



SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL EVALUATION OF MIXED LIGAND COMPLEXES OF MANGANESE(II), COBALT(II), COPPER(II), NICKEL(II) AND MERCURY(II) WITH 1,10-PHENANTHROLINE AND A BIDENTATE SCHIFF BASE

Rehab K. Al-Shemary^{[a]*}, Ahmed T. Numan^[a] and Eman Mutar Atiyah^[a]

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A Schiff base (L, [2,2'-(1E,1'E)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dibenzaldehyde]) has been synthesized by reacting *o*-phthalaldehyde with ethylenediamine and characterized with spectral studies and elemental analysis. Mixed ligands complexes of Mn (II), Co (II), Cu (II), Ni (II) and Hg (II) with 1,10-phenanthroline and the Schiff base have been prepared and characterized. The results indicated tetrahedral and square planar structure for the complexes. Biological activity of the ligands and complexes against four selected bacteria viz. *Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli* and *Pseudomonas* were also examined. Some of the complexes exhibit good antibacterial activities.

* Corresponding Authors

E-Mail: drrehabalshemary@gmail.com

[a] Department of Chemistry, College of Education for Pure Sciences, Ibn -Al-Haitham, University of Baghdad, Baghdad, Iraq

Introduction

In recent years, there has been renewed interest in the synthesis and study of mixed ligand transition metal complexes. The utility aspects of these complexes have received their share of attention as these have found applications in diverse fields.¹ Chiral metal complexes are well known for their use as catalysts, especially in asymmetric synthesis.² Organic compound containing imino group have both salt forming and coordinating properties. The resulting imino complexes are generally insoluble in polar solvents and soluble in non-polar solvents and hence are very important from analytical point of view the studies of simple metal-imino complexes are available in the literature but a very little work has been done on their mixed ligand complexes.^{3,4}

Schiff bases derived from aromatic aldehydes and substituted aliphatic amines and have a large diversity of enforcements in many ranges, e.g. analytical,⁶ inorganic⁷ and biological chemistry.⁸ Schiff bases and their metal complexes are renowned to offer anticancer,⁹ antioxidant¹⁰ and anti-inflammatory activities.¹¹ Many transition metal complexes with oxygen and nitrogen donor Schiff bases possess unusual configuration, structural liability and are sensitive to the molecular environment.¹² Schiff bases are a significant class of ligand in coordination chemistry and find extensive utilities in different fields.¹³ Schiff bases derived from pyridoxal and amino acids are considered very important ligands from the biological point of view.¹⁴ Transition metal complexes of such ligands are important enzyme models.¹⁵ The rapid development of these ligands

resulted in an enhanced research activity in the field of coordination chemistry leading to very interesting conclusions.¹⁶ Mixed ligand complexes have been found to act as an active catalyst in reactions of industrial importance including hydrogenation, hydrogen formation, and oxidative hydrolysis of olefins and carboxylation of methanol.¹⁷ These complexes have also shown catalytic activity in various oxidation reactions of environmental and biological importance.¹⁸ Presently, we have been undertaken a study of mixed ligand complexes of some transition metal ions with 1,10-phenanthroline (phen) and a Schiff base (L) derived from *o*-phthalaldehyde and ethylenediamine.

Experimental

Material

All materials applied in this research are of analytical reagent grade and were applied as received.

Methods

NMR spectra of the compounds were determined on "Bruker Spectrospin Ultrashield Magnets 300 MHz" instrument using TMS as an internal standard and DMSO-d₆ as a solvent at Sharif University of Technology in Iran. The shifts are expressed as δ ppm. FT-IR spectra were recorded on "SHIMADZU FTIR-8400 spectrophotometer" on KBr disc. The chloride content for complexes was determined using potentiometric titration method on 686-Titro Processor-665 Dosim A-Metrohm /Swiss. {Magnetic susceptibility} instrument measurements were recorded applying Bruker BM6 instrument at 298 K. Elemental analysis (C, H, and N) was put into Perkin Elmer 2400 series II CHN Analyzer. Melting points were determined by applying Digimelt kind start melting point instrument. The proposed molecular structures of the compounds were drawn by using chem. Office program, 3DX (2006).

Table 1. Some physical properties of the ligand (L) and its complexes.

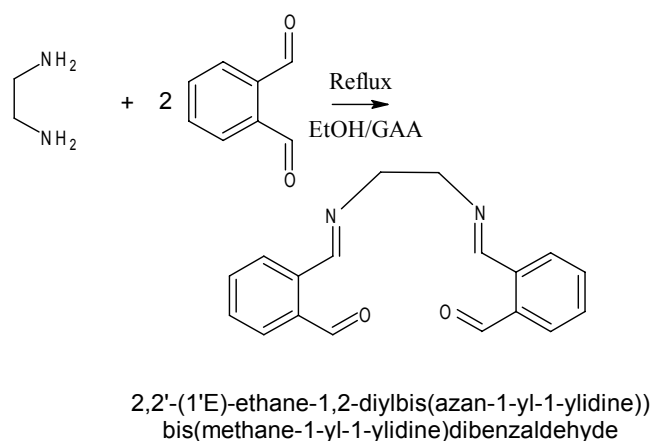
Compounds	Empirical formula	MW	Yield, %	M. p. °C	Colour	Analysis (Calc.), Found			
						C	H	N	Metal
L	C ₁₈ H ₁₆ N ₂ O ₂	292.33	81	171	Dark brown	(73.95) 73.67	(5.52) 5.40	(9.58) 9.21	-
[Co(phen)(L)]Cl ₂	C ₃₂ H ₂₈ Cl ₂ CoN ₄ O ₂	630.43	70	232	Greenish blue	(60.97) 60.38	(4.48) 4.21	(8.89) 8.08	(9.35) 9.20
[Ni(phen)(L)]Cl ₂	C ₃₂ H ₂₈ Cl ₂ N ₄ NiO ₂	630.19	68	267	Greenish yellow	(60.99) 60.64	(4.48) 4.21	(8.89) 8.60	(9.31) 9.30
[Mn(phen)(L)]Cl ₂	C ₃₂ H ₂₈ Cl ₂ MnN ₄ O ₂	626.43	75	261	Pale brown	(61.35) 60.88	(4.51) 4.47	(8.94) 8.74	(8.77) 8.35
[Cu(phen)(L)]Cl ₂	C ₃₂ H ₂₈ Cl ₂ CuN ₄ O ₂	635.04	77	208	Green	(60.52) 60.19	(4.44) 4.32	(8.82) 8.56	(10.01) 9.80
[Hg(phen)(L)]Cl ₂	C ₃₂ H ₂₈ Cl ₂ HgN ₄ O ₂	772.09	82	221	Off -white	(49.78) 49.69	(3.66) 3.32	(7.26) 7.16	(25.98) 25.35

Table2. Infrared spectral data (cm⁻¹) for the ligand (L) and its complexes.

Compounds	$\nu(\text{C-H})_{\text{arom}}$	$\nu(\text{C-H})_{\text{aliph}}$	$\nu(\text{C=O})$	$\nu(\text{C=N})_{\text{imine}}$	$\nu(\text{C=C})$	M – N	M – O
L	3007	2906	1710	1639	1535	-	
[Co(phen)(L)]Cl ₂	3059	2920	1712	1624, 1581	1527	528	424
[Ni(phen)(L)]Cl ₂	3034	2920	1712	1623, 1582	1528	523	448
[Mn(phen)(L)]Cl ₂	3024	2922	1712	1621, 1580	1531	502	428
[Cu(phen)(L)]Cl ₂	3003	2935	1712	1672, 1666	1529	527	438
[Hg(phen)(L)]Cl ₂	3041	2937	1712	1622, 1586	1530	517	450

Synthesis of Schiff base ligand

The ligand (L) was synthesized, as given in Scheme 1, by the usual condensation reaction¹⁰ in which (0.27g, 2 mmol) of *o*-phthalaldehyde, dissolved in 10 mL of methanol, was added to solution contain (0.06 g, 1 mmol) of ethylenediamine dissolved in 10 mL of methanol with continuous stirring. Three drops of glacial acetic acid was added. After complete addition, the reaction mixture was heated under reflux for about 4 h. The volume of reaction mixture was reduced by slow evaporation at room temperature. Then isolated compound was purified by recrystallization from a hot of ethanol (10 mL), to get a pure product of ligand, Yield: 81 %, m. P. 171 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ = 2.479 (DMSO), 5.38 (2H, CH₂), 7.31-8.28 (m, 5H, C₆H₅), 10.38 (1H, HCO), 8.78-8.85 (m, 1H, HC=N). ¹³C NMR δ = 40.8 (DMSO), 56.70, 61.84 (CH₂), 101.41(=C-N), 128.50-141.13(C₆H₅), 160.05(C=O), 192.87 (C=N).

**Scheme 1.** Synthesis of ligand L.

General procedure of preparation of metal complexes

An aqueous solution (1 mmol) of the metal salts was added gradually with stirring to a methanolic KOH solution (0.29 g, 1 mmol) of the Schiff base. A methanolic solution of 1,10-phenanthroline (0.18 g, 1 mmol) was added to the mixture keeping the stoichiometric ratio of 1:1:1 in each case. The mixture was refluxed with constant stirring for about 2 h. The mixture was cooled to room temperature. The coloured product formed was filtered then recrystallized from ethanol.¹¹

Antimicrobial Screening

The ligand and its complexes were tested against bacteria. Antibacterial testing was done by (MIC) the paper disc method.¹¹ The bacterial applied are *Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli* and *Pseudomonas aeruginosa* and *Escherichia coli*. Cultures of screen bacteria were preserved in nutritive agar environments and sub-cultured in Petri dishes prior to screening at 10⁻³ mol L⁻¹ concentration.

Results and Discussion

The compounds were soluble in ethanol, methanol, acetone, DMF and DMSO and insoluble in water. Some physical properties of ligand, L, and its complexes are given in Table 1. The important bands observed in the FT-IR of L and the complexes are given in Table 2. The ^1H and ^{13}C NMR spectra of Schiff base ligand can be seen in Figs. 1 and 2.

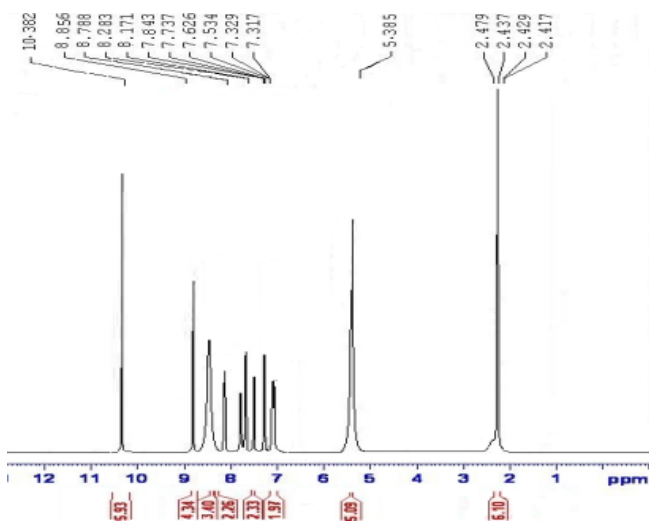


Figure 1. ^1H NMR spectrum of the Schiff base ligand

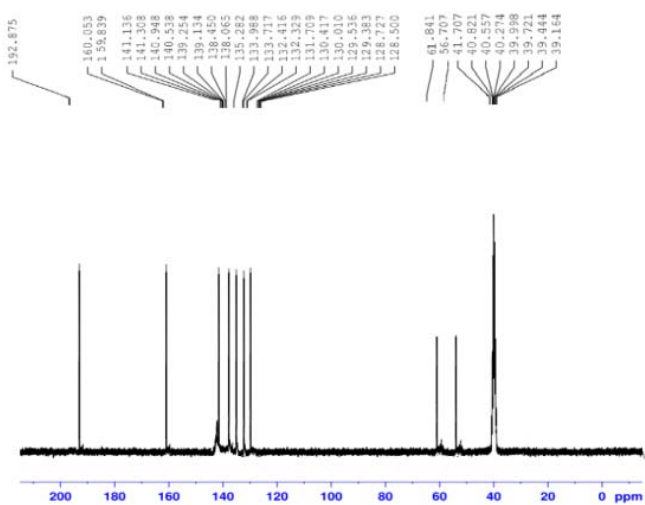


Figure 2. ^{13}C NMR spectrum of the Schiff base ligand

FT-IR spectra

The infrared spectra of L show intense band appearing at 1710 cm^{-1} was attributed to carbonyl group of the *o*-phthalaldehyde compound,¹² on complexation no shifting were observed from this band. In the free Ligand, the peak appeared at 1639 cm^{-1} was assigned to the $\nu(\text{C}=\text{N})$ stretching mod. In complexes this band was shifted to lower regions, 1621 cm^{-1} , 1624 cm^{-1} , 1623 cm^{-1} , 1626 cm^{-1} and 1622 cm^{-1} for Mn(II), Co(II), Ni(II), Cu(II) and Hg(II) complexes respectively, suggesting the coordination of azomethine nitrogen to metal the absorption band belonging vibration of $\nu(\text{C}=\text{N})$ imine group have been found in range between $1586\text{--}1580\text{ cm}^{-1}$ proposing

the potential of the chelation of 1,10-phenanthroline through the nitrogen atom at the imine mintoy.¹³ The FT-IR of prepared complexes have shown new bonds in range $528\text{--}502\text{ cm}^{-1}$ which were attributed to $\nu(\text{M-N})$ mode. The other new bonds in range $450\text{--}424\text{ cm}^{-1}$ which were attributed to $\nu(\text{M-O})$ mode. According to the results obtained and spectral analysis a tetrahedral and square planer have been suggested for these complexes.¹⁴

Electronic spectra, magnetic moments and conductivity measurements

The electronic spectrum of L exhibits high intense absorption peaks at 252 nm and 300 nm which have been assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transition respectively.¹⁵

The UV-Vis spectra of the complexes displayed absorption at the range 276-284 nm and 350-383 nm, assigned to the ligand field and charge transfer transitions.

In the UV-Vis spectrum of $[\text{Mn}(\text{phen})(\text{L})]\text{Cl}_2$, the band at 570 nm is attributed to (d-d) transition of type ${}^6\text{A}_{1(\text{P})}\rightarrow{}^4\text{E}_{(\text{G})}$, the $[\text{Co}(\text{phen})(\text{L})]\text{Cl}_2$ complex, showed band at 857 nm which has been attributed to d-d transition of types ${}^4\text{A}_2\rightarrow{}^4\text{T}_1$ transition.¹⁶ The electronic spectrum of $[\text{Cu}(\text{phen})(\text{L})]\text{Cl}_2$ showed one intense peak in 608 nm which is due to (d-d) transition of type ${}^2\text{B}_2\rightarrow{}^3\text{A}_{2(\text{F})}$ transition.¹⁷ The electronic spectrum of $[\text{Ni}(\text{phen})(\text{L})]\text{Cl}_2$ displayed one intense peak in 738 nm which is due to d-d transition of type ${}^4\text{T}_2\rightarrow{}^4\text{A}_2$ transition.¹⁸ The band at 363 nm in the spectrum of $[\text{Hg}(\text{phen})(\text{L})]\text{Cl}_2$ has been assigned to charge transfer, since Hg is a d^{10} system.

The magnetic moment of the complexes of Mn (II), Co (II) and Cu (II) are 4.96, 4.78 and 2.01 B.M., respectively, consistent with a tetrahedral geometry.¹⁹

The molar conductivities indicate that all metal complexes are 1:2 electrolytes in ethanol as a solvent. These data together with magnetic moment indicate tetrahedral geometry around the Mn(II), Co(II), Cu(II) and square planar geometry around Ni(II) atom.²⁰

Antibacterial activity studies

Finally, the antibacterial activity of the ligands and their complexes has also been tested against selected type of bacteria viz. *Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli* and *Pseudomonas aeruginosa*. The results (Table 3) show that all complexes have relatively high deactivating capacity. The ligand L possessed no activity towards the same species of bacteria.^{21,22}

Compound	<i>E. Coli</i>	<i>S. aureus</i>	<i>B. cereus</i>	<i>P. aeruginosa</i>
L	-	1	4	2
$[\text{Co}(\text{phen})(\text{L})]\text{Cl}_2$	3	7	10	13
$[\text{Ni}(\text{phen})(\text{L})]\text{Cl}_2$	5	8	11	9
$[\text{Mn}(\text{phen})(\text{L})]\text{Cl}_2$	9	12	9	12
$[\text{Cu}(\text{phen})(\text{L})]\text{Cl}_2$	6	10	6	8
$[\text{Hg}(\text{phen})(\text{L})]\text{Cl}_2$	7	8	12	10

Table 3. Diameter of zone of inhibition (mm).

The increase in the antimicrobial activity of the complexes may be due to the metal chelation. From comparative analysis as shown in the Table 3, it is absorbed that all the metal complexes are more potent biotical than the ligand.

Conclusion

The mixed complexes were obtained as coloured powdered materials and were characterized using FT-IR, electronic spectra, and magnetic measurements. The elemental analyses were in good agreement with the complexes. From the antimicrobial activity data, it is observed that the complexes exhibit higher activity than the free ligand. The increase in the antimicrobial activity of the complexes may be due to the metal chelation. From comparative analysis as shown in the Table 3 it is observed that all the metal complexes are more potent biotical than the free ligand.

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