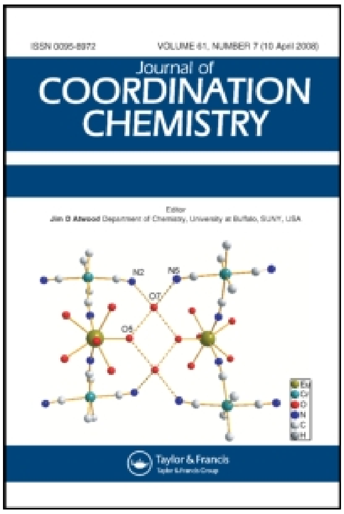

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Mixed ligand complexes of nickel(II) and cerium(III) ions with 4-(-3-methoxy-4-hydroxybenzylideneamino)-1, 3-dimethyl-2,6-pyrimidine-dione and some nitrogen/oxygen donor ligands

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Mixed ligand complexes of nickel(II) and cerium(III) ions with 4-(-3-methoxy-4-hydroxybenzylideneamino)-1, 3-dimethyl-2,6-pyrimidine-dione and some nitrogen/oxygen donor ligands

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Mononuclear mixed ligand complexes of Ni(II) and Ce(III) with 4-(-3-methoxy-4-hydroxybenzylideneamino)-1,3-dimethyl-2,6-pyrimidine-dione, 2-aminopyridine and 8-hydroxyquinoline have been prepared. The elemental analysis, molar conductance, spectral (IR, mass and solid reflectance), magnetic moment measurements and thermal study were utilized to investigate the coordination behavior. All metal complexes have metal-to-ligand ratios of 1 : 1 : 1 and the modes of bonding are consistent with N- and O-donation suggesting monomeric octahedral and square planar structures. The thermal behavior of these complexes was investigated and the thermal decomposition pathways postulated. The activation thermodynamic parameters, E*, ΔH*, ΔS* and ΔG* for the different thermal decomposition steps of the complexes were calculated using the Coats-Redfern equation. Antibacterial and antifungal properties of the metal complexes have also been examined against *Staphylococcus aureus* (ATCC 25923), *Streptococcus pyogenes* (ATCC 19615), *Pseudomonas fluorescens* (S 97), *Pseudomonas phaseolicola* (GSPB 2828), *Fusarium oxysporum* and *Aspergillus fumigatus*. The highest antimicrobial activity was observed for the Ce(III) complex, $[CeL(8\text{-}Oqu)(NO_3)_2] \cdot 1\tfrac{1}{2}H_2O$.

Keywords: 2-Aminopyridine; 8-Hydroxyquinoline; Mixed ligand complexes; Spectroscopic characterization; Thermal investigation and biological study

1. Introduction

Schiff bases derived from an amine and any aldehyde coordinate to metal ions via the azomethine nitrogen. Transition and non-transition metal complexes with Schiff-base ligands played a vital role in the development of coordination chemistry. Interest in Schiff bases and their metal complexes is enhanced by proteins and enzymes requiring metal ions for activity, catalytic activity in the hydrogenation of olefins, complexing ability towards toxic metals and so on [1–3]. Mixed ligand complexes containing N, O

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and/or S donor atoms are important with significant antifungal, antibacterial and anticancer activity [4]. Mixed ligand complexes with metal ions bound to two different and biochemically important ligands have aroused interest as models for metalloenzymes; mixed ligand complexes have been extensively studied following recognition that they play an important role in biological processes and serve as suitable models for valuable information in the elucidation of enzymatic processes of biological relevance [5, 6]. A large number of mixed ligand complexes involving heterocyclic bases such as pyridine [7–10], aminopyridine [11, 12], bipyridine [13–20], phenanthroline [16–21], hydroxyquinoline [17, 20–24], picoline [5, 9, 10] and imidazole [18, 25] were reported due to their bio-inorganic applications and thermal stability. Abd El-Wahab *et al.* [26–30] have prepared and isolated mixed ligand complexes of heterocyclic ligands of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III), Ce(III) and UO_2(IV) complexes. Review of the literature reveals that:

- Pyridine derivatives are widely applied in medicine and agriculture; for example, they are used as anticancer, antifungal, plant growth reagents, and pesticides [31]. 8-Hydroxyquinoline and its derivatives have many potential applications such as in waste water treatment for metal recovery, as water disinfectants and for biological activity [32].
- Transition and lanthanide metal complexes derived from Schiff-base ligands play a major role in the development of modern coordination chemistry providing examples of macrocyclic ligand systems and the effects of steric interactions on coordination geometries [33]. In addition, the activity of nickel is known because it is a component of a hydrolase (urease) and activates the genes of hydrogenases [6]. Cerium is industrially important, used in nuclear reactors and in alloys with nickel and chromium in microwave devices. Cerium is also used in agriculture, forestry, and animal husbandry [34].

We have synthesized mixed ligand complexes containing Ni(II) and Ce(III) ions with biochemically important ligands, 2-aminopyridine and 8-hydroxyquinoline, in addition to the Schiff-base ligand, 4-(3-methoxy-4-hydroxybenzylideneamino)-1,3-dimethyl-2,6-pyrimidine-dione (figure 1). All compounds under study have been screened for their biological activity against selected microbial strains.

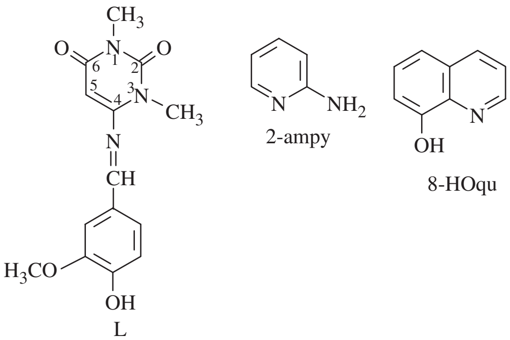


Figure 1. Structures of 4-(3-methoxy-4-hydroxybenzylideneamino)-1,3-dimethyl-2,6-pyrimidine-dione (L); 2-aminopyridine (2-ampy) and 8-hydroxyquinoline (8-HOqu).

2. Experimental

2.1. *Analysis and physical measurements*

All chemicals used were of highest available purity, 2-aminopyridine and 8-hydroxyquinoline (Sigma), nickel nitrate hexahydrates and cerium nitrate hexahydrates (BDH), absolute ethyl alcohol, diethylether, dimethylformamide and dimethylsulfoxide (Merck or Sigma). Concentrated nitric and perchloric acid were reagent grade and used as supplied. The Schiff-base ligand, 4-(-3-methoxy-4-hydroxybenzylideneamino)-1, 3-dimethyl-2,6-pyrimidine-dione, (L) has been described previously [35].

Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer 2408 CHN analyzer. Ni(II) and Ce(III) contents were determined complexometry and gravimetrically, respectively [36]. Melting or decomposition points were carried out on a melting point apparatus, Gallenkamp, England. IR spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer using KBr discs. Mass spectra were recorded in a range of m/e ratio between 0 and 1000 on a Jeol JMSAX-500 mass spectrometer. The solid reflectance spectra of metal complexes were recorded on a Jasco model V-550 UV–Vis spectrophotometer. Magnetic susceptibility of the metal complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alpha products, model MKI magnetic susceptibility balance and the effective magnetic moments were calculated using the relation $\mu_{\text{eff}} = 2.828 (\chi_m \cdot T)^{1/2}$ BM, where χ_m is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds. Molar conductance measurements were measured in solutions of the metal complexes in DMF (10^{-3} M) using WTWD-812 Weilheium-Conductivity meter model LBR, fitted with a cell model LTA100. The TG analysis (20–1000°C) was carried out in dynamic nitrogen atmosphere ($20\,\text{mL}\,\text{min}^{-1}$) with heating rate of $10^\circ\text{C}\,\text{min}^{-1}$ using α-Al_2O_3 as reference on a Shimadzu Thermogravimetric Analyzer (TGA-50H). The antimicrobial activity of the metal complexes was screened using the agar-disc diffusion technique [37].

2.2. *Synthesis of mononuclear mixed-ligand complexes*

Interaction of metal ion with Schiff-base ligand and 2-aminopyridine or 8-hydroxyquinoline in 1 : 1 : 1 molar ratio resulted in complexes **1**–**4**. An ethanolic solution of the Schiff-base ligand (L) (0.868 g; 3 mmol) was mixed with an ethanolic solution of 2-aminopyridine or 8-hydroxyquinoline (0.282 or 0.436 g, respectively, 3 mmol). Subsequently, an ethanolic solution of the hexahydrated metal nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ or $Ce(NO_3)_3 \cdot 6H_2O$ (0.872 or 1.303 g, respectively, 3 mmol) was added dropwise with stirring, the mixture was refluxed for 4 h on a water bath and then left to cool at room temperature. The resulting precipitate was filtered, washed several times with 50% (v/v) ethanol-water to remove any traces of unreacted materials, then washed with diethyl ether and dried in a vacuum desiccator over anhydrous calcium chloride. The obtained complexes were colored powders, stable at room temperature and insoluble in common organic solvents but soluble in DMF or DMSO. The elemental analyses and some physical properties of the isolated metal complexes are listed in table 1.

Table 1. Analytical data and some physical properties of Ni(II) and Ce(III) mixed ligand complexes.

Compd. No Empirical formula	M. wt Found (Calcd)[a]	Color	M.p. (°C)	Λ_m^b	$\mu_{eff.}$ (BM)[c]	Elemental analysis, found (Calcd %)			
						C	H	N	M
(**1**) [NiL(2-ampy)$(NO_3)_2(H_2O)$]; $NiC_{19}H_{21}N_7O_{10} \cdot H_2O$	584.00 (584.18)	Pale Green	182	15.48	3.02	39.27 (39.06)	3.66 (3.63)	16.38 (16.79)	10.00 (10.05)
(**2**) [NiL(8-Oqu)]$NO_3 \cdot H_2O$; $NiC_{23}H_{21}N_5O_8 \cdot H_2O$	572.00 (572.20)	Olive Green	300	88.00	Diamag	48.49 (48.28)	4.00 (3.71)	12.68 (12.24)	10.45 (10.26)
(**3**) [CeL(2-ampy)$(NO_3)_3$]$\cdot H_2O$; $CeC_{19}H_{21}N_8O_{13} \cdot H_2O$	729.00 (727.62)	Buff	224	10.11	2.43	31.11 (31.36)	3.00 (2.91)	15.21 (15.40)	19.29 (19.26)
(**4**) [CeL(8-Oqu)$(NO_3)_2$]$\cdot 1\frac{1}{2}H_2O$; $CeC_{23}H_{21}N_6O_{11} \cdot 1\frac{1}{2}H_2O$	724.00 (724.65)	Brown	290	8.91	2.52	38.75 (38.12)	3.12 (2.93)	12.09 (11.60)	19.64 (19.34)

L is 4-(-3-methoxy-4-hydroxybenzylideneamino)-1,3-dimethyl-2,6-pyrimidine-dione.

2-ampy = 2-aminopyridine.

8-Oqu = deprotonated form of 8-hydroxyquinoline.

[a] Found values obtained from mass spectra.

[b] Molar conductance ($Ohm^{-1}\,cm^2\,mol^{-1}$) of 1×10^{-3} M solution in DMF at room temperature.

[c] Room temperature effective magnetic moment.

2.3. *Antimicrobial assay*

The complexes, Schiff-base ligand, 2-aminopyridine and 8-hydroxyquinoline in addition to $Ni(NO_3)_2 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were screened for antibacterial and antifungal activity against *Staphylococcus aureus* (ATCC 25923) and *Streptococcus pyogenes* (ATCC 19615) as Gram positive bacteria, *Pseudomonas fluorescens* (S 97) and *Pseudomonas phaseolicola* (GSPB 2828) as Gram negative bacteria and the fungi *Fusarium oxysporum* and *Aspergillus fumigatus*. The antibiotics, *Cephalothin*, *Chloramphencol* and *Cycloheximide*, were used as standard references for Gram positive bacteria, Gram negative bacteria and fungi, respectively, using the agar-disc diffusion technique [37] described below.

The tested compounds were dissolved in dimethyl formamide (DMF) which has no inhibition activity to get concentrations of $2\,\mathrm{mg\,mL^{-1}}$ and $1\,\mathrm{mg\,mL^{-1}}$. The test was performed on medium potato dextrose agar (PDA) which contains 200 g potatoes, 6 g dextrose and 15 g agar. Uniform size filter article disks (three disks per compound) were impregnated by equal volume ($10\,\mu l$) from the specific concentration of dissolved tested compounds and carefully placed on inoculated agar surface. After incubation for 36 h at 27°C in the case of bacteria and for 48 h at 24°C in the case of fungi, inhibition of the organisms by the clear zone surrounding each disk was measured and used to calculate the mean inhibition zones.

3. Results and discussion

The reaction of Schiff-base ligand (L) with Ni(II) and Ce(III) ions in the presence of 2-aminopyridine (2-ampy) or 8-hydroxyquinoline (8-HOqu) produce the mixed ligand complexes (**1**–**4**) having compositions shown in table 1.

3.1. *Conductivity measurements*

The conductance measurements recorded for 10^{-3} M solutions in DMF are listed in table 1. All complexes, except one, are non-conducting with conductance values of $15.48–8.91\,\mathrm{Ohm^{-1}cm^2mol^{-1}}$ indicating their neutrality, so the nitrate is absent or situated inside the coordination sphere. The exception is nickel(II) complex $[NiL(8\text{-}Oqu)]NO_3 \cdot H_2O$, which showed conductance of $88.00\,\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$, indicating 1 : 1 electrolyte [2, 26].

3.2. *Infrared spectra*

The more relevant IR-bands of the mixed ligand complexes are presented in table 2.

The azomethine stretching band was shifted to lower energy at $1616–1612\,\mathrm{cm^{-1}}$ in all metal complexes compared to the free ligand ($1625\,\mathrm{cm^{-1}}$), confirming involvement of the azomethine nitrogen in complex formation [35, 38]. The position and intensity of $\nu(C_6{=}O)$ ($1744\,\mathrm{cm^{-1}}$ in the free ligand) change appreciably during complexation, observed at lower energy regions at $1693–1644\,\mathrm{cm^{-1}}$, indicating that this carbonyl oxygen is involved in the metal complexes [35, 39]. In the ν(O–H) region, the IR spectra

Table 2. Main IR spectral vibrations (cm^{-1}) and electronic spectral bands (cm^{-1}) with their assignment for Ni(II) and Ce(III) mixed ligand complexes.

Compd. No.[a]	IR spectral vibrations (cm^{-1})						Electronic spectral bands (cm^{-1})			
	ν_{O-H} (H_2O)	$\nu_{C(6)=O}$ (carbo.)	$\nu_{C=N}$ (azome.)	ν_{M-O}	ν_{M-N}	Nitrate-stretch	$\pi-\pi^*$	$n-\pi^*$	LMCT	d–d transitions/peak assignment
(**1**)	3576–3398	1693	1612	552	424	1450, 1300, 1076 (coord. NO_3)	28571	45662	26525	12121 $^3A_{2g}$ (F) → $^3T_{2g}$ (F) 18382 $^3A_{2g}$ (F) → $^3T_{1g}$ (F) 21978 $^3A_{2g}$ (F) → $^3T_{1g}$ (P)
(**2**)	3550–3398	1655	1612	548	413	1385, 826 (ionic NO_3)	39216	45246	34483	14970 $^1A_{1g} \rightarrow {}^1B_{1g}$ 18315 $^1A_{1g} \rightarrow {}^1B_{2g}$
(**3**)	3533–3422	1644	1616	513	424	1431, 1304, 1072 (coord. NO_3)	28490	46296	18711	
(**4**)	3564–3418	1690	1612	509	480	1461, 1304, 1099 (coord. NO_3)	30395	45045	20325	

[a] Represent the complex number as in table 1.

of **1**–**4** show a broad band at 3576–3398 cm^{-1} attributed to the ν(O–H) phenolic (Schiff-base ligand) and coordinated/lattice water molecules associated with complex formation [22, 35]. The IR spectra of **1** and **3** show that the NH_2 bands at 3342 and 3145 cm^{-1} in 2-aminopyridine [27] appear without significant change, indicating no role in coordination to the metal ions; the only change in 2-aminopyridine complexes was the stretching vibration for the ring nitrogen at 1512–1501 cm^{-1} and 907–903 cm^{-1} characteristic to pyridine ring vibration and pyridine ring breathing mode, respectively, indicating the involvement of pyridine ring nitrogen in coordination and 2-aminopyridine as a neutral monodentate ligand [27, 40]. The IR-spectrum of the free 8-hydroxyquinoline shows a strong band at 1586 cm^{-1} due to stretching of the C=N [17]. This band shifted to 1522–1508 cm^{-1} on coordination for **2** and **4** suggesting that the lone pair on nitrogen is involved in formation of a bond with metal. The broad stretching vibration at 3242 cm^{-1} due to O–H of the free 8-HQ [17] was absent in the metal complexes, suggesting formation of the M–O bond with 8-hydroxyquinolate. Thus, 8-hydroxyquinolate in these complexes is monobasic bidentate chelating. IR spectra of metal **1**, **3** and **4** show three bands at 1461–1431 cm^{-1}, 1304–1300 cm^{-1} and 1099–1072 cm^{-1} attributed to unidentate coordination of nitrate while **2** has characteristic strong and medium absorption bands at 1385 and 826 cm^{-1} assigned to ionic nitrate [41, 42]. The mode of coordination is further supported by new medium and/or weak bands at 552–509 cm^{-1} and 480–413 cm^{-1} due to ν(M–O) and ν(M–N), respectively [26].

3.3. *Magnetic susceptibility and electronic spectra*

The magnetic moment values at room temperature, table 1, show **1** with a magnetic moment value of 3.02 BM corresponding to two unpaired electrons consistent with six-coordinate Ni(II) [2]. Complex **2** is diamagnetic at room temperature indicating square planar geometry [43]. At room temperature cerium(III) complexes (**3**, **4**) show magnetic moment values in the range 2.43–2.52 BM, close to those calculated for Ln(III) by Hund and Van-Vleck (2.54 and 2.56) and in the normal range of 2.14–2.46 BM [28].

Electronic spectra of the metal complexes, table 2, exhibit two spectral bands in the region 39216–28490 cm^{-1} and 46296–45045 cm^{-1}, attributed to π–π* and n–π* transitions, respectively, involving C=N and both benzene and heterocyclic rings. The intramolecular charge transfer and d–d transitions confirm coordination of the ligands to metal [35].

The electronic spectrum of **1** shows three bands in the regions 12121 cm^{-1} (υ_1), 18382 cm^{-1} (υ_2) and 21978 cm^{-1} (υ_3) in addition to a band at 26525 cm^{-1} (table 2), suggesting octahedral configuration. The ground state for nickel(II) octahedral coordination is $^3A_{2g}$. Thus, these transitions are attributed to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, respectively. The band at 26525 cm^{-1} is the charge transfer band [44]. Various ligand field parameters, $10D_q$, B and β, were calculated. The transition at 12121 cm^{-1} represents $10D_q$ and reduction in B-value from the free ion value (1080 cm^{-1}) to 712 cm^{-1} suggests covalent character of the metal-ligand bond. Additionally, β (0.66), β% (34.07) and LFSE (14545 cm^{-1}) values agree well with those reported for similar complexes [45]. The parameters $(\upsilon_2)/(\upsilon_1)$ (1.52) and D_q/B (1.70) further support the octahedral geometry. The spectrum of **2** shows absorption bands at 14970 cm^{-1} and 18315 cm^{-1} assignable to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1B_{2g}$, respectively, consistent with square planar geometry about nickel(II) [43].

Table 3. The most relevant mass spectral peaks of Ni(II) and Ce(III) mixed ligand complexes.

Compd. No.	*m/e* Found (Calcd)	Relative intensity %)	Loss moiety[a]	Peak assignment due to loss moiety
(**1**) [NiL(2-ampy)$(NO_3)_2(H_2O)$]	584.00 (584.18)	4.67	–	
	442.00 (442.14)	26.32	H_2O and $2NO_3$	[NiL(2-ampy)]
	347.00 (348.01)	7.30	2-ampy	[NiL]
	58.00 (58.69)	8.09	L	Ni
(**2**) [NiL(8-Oqu)]$NO_3 \cdot H_2O$	572.00 (572.20)	35.02	–	
	266.00 (264.86)	6.69	H_2O and L	[Ni(8-Oqu)]NO_3
	200.00 (202.85)	9.68	NO_3	[Ni(8-Oqu)]
	59.00 (58.69)	7.17	8-Oqu	Ni
(**3**) [CeL(2-ampy)$(NO_3)_3$]$\cdot H_2O$	729.00 (727.62)	51.20	–	
	649.00 (647.59)	52.55	H_2O and NO_3	[CeL(2-ampy)$(NO_3)_2$]
	359.00 (358.27)	40.50	L	[Ce(2-ampy)$(NO_3)_2$]
	294.00 (296.26)	62.81	NO_3	[Ce(2-ampy)(NO_3)]
	232.00 (234.25)	48.28	NO_3	[Ce(2-ampy)]
	141.00 (140.12)	62.48	2-ampy	Ce
(**4**) [CeL(8-Oqu)$(NO_3)_2$]$\cdot 1\frac{1}{2}H_2O$	724.00 (724.65)	41.01	–	
	492.00 (491.45)	3.90	$1\frac{1}{2}H_2O$,NO_3 and 8-Oqu	[CeL(NO_3)]
	430.00 (429.44)	5.69	NO_3	[CeL]
	139.00 (140.12)	23.62	L	Ce

[a] L represents the Schiff-base ligand.
2-ampy represents 2-aminopyridine.
8-Oqu represents the deprotonated form of 8-hydroxyquinoline.

Cerium(III) complexes (**3** and **4**) show absorption bands at 20325–18711 cm^{-1} from metal ligand charge transfer excitations [28]. The complexes are six coordinate, probably octahedral.

3.4. *Mass spectra*

The mass spectra of the complexes (Supplemental Information) and the molecular ion peaks have been used to confirm the proposed formulas. Calculated and found values of the molecular weights (table 1) indicate the monomeric nature. Fragmentation is described in the Supplemental Information with some detail in table 3.

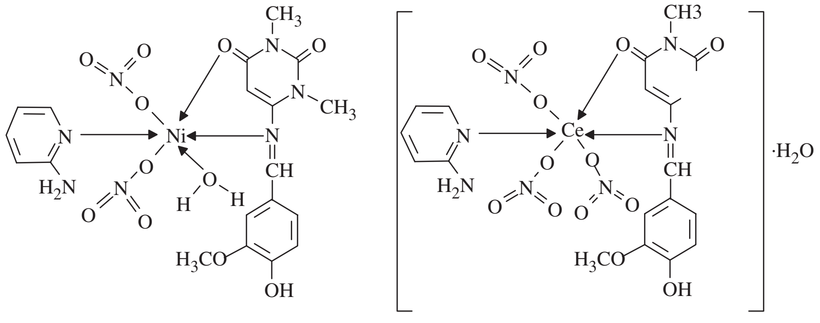
3.5. *Thermal behavior and kinetic aspects*

TG/DTG curves have been studied for all complexes. The TG curves (Supplemental Information) showed that the thermal decomposition of all complexes take place in three steps. The decomposition stages, temperature range, decomposition product as well as the found and calculated weight loss temperatures of the metal complexes are given in table 4. All these complexes undergo similar decomposition ending with formation of metal or metal oxide. The observed weight losses for all complexes are in good agreement with the calculated values from their chemical formulas given in table 1.

In the light of all results, the most reasonable structures of the mixed ligand complexes are shown in figures 2 and 3.

Table 4. Thermoanalytical results of of Ni(II) and Ce(III) mixed ligand complexes.

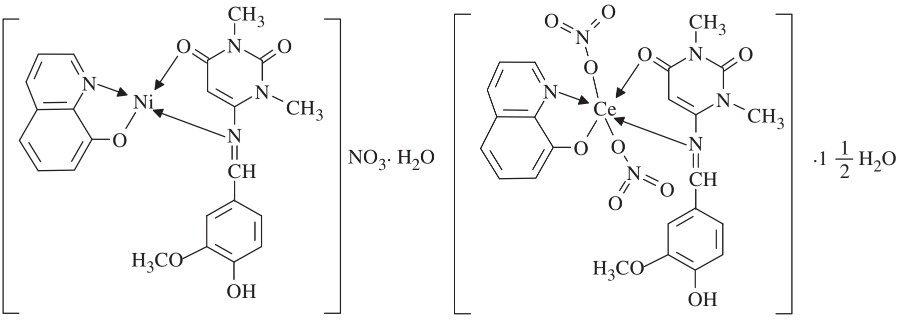
			Mass loss%			
Complex compound	Stage	Temp. range (°C)	Calcd	Found	Evolved moiety	Residue
(**1**) [NiL(2-ampy)$(NO_3)_2(H_2O)$]	I	44–220	13.70	13.40	H_2O (coord.) and NO_3	[NiL(2-ampy)(NO_3)]
	II	220–305	40.43	41.00	NO_3 and (2-ampy)	[NiL]
	III	305–568	87.22	87.00	$C_{14}H_{15}N_3O_3$	NiO
(**2**) [NiL(8-Oqu)]$NO_3 \cdot H_2O$	I	28–149	3.15	3.64	H_2O (hydr.)	[NiL(8-Oqu)]NO_3
	II	149–313	39.18	39.48	NO_3 and (8-Oqu)	[NiL]
	III	313–500	86.95	87.47	$C_{14}H_{15}N_3O_3$	NiO
(**3**) [CeL(2-ampy)$(NO_3)_3$]$\cdot H_2O$	I	25–125	2.48	2.72	H_2O (hydr.)	[CeL(2-ampy)$(NO_3)_3$]
	II	125–228	32.46	33.50	$2NO_3$ and (2-ampy)	[CeL(NO_3)]
	III	228–293	80.74	81.00	NO_3 and L	Ce
(**4**) [CeL(8-Oqu)$(NO_3)_2$]$\cdot 1\frac{1}{2}H_2O$	I	34–170	8.01	7.25	$1\frac{1}{2}H_2O$ (hydr.) and $\frac{1}{2}NO_3$	[CeL(8-Oqu)$\cdot 1\frac{1}{2}NO_3$]
	II	170–282	36.46	36.62	NO_3 and (8-Oqu)	[CeL$\cdot \frac{1}{2}NO_3$]
	III	282–385	80.66	80.00	$\frac{1}{2}NO_3$ and L	Ce



(1) : [NiL (2-ampy) $(NO_3)_2(H_2O)$]

(3) : [CeL (2-ampy)]$(NO_3)_3 \cdot H_2O$

Figure 2. Proposed structures of the 2-aminopyridine complexes, (**1**): Aquadinitrato-2-aminopyridine 4-(-3-methoxy-4-hydroxybenzylideneamino)-1,3-dimethyl-2,6-pyrimidine-dione nickel(II) complex; (**3**): Trinitrato-2-aminopyridine 4-(-3-methoxy-4-hydroxybenzylideneamino)-1,3-dimethyl-2,6-pyrimidine-dione cerium(III) complex.



(2) : [NiL(8-Oqu)]$NO_3 \cdot H_2O$

(4) : [CeL (8-oqu)]$(NO_3)_2 \cdot 1\frac{1}{2} H_2O$

Figure 3. Proposed structures of the 8-hydroxyquinoline complexes, (**2**): 8-Hydroxyquinolinato 4-(-3-methoxy-4-hydroxybenzylideneamino)-1,3-dimethyl-2,6-pyrimidine-dione nickel(II) nitrate complex; (**4**): Dinitrato-8-hydroxyquinolinato 4-(-3-methoxy-4-hydroxybenzylideneamino)-1,3-dimethyl-2,6-pyrimidine-dione cerium(III) complex.

Table 5. Antimicrobial screening results of all compounds under study.

	Gram-positive bacteria				Gram-negative bacteria				Fungi			
Organism	*Staphylococcusaureus* (ATCC 25923)		*Streptococcus pyogenes* (ATCC 19615)		*Pseudomonas phaseolicola* (GSPB 2828)		*Pseudomonas fluorescens* (S 97)		*Eusarium oxysporum*		*Aspergillus fumigatu*	
Conc.	1	2	1	2	1	2	1	2	1	2	1	2
Comp. No.	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$	$2\,mg\,ml^{-1}$	$1\,mg\,mL^{-1}$	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$	$2\,mg\,mL^{-1}$	$1\,mg\,mL^{-1}$
(**1**) $[NiL(2\text{-}ampy)(NO_3)_2(H_2O)]$	–	–	–	–	7	5	5	2	–	–	–	–
(**2**) $[NiL(8\text{-}Oqu)]NO_3 \cdot H_2O$	6	3	7	3	8	5	10	5	28	20	31	23
(**3**) $[CeL(2\text{-}ampy)(NO_3)_3] \cdot H_2O$	7	4	9	5	5	3	5	3	7	3	5	2
(**4**) $[CeL(8\text{-}Oqu)(NO_3)_2] \cdot 1\frac{1}{2}H_2O$	20	14	23	17	22	16	20	14	31	23	33	24
L	11	8	–	–	6	4	8	4	3	2	3	2
2-ampy	12	5	7	3	9	5	5	3	30	23	30	24
8-Hoqu	32	26	33	24	22	14	25	16	35	26	31	20
$Ni(NO_3)_2 \cdot 6H_2O$	22	14	24	15	30	20	30	22	6	4	6	4
$Ce(NO_3)_3 \cdot 6H_2O$	20	12	21	17	22	14	23	15	22	14	24	15
R.S	42	28	38	30	36	25	38	30	40	28	40	31

- Test done using the agar-disc diffusion method.
- % Activity indices are in parentheses.
- R.S; Reference standard: *Chloramphencol*, *Cephalothin* and *Cycloheximide* were used as standard references for Gram positive bacteria, Gram negative bacteria and antifungal, respectively.
- Inhibition values: – no effect; 3–13 low activity; 14–24 intermediate activity; 25–32 high activity and >32 very high activity.

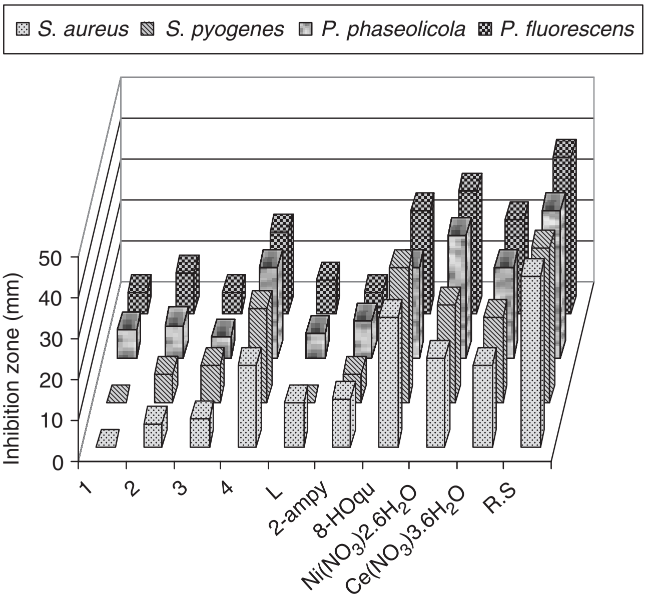


Figure 4. Antibacterial activity of compounds under study.

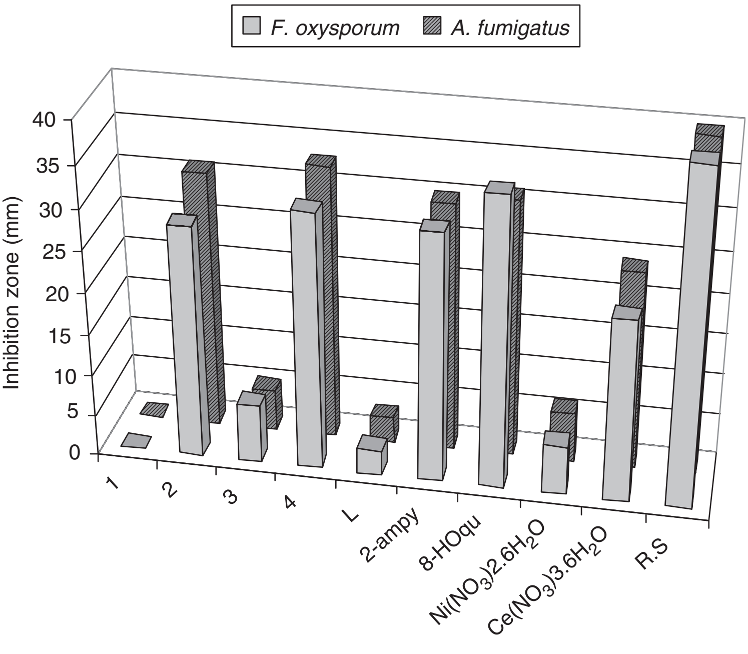


Figure 5. Antifungal activity of compounds under study.

3.6. *Antibacterial and antifungal assay*

The biological activity of a particular substance depends on a complex sum of the individual properties including the compound structure, the affinity of the target, survival in the medium of application or within the biological system, transport properties and state of the target organism. In this study we focused our attention on the structure-activity relationships.

The screening data obtained for the compounds under study against *S. aureus*, *S. pyogenes*, *P. fluorescens*, *P. phaseolicola*, *F. oxysporum* and *A. fumigatus* using the disc-agar diffusion technique [37] are summarized in table 5 and figures 4 and 5 showing the variation of inhibition zone values of all the compounds towards the tested bacteria and fungi.

A comparison of all tested compounds towards the different organisms show the following:

- The compounds inhibit the growth of organisms to a greater extent as the concentration is increased.
- The Schiff-base ligand (L) did not have any activity towards *S. pyogenes* but displays low activity against all other organisms.
- Generally activity of the free ligand increased upon complexation with Ni(II) and Ce(III) ions, explained by chelation theory [46].
- **1** has no effect against the two types of Gram positive bacteria and fungi but displays low activity against Gram negative bacteria.
- **2** displays low activity against both Gram positive and Gram negative bacteria strains but has high activity against fungi.
- **3** displays low activity against all organisms.
- **4** has a higher degree of activity than all the other metal complexes or the free Schiff-base ligand (L) against all types of bacteria and fungi. It displays intermediate activity against bacteria strains and high activity against fungi strains.
- On comparison of all metal complexes to each other; **2** containing 8-hydroxyquinoline shows higher activity than **1**. Complex **4** containing 8-hydroxyquinoline shows higher activity than **3**.

4. Conclusion

We have successfully synthesized four complexes of Ni(II) and Ce(III) with 4-(3-methoxy-4-hydroxybenzylideneamino)-1,3-dimethyl-2,6-pyrimidine-dione, 2-aminopyridine and 8-hydroxyquinoline. The structures of these metal complexes were confirmed by elemental analysis, molar conductance, magnetic moment, thermal analysis and spectral data (IR, mass and solid reflectance). The mass spectra support the monomeric nature of the complexes. The geometry and mode of bonding in these complexes are reached based on infrared, electronic spectra and magnetic susceptibility measurements to be octahedral and square planar structures and the mode of bonding is consistent with N- and O-donation. The antimicrobial activity of the complexes was studied against different strains of bacteria and fungi showing that the metal complexes containing 8-hydroxyquinoline are more active than those containing 2-aminopyridine.

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