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Unsymmetrical Schiff base (ON) ligand on complexation with some transition metal ions: Synthesis, spectral characterization, antibacterial, fluorescence and thermal studies

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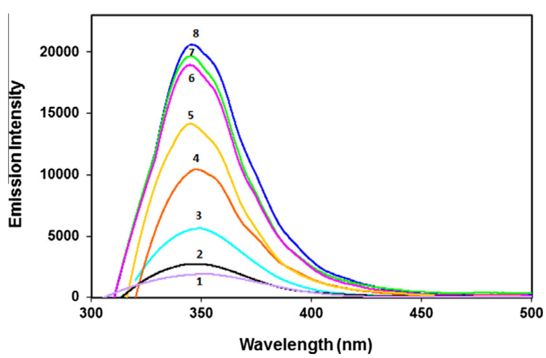
HIGHLIGHTS

- The complexes are characterized by different spectroscopic techniques.
- The Schiff base ligand exhibited efficient corrosion inhibitors.
- The ligand and its complexes exhibited intraligand (π–π^*) fluorescence and can potentially serve as photoactive materials.
- The thermal analyses confirmed high stability for all complexes.

GRAPHICAL ABSTRACT

Emission spectra of: (1) $[Sm(L)_3](ClO_4)_3H_2O$; (2) Ligand; (3) $[Hg(L)(AcO)_2]H_2O$; (4) $[La(L)(NO_3)_2]$ NO_3H_2O; (5) $[Zn(L)(AcO)_2]H_2O$; (6) $[Co(L)(Cl)_2(H_2O)_2]2H_2O$; (7) $[Ni(L)(Cl)_2]2H_2O$; (8) $[Cu(L)(Cl)_2]\cdot H_2O$



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ABSTRACT

A series of eight metal Schiff base complexes were synthesized by the thermal reaction of Cu(II), Ni(II), Fe(III), Co(II), Zn(II), Hg(II), La(III) or Sm(III) with a Schiff base "L" produced by the condensation of furfuraldehyde and 1,2-diaminobenzene. These compounds were characterized by elemental analysis, UV–Vis, FT-IR, molar conductance, mass spectrometry, thermal and fluorescence studies. The studies suggested the coordination of the ligand L to metal through azomethine imine nitrogen and furan oxygen atoms of Schiff base moiety. Thermogravimetric (TG/DTG) analyses data were studied and indicated high stability for all complexes and suggested the presence of lattice and/or coordinated water molecules in the complexes. Coats–Redfern method has been used to calculate the kinetic and thermodynamic parameters of the metal complexes. The spectral and thermal analysis reveal that all complexes have octahedral geometry except Cu(II) and Ni(II) complexes which can attain a square planner arrangements. The ligand and its complexes exhibited intraligand (π–π^*) fluorescence and can potentially serve as photoactive materials. Both the ligand and its complexes have been screened for antibacterial activities.

Introduction

For decades, coordination chemistry of Schiff base ligands has been the subject of great interest. This interest comes from the fact

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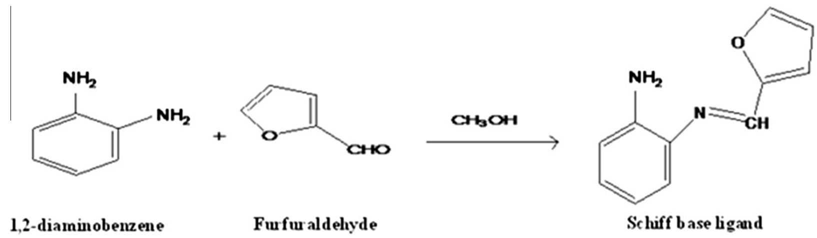

Scheme 1. Preparation of L ligand.

Table 1
Analytical and physical data of ligand and its complexes.

Compound	Color (% yield)	M.Wt.	M.p. (°C)	Found (calculated)			Λ_m (Ω^{-1} mol^{-1} cm^2)
				% C	% H	% N	
L ($C_{11}H_{10}N_2O$)	Brown (85)	186.21	180	70.86 (70.95)	5.32 (5.41)	15.05 (15.04)	–
$CuC_{11}H_{12}N_2O_2Cl_2$	Black (60)	338.67	>300	39.19 (39.01)	3.94 (3.57)	8.50 (8.27)	12
$NiC_{11}H_{14}N_2O_3Cl_2$	Dark brown (70)	351.86	>300	37.66 (37.55)	4.37 (4.01)	7.40 (7.96)	15
$FeC_{11}H_{14}N_2O_3Cl_3$	Black (80)	384.45	>300	34.54 (34.37)	3.05 (3.67)	7.39 (7.29)	10
$CoC_{11}H_{18}N_2O_5Cl_2$	Dark brown (55)	388.11	>300	34.34 (34.04)	5.72 (4.67)	7.22 (7.22)	16
$ZnC_{15}H_{18}N_2O_6$	Black (60)	387.69	>300	46.27 (46.47)	4.44 (4.68)	7.54 (7.22)	15
$HgC_{15}H_{18}N_2O_6$	Dark brown (70)	522.91	>300	34.78 (34.47)	3.23 (3.47)	5.11 (5.36)	20
$LaC_{11}H_{12}N_5O_{11}$	Black (85)	529.15	>300	24.87 (24.97)	2.20 (2.28)	13.77 (13.24)	87
$SmC_{33}H_{32}N_6O_{16}Cl_3$	Black (65)	1025.35	>300	38.12 (38.66)	3.59 (3.15)	8.22 (8.19)	320

that their metal complexes have found various applications and play an important role in biological systems [1–3]. Heterocyclic compounds such as furan and related molecules are good ligands due to the presence of one or more ring oxygen atoms with a localized pair of electrons [4–7]. Also, these heterocyclic compounds have found increased interest in the context of bioinorganic chemistry [8,9]. The high affinity for the chelation of the Schiff bases towards the transition metal ions is used in preparing their solid complexes. Schiff base ligands are able to coordinate many different metals [10–17] and to stabilize them in various oxidation states. Moreover, luminescent compounds are attracting much current research interest because of their many applications including emitting materials for organic light emitting diodes, light harvesting materials for photocatalysis and fluorescent sensors for organic or inorganic analyses [16–20]. Several Schiff bases have recently been investigated as corrosion inhibitors for various metals and alloys in acid media [21–27]. Inhibitors are generally used to reduce corrosive attack of the acid solutions on metallic material. Many symmetrical bis tetradentate Schiff bases of 1,2-diamines with *o*-hydroxy aldehydes/ketones have been prepared and studied intensively [28]. However, much less attention has been focused on unsymmetrical Schiff bases derived from 1,2-diamines and different aldehydes/ketones. The present study deals with the preparation and characterization of heterocyclic Schiff base ligand, 2-[(2-furylmethylene)]phenylenediamine, and its complexes with Cu(II), Ni(II), Fe(III), Co(II), Zn(II), Hg(II), La(III) and Sm(III).

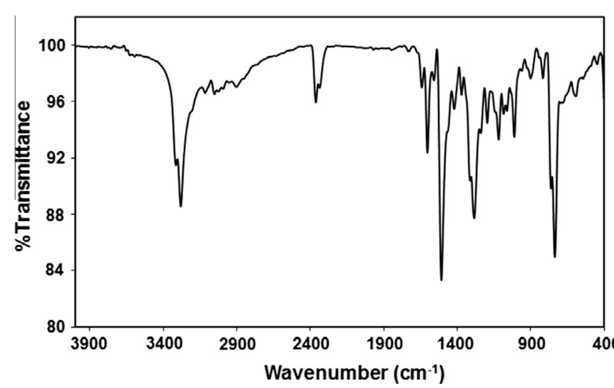

Fig. 1. IR spectrum of L ligand.

Table 2
IR data (4000–400 cm^{-1}) of the Schiff base ligand and its complexes.

Compound	IR data[a] (cm^{-1})					
	$\nu_{(NH2)}$ or $\nu_{(OH)}$	$\nu_{C=N}$	ν_{C-O-C} (furan)	ν_{M-O} (furan)	ν_{M-N}	Other bands
L	3315(s) 3282(s)	1603(s)	1240(m)	–	–	–
$[Cu(L)(Cl)_2]\cdot H_2O$	3418(b)	1613(s)	1253(m)	464(w)	444(w)	–
$[Ni(L)(Cl)_2]\cdot 2H_2O$	3352(b)	1617(s)	1235(m)	532(w)	449(w)	–
$[Fe(L)(Cl)_3H_2O]H_2O$	3372(b)	1608(s)	1254(w)	527(w)	479(m)	–
$[Co(L)(Cl)_2(H_2O)_2]\cdot 2H_2O$	3365(b)	1623(s)	1251(w)	546(w)	465(w)	–
$[Zn(L)(AcO)_2]H_2O$	3315(s) 3275(s) 3190(b)	1600(w)	1245(w)	545(w)	453(w)	1509; $\nu_{as}(COO^-)$, 1448; $\nu_s(COO^-)$ bidentate
$[Hg(L)(AcO)_2]H_2O$	3190(b)	1612(s)	1250(m)	530(w)	447(w)	1496; $\nu_{as}(COO^-)$, 1405; $\nu_s(COO^-)$ bidentate
$[La(L)(NO_3)_2]NO_3H_2O$	3388(b)	1644(s)	1243(w)	528(w)	450(w)	1461, 1145, 1331, 814; $\nu(NO_3^-)$ bidentate 1384; $\nu(NO_3^-)$ ionic
$[Sm(L)_3](ClO_4)_3H_2O$	3171(b)	1599(s)	1258(m)	531(w)	457(w)	1102, 623; $\nu(ClO_4^-)$ ionic

[a] s, Strong; m, medium; w, weak; b, broad.