

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

^aZ. H. ABD EL-WAHAB*, ^bM. M. MASHALY, and ^aA. A. FAHEIM

^aDepartment 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

Received 7 October 2003

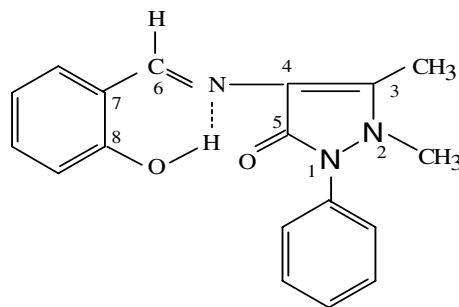
Accepted for publication 25 June 2004

New series of Co(II), Ce(III), and UO₂(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 UO₂(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-aminoantipyrine 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-hydroxy-quinoline (8-OHqu), and oxalic acid (Ox) with the metal ions Co²⁺, Ce³⁺, and UO₂⁶⁺ 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, Analar 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,

*The author to whom the correspondence should be addressed.

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. ^1H 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), model MKI magnetic susceptibility balance. The effective magnetic moments were calculated using the relation $\mu_{\text{eff}} = 2.828 (\chi_m \cdot T)^{1/2}$ B.M. where χ_m is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds. Electronic spectra of both ligand, HL, and its metal complexes were recorded in DMF solutions or as Nujol mulls on a Jasco model V-550 UV VIS spectrophotometer, the conductivities of 10^{-3} M solution of the metal complexes in DMF were measured using WTWD-812 Weilheium conductivity meter, model LBR, fitted with a cell model LTA100.

Binary Schiff Base Metal Complexes

The complexes were prepared by adding the appropriate amount of the metal salt (3 mmol), namely $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{UO}_2(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ dissolved in the least amount of bidistilled water to a mixture of 0.126 g (3 mmol) of $\text{LiOH} \cdot \text{H}_2\text{O}$ and 0.922 g (3 mmol) of HL dissolved in 50 cm^3 of methanol. The reaction mixture was refluxed for 3 h with constant stirring. The precipitated solid complexes were filtered, washed several times with 50 vol. % methanol to remove any traces of the unreacted starting materials. Finally, the complexes were washed with diethyl ether and dried in a vacuum desiccator over anhydrous CaCl_2 . The obtained complex compounds were found to be amorphous coloured compounds stable at room temperature and soluble in DMF and DMSO.

Mixed Ligand Complexes

The complexes were prepared in a similar way to the previous method except the presence of the secondary ligands. The materials used to act as

secondary ligands are 2-aminopyridine (2-Ampy), 8-hydroxyquinoline (8-OHqu), and oxalic acid (Ox), typically a mixture of 0.126 g (3 mmol) of $\text{LiOH} \cdot \text{H}_2\text{O}$, 0.922 g (3 mmol) of HL, and 0.282 g (3 mmol) of 2-Ampy in 50 cm^3 of methanol was added to the metal salt (3 mmol), dissolved in the least amount of bidistilled water. The reaction mixture was refluxed for 5 h with constant stirring to ensure the complete formation of the metal complexes. The precipitated solid complexes were filtered, washed several times with 50 vol. % methanol to remove any traces of the unreacted starting materials. Finally, the complexes were washed with diethyl ether and dried in a vacuum desiccator over anhydrous CaCl_2 . The same procedure was repeated with 8-hydroxyquinoline and oxalic acid. The obtained coloured complex compounds are stable at room temperature and soluble in DMF and DMSO.

Determination of Biological Activity

Diffusion method [15—19] was used to evaluate the antimicrobial activities of the tested compounds as follows: 0.5 cm^3 of spore suspension (10^6 — 10^7)/ cm^3 of each of the investigated organisms was added to a sterile agar medium just before solidification, then poured into sterile Petri dishes (9 cm in diameter) and left to solidify. Using sterile cork borer (6 mm in diameter), three holes (wells) were made in each dish, then 0.1 cm^3 of the tested compounds dissolved in DMF (100 $\mu\text{g cm}^{-3}$) was poured into these holes. Finally the dishes were incubated at 37°C for 48 h for bacteria and at 30°C for 72 h for fungi, where clear or inhibition zones were detected around each hole.

0.1 cm^3 of DMF alone was used as a control under the same conditions for each organism and by subtracting the diameter of inhibition zone resulting with DMF from that obtained in each case, both antibacterial and antifungal activities can be calculated as a mean of three replicates.

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, $\text{UO}_2(\text{VI})$ in the presence of LiOH as a deprotonating agent, yielded different products of the binary mononuclear complexes (Formula 1, structures I, IV, and VII).

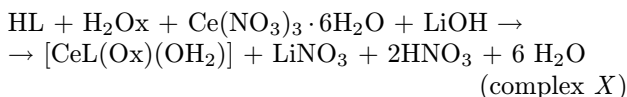
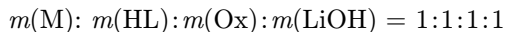
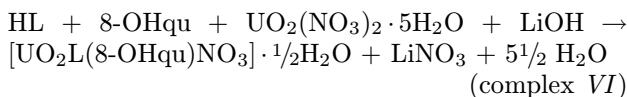
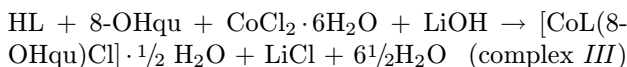
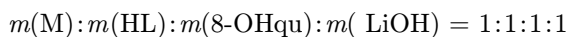
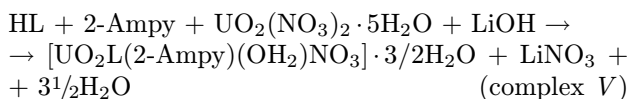
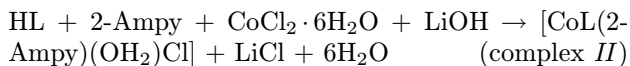
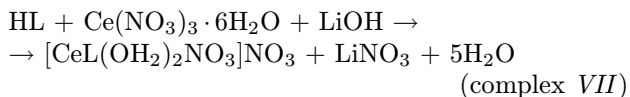
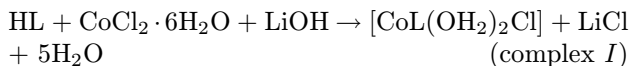
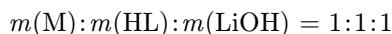
The binary complexes are active towards the mixed ligands, 2-Ampy, 8-OHqu, and Ox to form the mixed ligand complexes. The addition of metal salt to a mixture of Schiff base, secondary ligands, and LiOH (1 : 1 : 1) yielded different products of mononuclear mixed

Table 1. Analytical and Physical Data of the Compounds Studied

Compound	Formula	M_r	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$					Yield %	M.p. °C	Colour
			C	H	N	Cl	Metal			
HL	$C_{18}H_{17}N_3O_2$	307.35	70.30 70.34	5.50 5.57	13.90 13.67	—	—	85	199	Bright yellow
Cobalt complexes										
<i>I</i> [CoL(OH ₂) ₂ Cl]	$C_{18}H_{20}N_3O_4CoCl$	436.76	49.21 49.50	4.40 4.61	9.33 9.62	8.15 8.12	13.15 13.49	90	> 300	Deep brown
<i>II</i> [CoL(2-Ampy)(OH ₂)Cl]	$C_{23}H_{24}N_5O_3CoCl$	512.86	53.90 53.86	4.91 4.72	13.70 13.65	6.71 6.91	11.60 11.49	83	> 300	Orange
<i>III</i> [CoL(8-OHqu)Cl] · 1/2H ₂ O	$C_{27}H_{24}N_4O_{3\frac{1}{2}}CoCl$	554.90	58.51 58.44	4.66 4.36	9.92 10.10	6.11 6.39	10.32 10.62	81	> 300	Brown
Uranyl complexes										
<i>IV</i> [UO ₂ L(OH ₂) ₂ NO ₃]	$C_{18}H_{20}N_4O_9U$	674.40	32.10 32.06	3.11 2.99	8.10 8.31	—	35.10 35.29	85	> 300	Orange
<i>V</i> [UO ₂ L(2-Ampy)(OH ₂)NO ₃] · 3/2H ₂ O	$C_{23}H_{27}N_6O_{9\frac{1}{2}}U$	977.53	35.15 35.53	3.25 3.50	10.67 10.81	—	30.30 30.61	82	> 300	Orange
<i>VI</i> [UO ₂ L(8-OHqu)NO ₃] · 1/2H ₂ O	$C_{27}H_{24}N_5O_{8\frac{1}{2}}U$	792.54	40.63 40.92	2.92 3.05	8.61 8.84	—	30.20 30.03	86	> 300	Brick red
Cerium complexes										
<i>VII</i> [CeL(OH ₂) ₂ NO ₃]NO ₃	$C_{18}H_{20}N_5O_{10}Ce$	606.50	35.41 35.65	3.25 3.32	11.20 11.55	—	22.81 23.10	90	> 300	Pale brown
<i>VIII</i> [CeL(2-Ampy)(OH ₂)NO ₃]NO ₃ · 1/2H ₂ O	$C_{23}H_{25}N_7O_{9\frac{1}{2}}Ce$	691.61	39.71 39.94	3.32 3.64	13.91 14.18	—	20.51 20.26	83	> 300	Brown
<i>IX</i> [CeL(8-OHqu)NO ₃] · 2H ₂ O	$C_{27}H_{26}N_5O_8Ce$	688.65	47.00 47.09	3.63 3.80	10.25 10.17	—	20.53 20.35	87	> 300	Black
<i>X</i> [CeL(Ox)(OH ₂)]	$C_{20}H_{18}N_3O_7Ce$	552.50	43.60 43.48	3.10 3.28	7.42 7.60	—	25.20 25.36	85	> 300	Brown
Heated products										
<i>XI</i> [UO ₂ L(NO ₃)]	$C_{18}H_{16}N_4O_7U$	638.37	33.93 33.87	2.58 2.53	8.43 8.77	—	37.10 37.29	93	> 300	Pale brown
<i>XII</i> [Ce ₂ (μ-L) ₂ (NO ₃) ₄]	$C_{36}H_{32}N_{10}O_{16}Ce_2$	559.81	37.80 37.90	3.00 2.83	12.00 12.28	—	24.50 24.56	92	> 300	Deep brown

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:



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

Table 2. Characteristic IR Bands ($\bar{\nu}/\text{cm}^{-1}$) of the Compounds Studied

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{O})$	$\text{N}(\text{M}-\text{N})$	Additional bands
HL	3287 br	1658 s	1543 s	1034 m	—	—	—
I	—	1602 s	1503 s	1041 m	633 m, 579 m, 548 m	478 m	3441 br (coordinated water), 359 m $\nu(\text{Co}-\text{Cl})$
II	—	1602 s	1513 s	1041 m	633 m, 579 m, 548 m	478 m, 447 w	3440 br (coordinated water), 3186 br (coordinated NH_2 group), 1695 m (skeletal vibration of the pyridine ring), 972 s (pyridine ring breathing mode), 362 m $\nu(\text{Co}-\text{Cl})$
III	—	1605 s	1497 s	1034 m	602 m, 579 m, 547 m	473 w, 442 m	3348 br (lattice water), 3470 s (coordinated OH of 8-OHqu), 1579 s (coordinated $\text{C}=\text{N}$ of 8-OHqu), 357 m $\nu(\text{Co}-\text{Cl})$
IV	—	1605 s	1489 s	1037 m	674 m, 640 m, 602 m, 563 m	477 m	3433 br (coordinated water), 1296 s, 1011s $\nu(\text{NO}_3)$ (coordinated), 915 s (antisymmetric $\nu_3(\text{O}=\text{U}=\text{O})$)
V	—	1605 s	1497 s	1037 m	640 m, 591 m, 560 m	488 m, 472 w	3512 br (coordinated water), 3360 br (lattice water), 3160 br (coordinated NH_2 group), 1680 s (skeletal vibration of the pyridine ring), 895 s (pyridine ring breathing mode), 1319 s, 1011s $\nu(\text{NO}_3)$ (coordinated), 916 s (antisymmetric $\nu_3(\text{O}=\text{U}=\text{O})$)
VI	—	1605 s	1499 s	1034 m	632 m, 602 m, 563 m	486 m, 448 w	3360 br (lattice water), 3418 s (coordinated OH of 8-OHqu), 1547 s (coordinated $\text{C}=\text{N}$ of 8-OHqu), 1319 s, 1011 s $\nu(\text{NO}_3)$ (coordinated), 917 m (antisymmetric $\nu_3(\text{O}=\text{U}=\text{O})$)
VIII	—	1597 s	1492 s	1036 m	633 m, 586 m, 552 m	470 w, 432 m	3480 br (coordinated water), 3340 br (lattice water), 3180 br (coordinated NH_2 group), 1646 s (skeletal vibration of the pyridine ring), 963 s (pyridine ring breathing), 1388 s ionic NO_3 group, 1296 s, 1006 s $\nu(\text{NO}_3)$ (coordinated)
IX	—	1605 s	1497 s	1034 m	633 m, 586 m, 560 w	438 w, 424 w	3348 br (lattice water), 1574 s (coordinated $\text{C}=\text{N}$ of 8-OHqu), 1311 s, 1103 s $\nu(\text{NO}_3)$ (coordinated)
X	—	1605 s	1489 s	1033 m	694 m, 623 m, 594 m, 532 w	493 m	3494 br (coordinated water), 1646 m $\nu(\text{C}=\text{O})$ of oxalic acid
XI	—	1602 s	1492 s	1034 m	643 m, 614 m, 579 w	462 m	1293 s, 1014s $\nu(\text{NO}_3)$ (coordinated) 917 s (antisymmetric $\nu_3(\text{O}=\text{U}=\text{O})$)
XII	—	1596 s	1493 s	1012 m	654 m, 597 m, 548 m	468 m, 431 m	1296 s, 1017 s $\nu(\text{NO}_3)$ (coordinated)

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 ($30\text{--}54 \text{ cm}^{-1}$). 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 $\text{N}-\text{N}$ 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 group, 8-hydroxyquinoline has hydroxyl group and quinoline ring nitrogen while oxalic acid has two carboxyl 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 NH_2 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 $\nu(\text{C}=\text{O})$ of oxalato group at $\tilde{\nu} = 1646 \text{ cm}^{-1}$. 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 $-\text{NO}_3$ group in complexes *IV*–*IX* showed two bands at $\tilde{\nu} = 1006$ – 1103 cm^{-1} and 1296 – 1319 cm^{-1} , which may be assigned to the asymmetric and symmetric stretches ν_1 and ν_2 of the nitrate group. We can conclude that the NO_3 group is coordinated in a unidentate manner [22]. Complexes *VII* and *VIII* showed new bands at 1389 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 $\nu_3(\text{O}=\text{U}=\text{O})$ vibration.

The IR spectra of complexes show new bands at 532 – 694 cm^{-1} and 424 – 493 cm^{-1} assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$, respectively [25, 26]. The complexes *I*–*III* showed a new band at 357 – 362 cm^{-1} , due to $\nu(\text{M}-\text{Cl})$. 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 ($10^{-3} \text{ mol dm}^{-3}$) 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 $\delta = 12.98$ (1H) due to the phenolic group proton. This signal is absent in the complexes $[\text{UO}_2\text{L}(\text{OH}_2)_2\text{NO}_3]$ (*IV*), $[\text{UO}_2\text{L}(2\text{-Ampy})(\text{OH}_2)\text{NO}_3] \cdot 3/2\text{H}_2\text{O}$ (*V*) and $[\text{UO}_2\text{L}(8\text{-OHqu})\text{NO}_3] \cdot 1/2\text{H}_2\text{O}$ (*VI*). This indicates the deprotonation of the phenolic group during the formation of the metal complexes.

The free ligand also showed signals at $\delta = 6.97$ (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 $\delta = 10.22$ (2H) due to coordinated NH_2 group of 2-Ampy. The mixed 8-hydroxyquinoline complex *VI* showed a signal at $\delta = 11.18$ (1H) assigned to coordinated OH group of 8-OHqu.

The lattice and coordinated water molecules were observed at $\delta = 3.16$ – 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 ($I_r = 83.17 \%$) corresponding to the molecular ion (calculated value 307.35), which loses $\text{C}_6\text{H}_4\text{OH}$ to give the fragment $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}^+$, m/z 215 ($I_r = 31.20 \%$), followed by the loss of HCN molecule to give the fragment $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}^+$, m/z 187 ($I_r = 20.80 \%$) and finally the fragment due to benzene molecule is present at m/z 77.00 ($I_r = 38.20 \%$).

The UV VIS spectra of the free ligand (HL) and its metal complexes were taken in DMF ($10^{-3} \text{ mol dm}^{-3}$) solutions. The values of band positions (nm) and molar absorptivities ($\epsilon_{\text{max}}/(\text{dm}^3 \text{ cm}^{-1} \text{ mol}^{-1})$) 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 $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ 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 $d \rightarrow d$ 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. ^1H NMR Data for the Compounds Studied

Compound ^a	$\delta(\text{OH})$	$\delta(\text{CH})$	$\delta(\text{CH})$ aromatic	$\delta(\text{CH})$ of CH_3	Additional signals
HL	12.98 (1H)	6.97 (H)	7.28—7.59 (9H)	2.40—2.72 (6H)	—
IV	—	6.92 (H)	7.26—7.61 (9H)	2.41—2.75 (6H)	δ 3.38 (4H) coordinated water molecules
V	—	6.93 (H)	7.45—7.86 (13H)	2.42—2.52 (6H)	δ 10.22 (2H) coordinated amino group, δ 3.59 (2H) coordinated water molecule, and δ 3.29 (3H) lattice water molecules
VI	—	6.82 (H)	7.29—7.84 (15H)	2.42—2.61 (6H)	δ 11.18 (H) coordinated OH group of 8-OHqu and δ 3.16 (H) lattice water molecule

a) Chemical shifts with reference to TMS.

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

Compound	Molar conductivity ^a $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	μ_{eff}^b B.M.	$\lambda_{\text{max}}^a/\text{nm}$ $\epsilon_{\text{max}}/(\text{dm}^{-3} \text{cm}^{-1} \text{mol}^{-1})$	
			$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and charge transfer transitions	$d \rightarrow d$ transitions
HL	—	—	269, 320, 370 2300, 1540, 1500	—
I	12	4.22	280, 330, 370 1910, 2380, 1420	472, 540 210, 280
II	18	4.51	236, 316, 347 3100, 1830, 2310	480, 539 138, 127
III	9	4.60	219, 240, 311, 344 1530, 1280, 790, 880	483, 539 142, 132
IV	14	Diam	230, 300, 318, 333, 410 1604, 695, 701, 669, 623	—
V	6	Diam	234, 326, 362, 401 2956, 1632, 1200, 971	—
VI	9	Diam	213, 234, 319, 333, 412 1974, 2846, 1554, 1615, 1167	—
VII	59	2.34	226, 320, 334, 410 2810, 1400, 1370, 970	—
VIII	84	2.53	233, 319, 334, 412 1570, 840, 870, 730	—
IX	18	2.57	228, 251, 318, 443 2340, 3390, 1520, 528	—
X	16	2.54	212, 235, 288, 404 1790, 2130, 1320, 827	—
XI	9	Diam	235, 281, 318, 370, 420 2470, 1900, 1960, 1430, 710	—
XII	14	1.87	228, 251, 318, 463 3130, 3710, 1530, 475	—

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

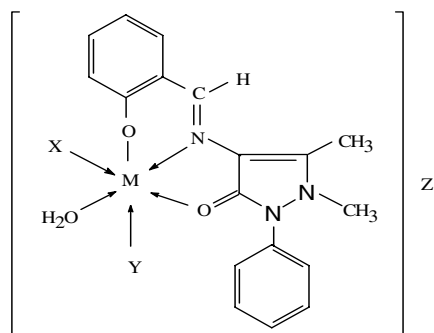
540 nm. These bands are assigned to $^4T_{1g}(\text{F}) \rightarrow ^4A_{2g}(\text{F})$ (ν_2) and $^4T_{1g}(\text{F}) \rightarrow ^4T_{1g}(\text{P})$ (ν_3) transitions, respectively. The ν_1 transition is expected to appear at larger λ (beyond 1000 nm) and hence it could not be observed, while the observed 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, μ_{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.

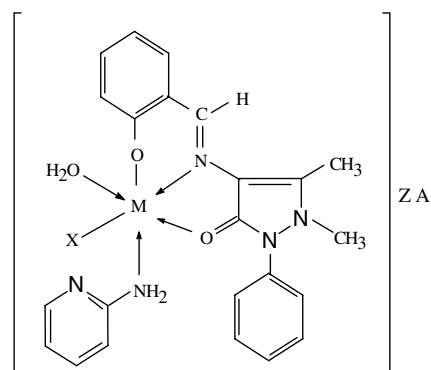
All cerium(III) complexes show a new absorption band at 404—443 nm which may be related to metal-ligand charge transfer excitations [32]. The complexes have a coordination number 6 and may exist in octahedral geometries (Formulae 1—4).

The electronic absorption spectra of the diamag-



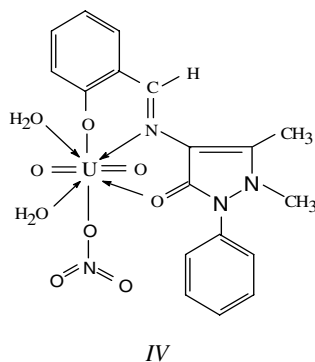
M = Co, X = H₂O, Y = Cl, Z = absent, I

M = Ce, X = H₂O, Y = NO₃, Z = NO₃, VII



M = Co, X = Cl, Z = A = absent, II

M = Ce, X = NO₃, Z = NO₃, A = 1/2 H₂O, VIII



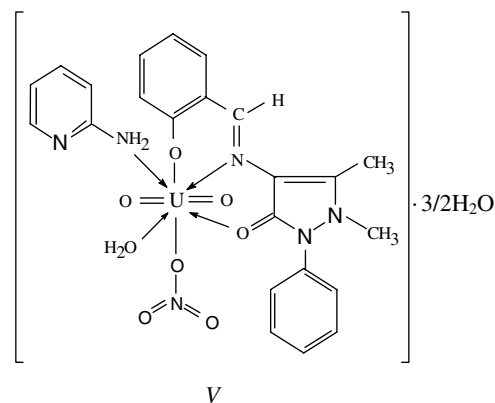
Formula 1. Suggested structures of the binary mononuclear complexes containing L as monoanionic tridentate ligand.

netic 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 (Formulae 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 (ΔH , 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



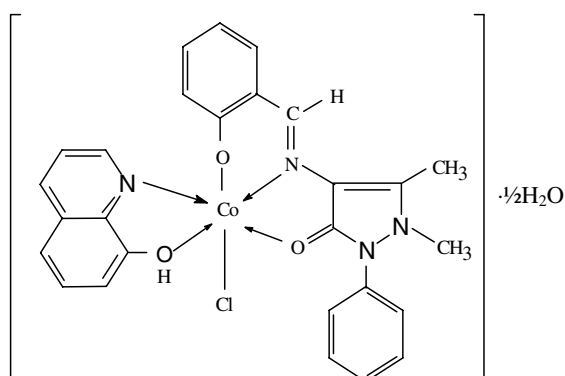
Formula 2. Suggested structures of the mixed ligand complexes containing L and 2-Ampy.

complexes, [UO₂L(NO₃)] and [Ce₂(μ -L)₂(NO₃)₄], 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 HNO₃, C₅H₆N₂ or C₂N₂ molecules and this process led to nonisolable complexes.

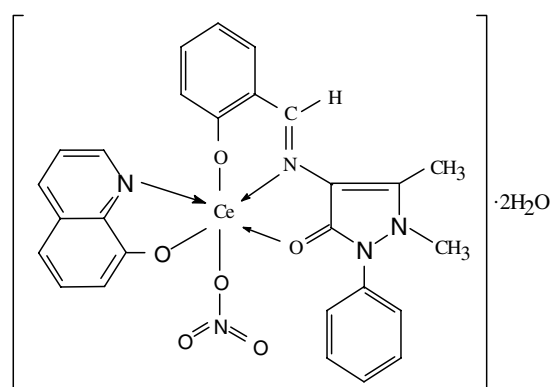
The removal of an HCl molecule from complexes I and II was accompanied by the loss of a part of organic moiety in the temperature range 560—664°C and led to nonisolable complexes.

The removal of an HNO₃ molecule from complexes VI and IX occurred in one step at 368°C and 274°C, respectively. The elimination of HNO₃ molecule from complexes IV, V, VII, and VIII was accompanied by the removal of another molecules such as C₂N₂, C₆H₅.C₆H₅ and coordinated water. This step occurred at a temperature range 328—620°C.

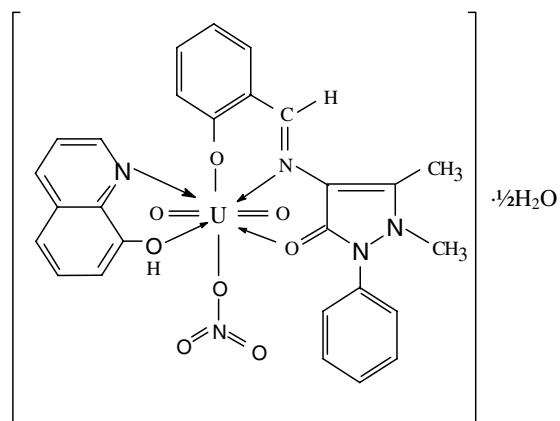
The mixed ligand complexes are thermally stable to the temperature > 250°C. The complexes start to decompose at a relatively higher temperature (> 270°C) and the organic ligand loses C₂N₂, C₆H₅ ·



III



IX

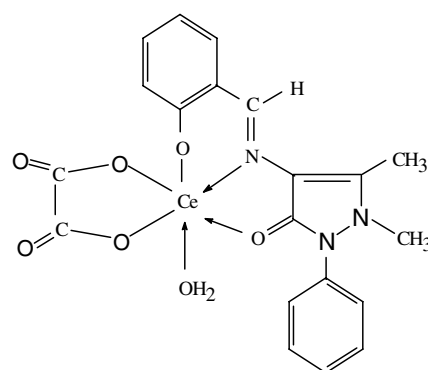


VI

Formula 3. Suggested structures of the mixed ligand complexes containing L and 8-OHqu.

C_6H_5 , CO_2 , 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 $350^\circ C$. The heating rate did not exceed $5^\circ C \text{ min}^{-1}$. 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



X

Formula 4. Suggested structure of the octahedral configuration of the Ce(III) mixed ligand complex containing L and Ox.

for further $1/2$ 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 $\nu(M-O)$ and $\nu(M-N)$ at $548-654 \text{ cm}^{-1}$ and $431-468 \text{ cm}^{-1}$, respectively.

$[UO_2L(NO_3)]$ (*XI*) was prepared by heating complex $[UO_2L(OH_2)_2NO_3]$ (*IV*) to $252^\circ C$ 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].

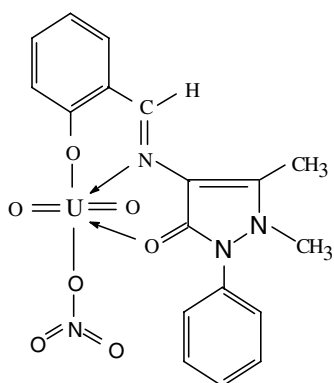
From the previous results and the elemental analyses, the heated product *XI* (Formula 5) has a coordination number 6 and may be in octahedral configuration.

$[Ce_2(\mu-L)_2(NO_3)_4]$ (*XII*) was prepared by heating the complex $[CeL(OH_2)_2NO_3]NO_3$ (*VII*) at $318^\circ C$ 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-

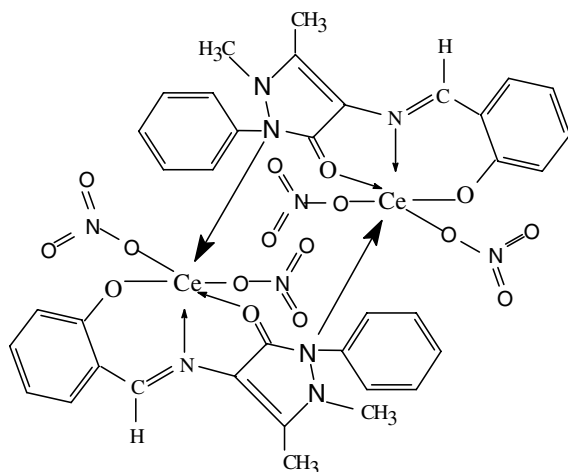
Table 5. Thermal Analysis of Complexes

Compound	Temperature		Mass loss found/% (Mass loss calc./%)	DSC Peak/°C		$\frac{\Delta H}{J\ g^{-1}}$	Composition of the residue	Probable composition of the expelled groups
	°C	°C		Endo	Exo			
<i>I</i>	80–262	197	8.43 (8.25)	–	–	7.26	[CoLCl]	Two molecules of coordinated water
	262–560	504	40.42 (40.18)	–	–	13.96	[Co(C ₁₁ H ₁₀ N ₂ O ₂)]	One molecule of HCl, half molecule of C ₂ N ₂ , and half molecule of C ₆ H ₅ .C ₆ H ₅
<i>II</i>	50–143	143	3.70 (3.51)	–	–	133.50	[CoL(2-Ampy)Cl]	One molecule of coordinated water
	143–652	503	49.30 (49.06)	–	–	15.58	[Co(C ₁₁ H ₁₀ N ₂ O ₂)]	One molecule of HCl, one molecule of C ₅ H ₆ N ₂ , half molecule of C ₂ N ₂ , and half molecule of C ₆ H ₅ .C ₆ H ₅
<i>III</i>	30–107	97	2.0 (1.98)	–	–	59.69	[CoL(8-OHqu)Cl]	Half molecule of lattice water
	107–664	504	64.54 (64.33)	–	–	17.83	[Co(C ₁₁ H ₁₁ N ₂ O ₂)]	One molecule of HCl, one molecule of C ₉ H ₆ NO, half molecule of C ₂ N ₂ , and half molecule of C ₆ H ₅ .C ₆ H ₅
<i>IV</i>	50–252	–	5.40 (5.34)	–	252	–228.0	[UO ₂ L(NO ₃)]	Two molecules of coordinated water
	252–620	505	30.20 (29.96)	–	–	21.09	[UO ₂ (C ₁₁ H ₁₀ N ₂ O ₂)]	One molecule of HNO ₃ , half molecule of C ₂ N ₂ , and half molecule of C ₆ H ₅ .C ₆ H ₅
<i>V</i>	30–79	79	2.90 (2.76)	–	–	523.70	[UO ₂ L(2-Ampy)(OH ₂)NO ₃]	One and half molecules of lattice water
	79–353	–	11.22 (11.05)	–	309	–138.67	[UO ₂ (C ₁₈ H ₁₅ N ₃ O ₂)(2-Ampy)]	One molecule of coordinated water and one molecule of HNO ₃
<i>VI</i>	353–530	504	31.40 (31.21)	–	–	12.43	[UO ₂ (C ₁₁ H ₁₀ N ₂ O ₂)]	One molecule of C ₅ H ₆ N ₂ , half molecule of C ₂ N ₂ , and half molecule of C ₆ H ₅ .C ₆ H ₅
	40–109	92	1.20 (1.14)	–	–	33.21	[UO ₂ L(8-OHqu)NO ₃]	Half molecule of lattice water
<i>VII</i>	109–368	–	9.16 (9.08)	–	342.70	–12.71	[UO ₂ L(8-OHqu)]	One molecule of HNO ₃
	368–509	505	40.62 (40.27)	–	–	24.92	[UO ₂ (C ₁₁ H ₁₁ N ₂ O ₂)]	One molecule of C ₉ H ₆ NO, half molecule of C ₂ N ₂ , and half molecule of C ₆ H ₅ .C ₆ H ₅
<i>VIII</i>	50–318	–	6.10 (5.94)	–	318	–534.08	[Ce(μ-L) ₂ (NO ₃) ₄]	Four molecules of coordinated water out of two complex molecules
	318–526	504	43.90 (43.69)	–	–	26.77	[Ce ₂ (C ₁₁ H ₁₀ N ₂ O ₂) ₂]	Four molecules of HNO ₃ , one molecule of C ₂ N ₂ , and one molecule of C ₆ H ₅ .C ₆ H ₅ out of two complex molecules
<i>IX</i>	30–92	92	1.46 (1.30)	–	–	19.20	[CeL(2-Ampy)(OH ₂)NO ₃]NO ₃	Half molecule of lattice water
	92–328	–	30.70 (30.38)	–	316	–510.36	[Ce(C ₁₇ H ₁₅ N ₂ O ₂)]NO ₃	One molecule of coordinated water, one molecule of C ₅ H ₆ N ₂ , one molecule of HNO ₃ , and half molecule of C ₂ N ₂
<i>X</i>	328–530	503	50.80 (50.48)	–	–	17.05	[Ce(C ₁₁ H ₁₀ N ₂ O ₂)]	One molecule of NO ₃ and half molecule of C ₆ H ₅ .C ₆ H ₅
	30–106	94	5.30 (5.23)	–	–	289.45	[CeL(8-OHqu)NO ₃]	Two molecules of lattice water
<i>XI</i>	106–274	–	14.39 (14.38)	–	269	–503.47	[CeL(8-OHqu)]	One molecule of HNO ₃
	274–763	505	50.64 (50.27)	–	–	20.24	[Ce(C ₁₁ H ₁₁ N ₂ O ₂)]	One molecule of C ₉ H ₆ NO, half molecule of C ₂ N ₂ , and half molecule of C ₆ H ₅ .C ₆ H ₅
<i>XII</i>	50–148	148	3.45 (3.26)	–	–	324.70	[CeL(Ox)]	One molecule of coordinated water
	148–273	249	19.40 (19.19)	–	–	19.84	[CeL]	Two molecules of CO ₂
<i>XIII</i>	273–416	403	38.20 (37.83)	–	–	77.09	[Ce(C ₁₁ H ₁₁ N ₂ O ₂)]	Half molecule of C ₂ N ₂ and half molecule of C ₆ H ₅ .C ₆ H ₅



XI

Formula 5. Structure of $[UO_2L(NO_3)]$.



XII

Formula 6. Structure of $[Ce_2(\mu-L)_2(NO_3)_4]$.

pearance of bands at 3410^{-1} cm and 1389^{-1} cm due to coordinated water molecules and ionic $-NO_3$ 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 $-NO_3$ 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 analy-

ses 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 $-NO_3$ 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, Augmentin, 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

Compound	Fungi				
	<i>Aspergillus fumigatus</i>	<i>Penicillium italicum</i>	<i>Syncephlastrum racemosum</i>	<i>Alternaria alternata</i>	<i>Candida albicans</i>
H ₂ L	++	+++	+++	+++	++
I	+++	++	+++	+++	+
IV	++	++	+	0	+
VII	++	++	++	++	++
Terbinafin	+++	+++	+++	+++	++

Table 7. Antibacterial Activity of Complexes

Compound	Gram +ve		Gram -ve	
	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>	<i>Pseudomonas aeruginosa</i>	<i>Escherichia coli</i>
H ₂ L	++	+++	+++	++
I	++	+++	++	++
IV	++	+	0	+
VII	++	+	++	+
Chloramphenicol	++	++	+++	+++

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

Antibiotic	Cocci (Gram +ve)	Bacilli (Gram -ve)	
	<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Escherichia coli</i>
Amikacin	R	+++	+++
Doxycillin	+++	R	+++
Augmantin	+++	R	+++
Sulperazon	+++	+++	+++
Unasyn	+++	R	R
Septin	R	R	++
Cefoboid	R	R	R
Ampicillin	R	++	R
Nitrofurantion	+++	R	+++
Tarivid	R	R	+++
Erythromycin	+++	R	R

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 ONO 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 tetridentate 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

1. Turan-Zitouni, G., Sivaci, M., Kilic, F. S., and Erol, K., *Eur. J. Med. Chem.* **36**, 685 (2001).
2. Sondhi, S. M., Sharma, V. K., Singhal, N., Verma, R. P., Shukla, R., Raghur, R., and Dubey, M. P., *Phosphorus, Sulfur, Silicon Relat. Elem.* **156**, 21 (2000).
3. Yoshioka, S., Ogata, H., Shibazaki, T., and Ejima, A., *Chem. Pharm. Bull.* **29**, 1179 (1981).
4. Burdulene, D., Palaima, A., Stumbryavichyute, Z., and Talaikite, Z., *Pharm. Chem. J.* **33**, 191 (1999).
5. Evstopov, A. N., Yavorovskaya, V. E., Vorobev, E. S., Kudonogova, Z. P., Gritsenko, L. N., Schmidt, E. N., Medvedeva, S. G., Filimonov, D. V., Prishchep, T. P., and Saratikov, A. S., *Pharm. Chem. J.* **26**, 426 (1992).
6. Sayed, G. H., Radwan, A., Mohamed, S. M., Shiba, S. A., and Kalil, M., *Chin. J. Chem.* **10**, 475 (1992).
7. Cosmetic, Toiletry, and Fragrance Association, *J. Am. Coll. Toxicol.* **11**, 475 (1992).
8. Verleye, M., Heurald, I., and Gillardin, J. M., *Pharmacol. Res.* **41**, 539 (2000).
9. Saraswathi, K., Naidu, N. V. S., Kumari, K. M., and Padmaja, K. P., *Chem. Environ. Res.* **8**, 271 (1999).
10. Singh, L., Sharma, A., and Sindhu, S. K., *Asian J. Chem.* **11**, 1445 (1999).
11. Zhang, Y., Yizhi, L., Hanbin, T., and Loggen, Z., *Acta Crystallogr. E* **58**, 24 (2002).
12. Radmakrishnan, T., Joseph, P. T., and Prabhakaran, C. P., *J. Inorg. Nucl. Chem.* **38**, 2217 (1976).
13. Shankar, G., Premkumar, R. R., and Ramalingam, S. K., *Polyhedron* **5**, 991 (1986).
14. Bassett, G., Denny, R. C., Geffery, G. H., and Mendhan, J., *Vogel's Textbook of Quantitative Inorganic Analysis, 4th Edition*. Longman, London, 1982.
15. Prasad, R. N., Agrawal, M., and Sharma, M., *J. Serb. Chem. Soc.* **67**, 229 (2002).
16. Li, Y. T., Yan, C. W., and Zeng, X. C., *Pol. J. Chem.* **74**, 631 (2000).
17. Jayabalakrishnan, C. and Natarajan, K., *Transition Met. Chem.* **27**, 75 (2002).
18. Viswanathamurthi, P. and Natarajan, K., *Transition Met. Chem.* **24**, 638 (1999).
19. Khera, B., Sharma, A. K., and Kaushik, N. K., *Polyhedron* **2**, 1177 (1983).
20. Ramesh, R., Suganthy, P. K., and Natarajan, K., *Synth. React. Inorg. Met.-Org. Chem.* **26**, 47 (1996).
21. Ali, M. A., Mirza, A. H., Nazimuddin, M., Dhar, P. K., and Butcher, R. J., *Transition Met. Chem.* **27**, 27 (2002).
22. Khan, T. A., Rather, M. A., Jahan, N., Vankey, S. P., and Shakir, M., *Synth. React. Inorg. Met.-Org. Chem.* **27**, 843 (1997).
23. Subramanian, P. S., Dave, P. C., Boricha, V. P., and Srinivas, D., *Polyhedron* **17**, 443 (1998).
24. Miodragovic, Z. M., Vuckovic, G., Leove, V. M., and Buzash, V. M., *Synth. React. Inorg. Met.-Org. Chem.* **30**, 57 (2000).
25. Alemi, A. A. and Shaabani, B., *Acta Chim. Solv.* **47**, 363 (2000).
26. Chang, C. J., Connick, W. B., Low, D. W., Day, M. W., and Gray, H. B., *Inorg. Chem.* **37**, 3107 (1998).
27. Mashaly, M. M., *Synth. React. Inorg. Met.-Org. Chem.* **26**, 211 (1996).
28. Mashaly, M. M., *Synth. React. Inorg. Met.-Org. Chem.* **32**, 373 (2002).
29. Khan, T. A. and Shahjahan, A., *Synth. React. Inorg. Met.-Org. Chem.* **31**, 1023 (2001).
30. Lever, A. B. P., *Inorganic Electronic Spectroscopy*, 2nd Edition. Elsevier, New York, 1984.
31. Liethr, A. D., *J. Phys. Chem.* **67**, 1314 (1967).
32. Abd El-Wahab, Z. H., Mashaly, M. M., Salman A. A., El-Shetary, B. A., and Faheim, A. A., *Spectrochim. Acta, Part A* **60**, 2861 (2004).