>90</td>
<td>&gt; 300</td>
<td>Pale brown</td>
<td></td>
</tr>
<tr>
<td>VIII [CeL(2-Ampy)(OH)(_2)]NO(<em>3)]NO(<em>3)·(</em>{1/2})H(</em>{2})O</td>
<td>C(<em>{23})H(</em>{25})N(<em>{7})O(</em>{9})(_{1/2})Ce</td>
<td>691.61</td>
<td>39.71</td>
<td>3.32</td>
<td>13.91</td>
<td>–</td>
<td>20.51</td>
<td>83</td>
<td>&gt; 300</td>
<td>Brown</td>
<td></td>
</tr>
<tr>
<td>IX [CeL(8-OHqu)NO(<em>3)]·2H(</em>{2})O</td>
<td>C(<em>{27})H(</em>{26})N(<em>{5})O(</em>{2})Ce</td>
<td>688.65</td>
<td>47.00</td>
<td>3.63</td>
<td>10.25</td>
<td>–</td>
<td>20.53</td>
<td>87</td>
<td>&gt; 300</td>
<td>Black</td>
<td></td>
</tr>
<tr>
<td>X [CeL(Ox)(OH)(_2)]</td>
<td>C(<em>{26})H(</em>{18})N(<em>{2})O(</em>{2})Ce</td>
<td>552.50</td>
<td>43.60</td>
<td>3.10</td>
<td>7.42</td>
<td>–</td>
<td>25.20</td>
<td>85</td>
<td>&gt; 300</td>
<td>Brown</td>
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<td>Heated products</td>
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<td></td>
</tr>
<tr>
<td>XI [UO(_2)L(NO(_3))]</td>
<td>C(<em>{18})H(</em>{16})N(<em>{2})O(</em>{7})U</td>
<td>638.37</td>
<td>33.93</td>
<td>2.58</td>
<td>8.43</td>
<td>–</td>
<td>37.10</td>
<td>93</td>
<td>&gt; 300</td>
<td>Pale brown</td>
<td></td>
</tr>
<tr>
<td>XII <a href="NO(_3)">Ce(<em>{2})(μ-L)(</em>{2})</a>(_{4})</td>
<td>C(<em>{36})H(</em>{32})N(<em>{10})O(</em>{16})Ce(_{2})</td>
<td>559.81</td>
<td>37.80</td>
<td>3.00</td>
<td>12.00</td>
<td>–</td>
<td>24.50</td>
<td>92</td>
<td>&gt; 300</td>
<td>Deep brown</td>
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</tr>
</tbody>
</table>

ligand complexes (Formulae 2—4, structures II, III, V, VI, VIII, IX, and X).

The following representative equations illustrate the formation of some of the complexes obtained:

\[ \text{m(M): m(HL): m(LiOH) = 1:1:1} \]

\[ \text{HL + CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{LiOH} \rightarrow [\text{CoL(OH)}_2\text{Cl}] + \text{LiCl} + 5\text{H}_2\text{O} \quad \text{(complex I)} \]

\[ \text{HL + Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O} + \text{LiOH} \rightarrow [\text{CeL(OH)}_2\text{NO}_3]\text{NO}_3 + \text{LiNO}_3 + 5\text{H}_2\text{O} \quad \text{(complex VII)} \]

\[ \text{m(M): m(HL): m(2-Ampy): m(LiOH) = 1:1:1:1} \]

\[ \text{HL + 2-Ampy + CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{LiOH} \rightarrow [\text{CoL(2-Ampy)(OH)}_2\text{Cl}] + \text{LiCl} + 6\text{H}_2\text{O} \quad \text{(complex II)} \]

\[ \text{m(M): m(HL): m(8-OHqu): m(LiOH) = 1:1:1:1} \]

\[ \text{HL + 8-OHqu + CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{LiOH} \rightarrow [\text{CoL(8-OHqu)Cl}] \cdot \frac{1}{2} \text{H}_2\text{O} + \text{LiCl} + 6\frac{1}{2}\text{H}_2\text{O} \quad \text{(complex III)} \]

\[ \text{HL + 8-OHqu + UO}_2\text{(NO}_3)_2 \cdot 5\text{H}_2\text{O} + \text{LiOH} \rightarrow [\text{UO}_2\text{L}(8\text{-OHqu})\text{NO}_3] \cdot \frac{1}{2}\text{H}_2\text{O} + \text{LiNO}_3 + 5\frac{1}{2}\text{H}_2\text{O} \quad \text{(complex VI)} \]

\[ \text{HL + H}_2\text{Ox + Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O} + \text{LiOH} \rightarrow [\text{CeL(Ox)(OH)}_2] + \text{LiNO}_3 + 2\text{HNO}_3 + 6\text{H}_2\text{O} \quad \text{(complex X)} \]

The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation, all data are listed in Table 2. The band at \( \tilde{\nu} = 1658 \text{ cm}^{-1} \) is characteristic of the carbonyl group present in the free Schiff base ligand. This group was shifted to lower wavenumbers (53—62 cm\(^{-1}\)) in all complexes, binary.
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Table 2. Characteristic IR Bands (ν/cm$^{-1}$) of the Compounds Studied

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν (OH)</th>
<th>ν (C=O)</th>
<th>ν (C=N)</th>
<th>ν (N=N)</th>
<th>ν (M=O)</th>
<th>N(M—N)</th>
<th>Additional bands</th>
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<tr>
<td>HL</td>
<td></td>
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<td></td>
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<tr>
<td>I</td>
<td>3287 br</td>
<td>1658 s</td>
<td>1543 s</td>
<td>1034 m</td>
<td>–</td>
<td>–</td>
<td>478 m (coordinated water), 359 m ν(Co—Cl)</td>
</tr>
<tr>
<td>II</td>
<td></td>
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<td>III</td>
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<td>IV</td>
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<td>X</td>
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<td>XI</td>
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<tr>
<td>XII</td>
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</tr>
</tbody>
</table>

and mixed ligand complexes, which indicates the involvement of the carbonyl oxygen in coordination [12, 13, 20]. The band assigned to the azomethine group in the free Schiff base ligand was observed at 1543 cm$^{-1}$ and shifted to lower wavenumbers in all complexes (30—54 cm$^{-1}$). This indicates the participation of the nitrogen atom of the azomethine group in coordination [12, 13, 21]. A broad vibration band at 3287 cm$^{-1}$ in the free ligand is assigned to phenolic OH group. The disappearance of this peak in the spectra of all the complexes indicates the deprotonation of phenol proton prior to coordination. The stretching wavenumbers due to N—N in the free ligand were observed at 1034 cm$^{-1}$. This band was slightly affected in all metal complexes, indicating unsharing of this linkage in coordination to the central metal ion. From
the previous results we can conclude that the Schiff base ligand behaves as monobasic terdentate ligand through the oxygen of phenolic OH group, nitrogen of the azomethine group, and the oxygen of the carbonyl group.

In the mixed ligand complexes, the point of interest here is that the coordination sites of the materials used to act as secondary ligand. All secondary ligands, 2-aminopyridine, 8-hydroxyquinoline, and oxalic acid may function as mono- or bidentate using either one or both of the two functional groups. 2-Aminopyridine has pyridine ring nitrogen and amine, either one or both of the two functional groups.2-Aminopyridine complex has pyridine ring nitrogen and amine group, 8-hydroxyquinoline has hydroxyl group and quinoline ring nitrogen while oxalic acid has two carbonyl groups.

The IR spectra of the mixed 2-aminopyridine complexes II, V, and VIII show three characteristic bands at 3160—3186 cm⁻¹, 1646—1695 cm⁻¹, and 895—972 cm⁻¹, the second and third bands assigned to skeletal vibration of the pyridine ring [22] and pyridine ring breathing mode while the first band is due to coordinated NH₂ group.

The mixed 8-hydroxyquinoline complexes III and VI show two new characteristic bands at 3418—3470 cm⁻¹ and 1574—1579 cm⁻¹ assigned to coordinated hydroxyl and azomethine groups of quinoline ring, respectively. Complex IX shows only a band at 1574 cm⁻¹ due to the azomethine group.

The mixed oxalato complex X showed the stretching vibration of ν(C=O) of oxalato group at ν = 1646 cm⁻¹. This indicates that the carbonyl group is free from coordination [23] to metal ion and the oxalato group acts as dianionic bidentate ligand.

The coordinated —NO₃ group in complexes IV—IX showed two bands at 1 = 1006—1103 cm⁻¹ and 1296—1319 cm⁻¹, which may be assigned to the asymmetric and symmetric stretches v₁ and v₂ of the nitrate group. We can conclude that the NO₃ group is coordinated in a unidentate manner [22]. Complexes VII and VIII showed new bands at 1398 cm⁻¹ and 1388 cm⁻¹, respectively, assigned to the ionic nitrate group [24].

The IR spectra of the uranyl complexes (IV—VI) show strong bands in the region 915—917 cm⁻¹ assigned to the antisymmetric v₃(O—U=O) vibration.

The IR spectra of complexes show new bands at 532—694 cm⁻¹ and 424—493 cm⁻¹ assigned to ν(M—O) and ν(M—N), respectively [25, 26]. The complexes I—III showed a new band at 357—362 cm⁻¹, due to ν(M—CI). The presence of a broad band at 3348—3512 cm⁻¹ in the spectra of all metal complexes is associated with coordinated and/or lattice water molecules supported from thermal analysis [25—28]. TGA and DSC demonstrates the nature of water molecules in the complexes (see later).

The conductances of solutions of the complexes in DMF (10⁻³ mol dm⁻³) are shown in Table 4. Complexes VII and VIII are 1:1 electrolytes [20, 21], while the other complexes are nonelectrolytes. This is consistent with the measured IR data.

The assignments of the main signals in the ¹H NMR spectra of the free ligand (HL) and its diamagnetic uranyl complexes are listed in Table 3. The free ligand showed a signal at δ = 12.98 (1H) due to the phenolic group proton. This signal is absent in the complexes [UO₂L(OH₂)₂NO₃] (IV), [UO₂L(2-Ampy)(OH₂)NO₃]·3H₂O (V) and [UO₂L(8-OHqu)NO₃]·1/2H₂O (VI). This indicates the deprotonation of the phenolic group during the formation of the metal complexes.

The free ligand also showed signals at δ = 6.97 (1H), 7.28—7.59 (9H), and 2.40—2.72 (6H) assigned to azomethine group proton, aromatic protons, and methyl groups protons, respectively. These signals were slightly shifted upfield or downfield in the complexes.

The mixed 2-aminopyridine complex V showed a signal at δ = 10.22 (2H) due to coordinated NH₂ group of 2-Ampy. The mixed 8-hydroxyquinoline complex VI showed a signal at δ = 11.18 (1H) assigned to coordinated OH group of 8-OHqu.

The lattice and coordinated water molecules were observed at δ = 3.16—3.29 and 3.38—3.59, respectively.

The mass spectrum fragmentation patterns of the free Schiff base ligand (HL) were in a good agreement with the suggested structure. The mass spectrum was characterized by intense peak at m/z 307.05 (Iₘ = 83.17 %) corresponding to the molecular ion (calculated value 307.35), which loses C₆H₄OH to give the fragment C₁₂H₁₁O₃⁺, m/z 215 (Iₘ = 31.20 %), followed by the loss of HCN molecule to give the fragment C₁₁H₁₂N₂O⁺, m/z 187 (Iₘ = 20.80 %) and finally the fragment due to benzene molecule is present at m/z 77.00 (Iₘ = 38.20 %).

The UV VIS spectra of the free ligand (HL) and its metal complexes were taken in DMF (10⁻³ mol dm⁻³) solutions. The values of band positions (nm) and molar absorptivities (εmax/(dm³ mol⁻¹ cm⁻¹)) together with the magnetic moments values are listed in Table 4.

The UV VIS spectra of the ligand (HL) showed three bands at 269 nm, 320 nm, and 370 nm assigned to π→π* and n→π* transitions within the molecule. In the spectra of the binary as well as mixed ligand complexes there are three or four bands observed due to the ligand (HL) and other mixed ligands. These bands were slightly shifted to blue or red regions in all complexes, while new bands were observed in the visible region for the Co(II) complexes due to d→d transitions.

The binary and mixed Co(II) complexes have magnetic moment values 4.22—4.60 B.M. which agrees well with the expected value for a high-spin Co(II) ion in an octahedral environment. The ligand spectra show two main bands at 472—483 nm and 539—
Table 3. $^1$H NMR Data for the Compounds Studied

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$(OH)</th>
<th>$\delta$(CH)</th>
<th>$\delta$(CH) aromatic</th>
<th>$\delta$(CH) of CH$_3$</th>
<th>Additional signals</th>
</tr>
</thead>
<tbody>
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<td>HL</td>
<td>12.98(1H)</td>
<td>6.97(H)</td>
<td>7.28—7.59(9H)</td>
<td>2.40—2.72(6H)</td>
<td>–</td>
</tr>
<tr>
<td>IV</td>
<td>–</td>
<td>6.92(H)</td>
<td>7.26—7.61(9H)</td>
<td>2.41—2.75(6H)</td>
<td>$\delta$ 3.38 (4H) coordinated water molecules</td>
</tr>
<tr>
<td>V</td>
<td>–</td>
<td>6.93(H)</td>
<td>7.45—7.86(13H)</td>
<td>2.42—2.52(6H)</td>
<td>$\delta$ 10.22 (2H) coordinated amino group, $\delta$ 3.59 (2H) coordinated water molecule, and $\delta$ 3.29 (3H) lattice water molecule</td>
</tr>
<tr>
<td>VI</td>
<td>–</td>
<td>6.82(H)</td>
<td>7.29—7.84(15H)</td>
<td>2.42—2.61(6H)</td>
<td>$\delta$ 11.18 (H) coordinated OH group of 8-OH$_2$ and $\delta$ 3.16 (H) lattice water molecule</td>
</tr>
</tbody>
</table>

$^a$) Chemical shifts with reference to TMS.

Table 4. Molar Conductivity, Magnetic Moment, and Electronic Spectral Data for the Compounds Studied

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar conductivity*</th>
<th>$\mu_{\text{eff}}$ B.M.</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\varepsilon_{\text{max}}$/ (dm$^{-3}$ cm$^{-1}$ mol$^{-1}$)</th>
<th>$\pi\rightarrow\pi^<em>$, $n\rightarrow\pi^</em>$ and charge transfer transitions</th>
<th>$d\rightarrow d$ transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>–</td>
<td>–</td>
<td>269, 320, 370</td>
<td>2300, 1540, 1500</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>I</td>
<td>12</td>
<td>4.22</td>
<td>280, 330, 370</td>
<td>472, 540</td>
<td>210, 280</td>
<td>–</td>
</tr>
<tr>
<td>II</td>
<td>18</td>
<td>4.51</td>
<td>236, 316, 347</td>
<td>480, 539</td>
<td>138, 127</td>
<td>–</td>
</tr>
<tr>
<td>III</td>
<td>9</td>
<td>4.60</td>
<td>219, 240, 311, 344</td>
<td>483, 539</td>
<td>1530, 1280, 790, 880</td>
<td>142, 132</td>
</tr>
<tr>
<td>IV</td>
<td>14</td>
<td>Diam</td>
<td>230, 300, 318, 333, 410</td>
<td>1604, 695, 701, 669, 623</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>V</td>
<td>6</td>
<td>Diam</td>
<td>234, 326, 362, 401</td>
<td>2956, 1632, 1200, 971</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>VI</td>
<td>9</td>
<td>Diam</td>
<td>213, 234, 319, 333, 412</td>
<td>1974, 2846, 1554, 1615, 1167</td>
<td>–</td>
<td>–</td>
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<tr>
<td>VII</td>
<td>59</td>
<td>2.34</td>
<td>226, 320, 334, 410</td>
<td>2810, 1400, 1370, 970</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>VIII</td>
<td>84</td>
<td>2.53</td>
<td>233, 319, 334, 412</td>
<td>1570, 840, 870, 730</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>IX</td>
<td>18</td>
<td>2.57</td>
<td>228, 251, 318, 443</td>
<td>2340, 3390, 1520, 528</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>X</td>
<td>16</td>
<td>2.54</td>
<td>212, 235, 288, 404</td>
<td>1790, 2130, 1320, 827</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>XI</td>
<td>9</td>
<td>Diam</td>
<td>235, 281, 318, 370, 420</td>
<td>2470, 1900, 1960, 1430, 710</td>
<td>–</td>
<td>–</td>
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<tr>
<td>XII</td>
<td>14</td>
<td>1.87</td>
<td>228, 251, 318, 463</td>
<td>3130, 3710, 1530, 475</td>
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<td>–</td>
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</tbody>
</table>

$^a$) DMF solutions, $1 \times 10^{-3}$ mol dm$^{-3}$ at 27°C; $b$) Measurements were taken at 26°C.

540 nm. These bands are assigned to $^4T_{1g}$(F) $\rightarrow$ $^4A_{2g}$(F) ($v_2$) and $^4T_{1g}$(F) $\rightarrow$ $^4T_{1g}$(P) ($v_3$) transitions, respectively. The $v_1$ transition is expected to appear at larger $\lambda$ (beyond 1000 nm) and hence it could not be observed, while the observed transitions are consistent with an octahedral geometry [29—31]. The proposed structures of the binary and mixed Co(II) complexes are shown in Formulae 1—3.

The magnetic moments values, $\mu_{\text{eff}}$ of the Ce(III) complexes are in the range 2.34—2.57 B.M., being consistent with mononuclear complexes and free from antiferromagnetism. All cerium(III) complexes show a new absorption band at 404—443 nm which may be related to metal-ligand charge transfer excitations [32]. The complexes have a coordination number 6 and may exist in octahedral geometries (Formulae 1—4).

The electronic absorption spectra of the dianag-

---

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The electronic absorption spectra of the dianag-
MIXED LIGAND COMPLEXES

\[ \text{M} = \text{Co}, \text{X} = \text{H}_2\text{O}, \text{Y} = \text{Cl}, \text{Z} = \text{absent}, I \]
\[ \text{M} = \text{Ce}, \text{X} = \text{H}_2\text{O}, \text{Y} = \text{NO}_3, \text{Z} = \text{NO}_3, VII \]

\[ \text{M} = \text{Co}, \text{X} = \text{Cl}, \text{Z} = \text{absent}, II \]
\[ \text{M} = \text{Ce}, \text{X} = \text{NO}_3, \text{Z} = \text{NO}_3, \text{A} = \frac{1}{2}\text{H}_2\text{O}, VIII \]

Formula 1. Suggested structures of the binary mononuclear complexes containing L as monoanionic tridentate ligand.

\[ \text{M} = \text{Co}, \text{X} = \text{H}_2\text{O}, \text{Y} = \text{Cl}, \text{Z} = \text{absent}, I \]
\[ \text{M} = \text{Ce}, \text{X} = \text{H}_2\text{O}, \text{Y} = \text{NO}_3, \text{Z} = \text{NO}_3, A = \frac{1}{2}\text{H}_2\text{O}, VIII \]

Formula 2. Suggested structures of the mixed ligand complexes containing L and 2-Ampy.

thermic uranyl complexes \( IV—VI \) show a new band in the region 401—412 nm. This band arises due to the charge transfer from equatorial donor atoms to the uranyl ion [15]. The complexes have a coordination number 8 and may have distorted dodecahedral geometries (Formules 1—3).

The results of TG—DSC analyses of the binary and mixed ligand complexes are shown in Table 5. The results show good agreement with the theoretical formulae as suggested from the analytical data (Table 1).

Complexes \( III, V, VI, VIII, \) and \( IX \) lost the molecules of lattice water in the temperature range 79—107°C and were accompanied by an endothermic peak (\( \Delta H, 19.20—523.70 \) J/g).

The coordinated water molecules were eliminated from their complexes at relatively higher temperature than those in the case of the lattice water molecules. There are two routes in removal of coordinated water molecules from the complexes. The first route was observed for complexes \( I, II, IV, VII, \) and \( X \) which lose only all the coordinated water molecules in a separate step in the temperature range 143—318°C. All the previous complexes lead to nonisolable complexes except complexes \( IV \) and \( VII \), which give the isolable complexes, \( [\text{UO}_2\text{L(NO}_3\text{)}_2] \) and \( [\text{Ce}_2(\mu-\text{L})_2(\text{NO}_3)_4]_2 \), respectively. The second route was observed for complexes \( V \) and \( VIII \), where the elimination of the coordinated water molecules was accompanied by the loss of \( \text{HNO}_3, \text{C}_2\text{H}_5\text{N}_2 \) or \( \text{C}_2\text{N}_2 \) molecules and this process led to nonisolable complexes.

The removal of an HCl molecule from complexes \( I \) and \( II \) was accompanied by the loss of a part of organic moiety in the temperature range 560—664°C and led to nonisolable complexes.

The removal of an \( \text{HNO}_3 \) molecule from complexes \( VI \) and \( IX \) occurred in one step at 368°C and 274°C, respectively. The elimination of \( \text{HNO}_3 \) molecule from complexes \( IV, V, VII, \) and \( VIII \) was accompanied by the removal of another molecules such as \( \text{C}_2\text{N}_2, \text{C}_6\text{H}_5 \).\( \cdot \text{C}_6\text{H}_5 \) and coordinated water. This step occurred at a temperature range 328—620°C.

The mixed ligand complexes are thermally stable to the temperature > 250°C. The complexes start to decompose at a relatively higher temperature (> 270°C) and the organic ligand loses \( \text{C}_2\text{N}_2, \text{C}_6\text{H}_5 \).
C₆H₅, CO₂, etc.

New solid metal complexes XI and XII were prepared pyrolytically by heating the mother complexes to the temperatures at which the exothermic peak is observed. The complex under investigation was placed in a porcelain crucible and heated slowly in an oven of a maximum temperature 350°C. The heating rate did not exceed 5°C min⁻¹. The heating was continued until it reached the temperature at which the exothermic peak was observed on the DSC curve of the original complex. The complex was kept at this temperature for further ½ h, to ensure the removal of all the liberated species and to avoid the occurrence of a backward reaction to the original complex. The new product was allowed to cool to room temperature and was characterized.

The structures of the obtained new products were elucidated on the basis of elemental analyses, IR and electronic absorption spectra, molar conductance, and magnetic moments (Tables 1, 2, and 4).

The UV VIS spectra of the heated products XI and XII showed the ligand bands as in the original complexes, but slightly shifted to longer or shorter wavelengths.

The pyrolytic products showed the bands due to ν(M—O) and ν(M—N) at 548—654 cm⁻¹ and 431—468 cm⁻¹, respectively.

[UO₂(L(NO₃)] (XI) was prepared by heating complex [UO₂(L(OH)₂)NO₃] (IV) to 252°C till constant mass. The colour of the complex was pale brown, which differed from the colour of the mother complex. The IR spectrum of the heated product is similar to that of the mother complex, except the disappearance of the band corresponding to coordinated water molecules. The conductance in DMF solution showed that the heated product is still nonelectrolyte. The electronic absorption spectrum of the diamagnetic heated product showed a visible band at 420 nm. This band arises due to the charge transfer from equatorial donor atoms to the uranyl ion [15].

From the previous results and the elemental analyses, the heated product XI (Formula 5) has a coordination number 6 and may be in octahedral configuration.

[Ce₂(µ-L)₂(NO₃)]₄ (XII) was prepared by heating the complex [Ce₂(L(OH)₂)₂NO₃]NO₃ (VII) at 318°C to a constant mass. The colour of the complex was deep brown which differed from the colour of the mother complex.

Comparison of the IR spectra of the heated product XII and its mother complex VII showed the disap-
<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature °C</th>
<th>Mass loss found/% (Mass loss calc./%)</th>
<th>DSC Peak/ °C</th>
<th>ΔH J g⁻¹</th>
<th>Composition of the residue</th>
<th>Probable composition of the expelled groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>80—262</td>
<td>8.43 (8.25)</td>
<td>197</td>
<td>7.26</td>
<td>[CoCl]</td>
<td>Two molecules of coordinated water</td>
</tr>
<tr>
<td></td>
<td>262—560</td>
<td>40.42 (40.18)</td>
<td>504</td>
<td>13.96</td>
<td>[Co(1H10N2O2)]</td>
<td>One molecule of HCl, half molecule of C2N2, and half molecule of C6H5,C6H3</td>
</tr>
<tr>
<td>II</td>
<td>50—143</td>
<td>3.70 (3.51)</td>
<td>143</td>
<td>133.50</td>
<td>[CoL(2-Ampy)Cl]</td>
<td>One molecule of coordinated water</td>
</tr>
<tr>
<td></td>
<td>143—652</td>
<td>49.30 (49.06)</td>
<td>503</td>
<td>15.58</td>
<td>[Co(1H10N2O2)]</td>
<td>One molecule of HCl, one molecule of C5H6N2O2, half molecule of C2N2, and half molecule of C6H5,C6H3</td>
</tr>
<tr>
<td>III</td>
<td>30—107</td>
<td>2.0 (1.98)</td>
<td>97</td>
<td>59.69</td>
<td>[CoL(8-OHquin)]</td>
<td>Half molecule of lattice water</td>
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<tr>
<td></td>
<td>107—664</td>
<td>64.54 (64.33)</td>
<td>504</td>
<td>17.83</td>
<td>[Co(1H11N2O2)]</td>
<td>One molecule of HCl, one molecule of C6H4NO, half molecule of C2N2, and half molecule of C6H5,C6H3</td>
</tr>
<tr>
<td>IV</td>
<td>50—252</td>
<td>5.40 (5.34)</td>
<td>–</td>
<td>252</td>
<td>-228.0 [UO2(L(NO3)]</td>
<td>Two molecules of coordinated water</td>
</tr>
<tr>
<td></td>
<td>252—620</td>
<td>30.20 (29.96)</td>
<td>505</td>
<td>21.09</td>
<td>[UO2(C11H10N2O2)]</td>
<td>One molecule of HNO3, half molecule of C2N2, and half molecule of C6H5,C6H3</td>
</tr>
<tr>
<td>V</td>
<td>30—79</td>
<td>2.90 (2.76)</td>
<td>79</td>
<td>523.70</td>
<td>[UO2L(2-Ampy)(OH2)NO3]</td>
<td>One and half molecules of lattice water</td>
</tr>
<tr>
<td></td>
<td>79—353</td>
<td>11.22 (11.05)</td>
<td>309</td>
<td>-138.67</td>
<td>[UO2(C18H15N3O2)(2-Ampy)]</td>
<td>One molecule of coordinated water and one molecule of HNO3</td>
</tr>
<tr>
<td></td>
<td>353—530</td>
<td>31.40 (31.21)</td>
<td>504</td>
<td>12.43</td>
<td>[UO2(C11H10N2O2)]</td>
<td>One molecule of C5H6N2, half molecule of C2N2, and half molecule of C6H5,C6H3</td>
</tr>
<tr>
<td>VI</td>
<td>40—109</td>
<td>1.20 (1.14)</td>
<td>92</td>
<td>33.21</td>
<td>[UO2L(8-OHquin)]</td>
<td>Half molecule of lattice water</td>
</tr>
<tr>
<td></td>
<td>109—368</td>
<td>9.16 (9.08)</td>
<td>342.70</td>
<td>-12.71</td>
<td>[UO2L(8-OHquin)]</td>
<td>One molecule of HNO3</td>
</tr>
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<td></td>
<td>368—509</td>
<td>40.62 (40.27)</td>
<td>505</td>
<td>24.92</td>
<td>[UO2(C11H11N2O2)]</td>
<td>One molecule of C5H6NO, half molecule of C2N2, and half molecule of C6H5,C6H3</td>
</tr>
<tr>
<td>VII</td>
<td>50—318</td>
<td>6.10 (5.94)</td>
<td>–</td>
<td>-534.08</td>
<td>[Ce(µ-L2)(NO3)]</td>
<td>Four molecules of coordinated water out of two complex molecules</td>
</tr>
<tr>
<td></td>
<td>318—526</td>
<td>43.90 (43.69)</td>
<td>504</td>
<td>26.77</td>
<td>[Ce2(C1H10N2O2)2]</td>
<td>Four molecules of HNO3, one molecule of C2N2, and one molecule of C6H5,C6H3 out of two complex molecules</td>
</tr>
<tr>
<td>VIII</td>
<td>30—92</td>
<td>1.46 (1.30)</td>
<td>92</td>
<td>19.20</td>
<td>[CeL(2-Ampy)(OH2)NO3]NO3</td>
<td>Half molecule of lattice water</td>
</tr>
<tr>
<td></td>
<td>92—328</td>
<td>30.70 (30.38)</td>
<td>316</td>
<td>-510.36</td>
<td>[Ce(1H15N2O2)NO3]</td>
<td>One molecule of coordinated water, one molecule of C5H6N2, one molecule of HNO3, and half molecule of C2N2</td>
</tr>
<tr>
<td></td>
<td>328—530</td>
<td>50.80 (50.48)</td>
<td>503</td>
<td>17.05</td>
<td>[Ce(C1H10N2O2)]</td>
<td>One molecule of NO3 and half molecule of C6H5,C6H3</td>
</tr>
<tr>
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<td>30—106</td>
<td>5.30 (5.23)</td>
<td>94</td>
<td>289.45</td>
<td>[CeL(8-OHquin)NO3]</td>
<td>Two molecules of lattice water</td>
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<tr>
<td></td>
<td>106—274</td>
<td>14.39 (14.38)</td>
<td>269</td>
<td>-503.47</td>
<td>[CeL(8-OHquin)]</td>
<td>One molecule of HNO3</td>
</tr>
<tr>
<td></td>
<td>274—763</td>
<td>50.64 (50.27)</td>
<td>505</td>
<td>20.24</td>
<td>[Ce(C11H11N2O2)]</td>
<td>One molecule of C5H6NO, half molecule of C2N2, and half molecule of C6H5,C6H3</td>
</tr>
<tr>
<td>X</td>
<td>50—148</td>
<td>3.45 (3.26)</td>
<td>148</td>
<td>324.70</td>
<td>[CeL(Ox)]</td>
<td>One molecule of coordinated water</td>
</tr>
<tr>
<td></td>
<td>273—416</td>
<td>38.20 (37.83)</td>
<td>403</td>
<td>77.09</td>
<td>[Ce(C11H11N2O2)]</td>
<td>Half molecule of C2N2 and half molecule of C6H5,C6H3</td>
</tr>
</tbody>
</table>
appearance of bands at 3410 $^{-1}$ cm and 1389 $^{-1}$ cm due to coordinated water molecules and ionic $-\text{NO}_3$ group, respectively. The stretching wavenumber due to N–N linkage was shifted to lower wavenumber (29 cm $^{-1}$) in the heated product. This indicates that the nitrogen atom of this linkage is involved in coordination to the cerium ion.

Conductivity measurements of the thermal product in DMF solution revealed the nonelectrolytic nature of the complex, which supports the transformation of $-\text{NO}_3$ group from the outer sphere to the inner sphere of the complex. The magnetic moment of the heated product was 1.87 B.M. The lowering in this value may be due to antiferromagnetism between two cerium ions. The visible spectrum of the heated product showed a band at 463 nm, which may be related to metal-ligand charge transfer excitations [32].

From the above results and the elemental analyses in Table 1 we can conclude that the heated product XII is a binuclear complex, where the two cerium ions are bridged through the nitrogen of N–N linkage and the outer-sphere $-\text{NO}_3$ group transferred into the inner sphere of the complex to compensate the eliminated coordinated water molecule. The proposed structure of XII (Formula 6) has an octahedral configuration.

The free ligand HL and its binary metal complexes were tested against the bacterial species *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, and *Escherichia coli*. Also the antifungal activity against *Aspergillus fumigatus*, *Penicillium italicum*, *Syncephalastrum racemosum*, *Alternaria alternata*, and *Candida albicans* was investigated. Some antibiotics were evaluated for their antibacterial activities and their results compared with the free ligand and its binary metal complexes.

The potency of the investigated ligand and its metal complexes as antimicrobial agents was screened in addition to the evaluation of some known antibiotics using Chloramphenicol as a standard antibacterial agent or reference (R) and Terbinafin as antifungal agent or reference (R). The results are tabulated in Tables 6–8.

The results showed that the binary cobalt(II) complex and HL exhibited the same activities towards all the tested bacteria. The cerium(III) and UO$_2$(VI) complexes are less active towards *Bacillus subtilis* and *Escherichia coli* in comparison to the free ligand, while UO$_2$(VI) complex has no effect against *Pseudomonas aeruginosa*.

The free ligand and the metal complexes showed higher and moderate antifungal activities. The binary cerium(III) complex showed no effect towards *Alternaria alternata* and less activity towards *Syncephalastrum racemosum* while the cerium(III) and UO$_2$(VI) complexes are less active towards *Candida albicans*.

The comparison of the biological activities of the synthesized compounds and some known antibiotics shows the following results:

1. The free ligand and its metal complexes show positive effect towards *Staphylococcus aureus* more than Amikacin, Septrin, Cefoboid, Ampicillin, and Tarivid.

2. The free ligand and cobalt(II) complex show higher antibacterial effect than that of Doxycillin, Augmantin, Unasyn, Septrin, Cefoboid, Nitrofurantion, Tarivid, and Erythromycin towards *Pseudomonas aeruginosa*.

3. The free ligand and some its metal complexes show an equal antimicrobial effect as that of some antibiotics.

From all of the above results we can conclude that the free ligand and its metal complexes show comparable antibacterial effects similar to those of the investigated antibiotics.
Table 6. Antifungal Activity of Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aspergillus fumigatus</th>
<th>Penicillium italicum</th>
<th>Syncphlastrum racemosum</th>
<th>Alternaria alternata</th>
<th>Candida albicans</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>++</td>
</tr>
<tr>
<td>I</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>IV</td>
<td>++</td>
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<td>+</td>
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<td>+</td>
</tr>
<tr>
<td>VII</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Terbinafin</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>++</td>
</tr>
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</table>

Table 7. Antibacterial Activity of Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Staphylococcus aureus</th>
<th>Bacillus subtilis</th>
<th>Pseudomonas aeruginosa</th>
<th>Escherichia coli</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
<td>++</td>
</tr>
<tr>
<td>I</td>
<td>++</td>
<td>+++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>IV</td>
<td>++</td>
<td>+</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>VII</td>
<td>++</td>
<td>+</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>Chloramphenicol</td>
<td>++</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
</tr>
</tbody>
</table>

The test done using the diffusion agar technique. Well diameter = 0.6 cm. Inhibition values 0.1—0.5 cm beyond control = + (less active). Inhibition values 0.6—1.0 cm beyond control = ++ (moderate active). Inhibition values 1.1—1.5 cm beyond control = +++ (highly active). Not active = 0.

Table 8. Antibacterial Activity of Some Known Antibiotics

<table>
<thead>
<tr>
<th>Antibiotic</th>
<th>Staphylococcus aureus</th>
<th>Pseudomonas aeruginosa</th>
<th>Escherichia coli</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amikacin</td>
<td>R</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Doxycillin</td>
<td>+++</td>
<td>R</td>
<td>+++</td>
</tr>
<tr>
<td>Augmantin</td>
<td>+++</td>
<td>R</td>
<td>+++</td>
</tr>
<tr>
<td>Sulperazon</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Unasyn</td>
<td>+++</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Septin</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Cefoboid</td>
<td>R</td>
<td>R</td>
<td>R</td>
</tr>
<tr>
<td>Ampicillin</td>
<td>R</td>
<td>+</td>
<td>R</td>
</tr>
<tr>
<td>Nitrofurantion</td>
<td>+++</td>
<td>R</td>
<td>+++</td>
</tr>
<tr>
<td>Tarivid</td>
<td>R</td>
<td>R</td>
<td>+++</td>
</tr>
<tr>
<td>Erythromycin</td>
<td>+++</td>
<td>R</td>
<td>R</td>
</tr>
</tbody>
</table>

R = resistance to the microorganism.

CONCLUSION

The reaction of the Schiff base ligand (HL) with the transition metal ion, Co(II), lanthanide ion, Ce(III) or actinide ion, UO₂(VI) in the presence of LiOH as a deprotonating agent, yielded different products of binary mononuclear complexes. The mixed 2-Ampy, 8-OHqu or Ox complexes were prepared also in the presence of LiOH.

HL behaves in the prepared binary or mixed ligand complexes as monoanionic tridentate ON ligand. The three bonding sites are the oxygen of the phenolic —OH group, nitrogen of the azomethine group, and the oxygen of the carbonyl group. In the pyrolytic product XII the Schiff base ligand works as monoanionic tetradeinate ONON ligand by the same previous mode of coordination in addition to the nitrogen of N—N linkage.

The mixed ligand 2-Ampy acts as a neutral monodentate ligand via the amino group, while the Ox works as dianionic bidentate ligand.

The mixed ligand 8-OHqu behaves as a neutral bidentate in the complexes of Co(II) and UO₂(VI), but in the case of mixed ligand complexes of Ce(III) it works as monoanionic bidentate ligand.

The binary and mixed ligand complexes of Co(II) and Ce(III) have an octahedral configuration. The binary and mixed ligand complexes of UO₂(VI) have coordination number 8 and exist as distorted dodecahedral geometries, while the heated product XI has an octahedral configuration.

Thermal studies explored the possibility of ob-
taining new complexes, which cannot be prepared from solution. Binuclear Ce(III) complex was prepared through the thermal transformation of mononuclear complex.

The free ligand and some of its metal complexes showed higher antibacterial effects than those of some of the investigated antibiotics.

REFERENCES