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Synthesis, Characterization and Antimicrobial Studies of Co(II), Ni(II) and Cu(II) Complexes Derived From α-Amino acetohydroxamic acid

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Abstract

A new Schiff base ligand 2,3-bis (α-imino acetohydroxamic acid) butane has been synthesized by the condensation of α-amino acetohydroxamic acid and Butane-2,3-dione. The transition metal complexes of Co(II), Ni(II) and Cu(II) with Schiff base have been prepared from metal salts in an alcoholic medium. The synthesized Schiff base and its transition metal complexes were characterized by elemental analysis, molar conductance measurements, magnetic susceptibility, FTIR and electronic absorption spectral data. The elemental analysis of the transition metal complexes indicate that the metal complexes are monomeric in nature. The metal complexes have general formula $[M(L)(X)_2]$, where X=water, ammonia, quinoline, phenyl isocyanide and pyridine. The lower molar conductance values of these metal complexes show their non-electrolytic in nature. The broad and strong band due to vibrations of ν(OH) and ν(N-H) of Schiff base located at 3160 cm^{-1} which disappears in all the metal complexes and a new broad band appears at 3320 cm^{-1} confirming the presence of at least one free -OH group with a very weak H-bonding even in the complexes. The band position due to ν(C=N) and ν(C-N) located at 1650 cm^{-1} and 1440 cm^{-1} in the ligand is also shifting to lower frequency in the complexes, which suggest the coordination of the two imine nitrogen atoms of the ligand in the complexes. The two nitrogen atoms of hydroxamic acid and two nitrogen atoms of azomethine group are the bonding sites of ligand. On the basis of elemental analysis, magnetic moment and spectral data indicates distorted high spin octahedral structure for metal complexes. The synthesized Schiff base complexes exhibit higher antimicrobial activity than the free Schiff base ligand due to chelation.

Keywords: Schiff base, Butane-2,3-dione, α-amino acetohydroxamic acid, Metal complexes, Antimicrobial activity.

Introduction

Schiff bases are formed when condensation of primary amines with carbonyl compounds under specific conditions and were first synthesized by Hugo Schiff in 1864. Schiff bases are represented as R – CH = N – R^1 where R and R^1 may be alkyl, aryl or heterocyclic. Azomethine functional group present in Schiff bases. Due to effective conjugation Schiff bases of aromatic aldehydes are more stable than aliphatic aldehydes. Ketones react slower than aldehydes in condensation reaction due to steric hinderance. Schiff bases are generally bidentate, tridentate, tetradentate and polydentate ligands to form stable complexes with transition metal ions. Schiff bases are effective ligands due to presence of azomethine group. Schiff bases derived from aromatic carbonyl compounds and primary amines have more applications in the fields of biological, analytical, inorganic chemistry, catalysis and optical materials. Schiff base ligands have donor atoms may be nitrogen, oxygen or Sulphur which provided binding sites through non- bonding electrons. The presence of ─ CH =N group in the transition metal complexes which contains donor nitrogen atom is responsible for stability, reactivity and biological activity of complexes. Transition metal Schiff base complexes are wide applications in medicinal chemistry, catalysis, polymerization reactions, dyes, corrosion, plant growth regulators and analytical chemistry. Due to chelation transition metal Schiff base complexes are more stable and have wide applications in antibacterial, antifungal, antiviral, anticancer, and anti-inflammatory. Schiff base ligands acts as chelating ligands and their biological activity enhanced on coordination. First of all, hydroxamic acid was reported due to the reaction of hydroxyl amine on diethyl oxalate by H. Lossen in 1869. Hydroxamic acids are prepared by the reaction of hydroxyl amine on organic esters or its derivatives in presence of sodium ethoxide. Yoe et al., have reported that hydroxamic acid behave as a bidentate chelating agent having complexing sites both of carbonyl and hydroxyl in which hydroxyl loses a proton on forming a chelate. The hydroxamic acids are acidic in nature like phenols and carboxylic acids.

The present aim of the work is to synthesize a Schiff base derived from α- amino acetohydroxamic acid and to prepare its transition metal complexes, characterize them and study their antibacterial and antifungal activities.

Experimental

Chemicals and Reagents

The chemicals used in present work were obtained From BDH and were used without purification. DMF, ethanol, glycine ethyl ester hydrochloride, hydroxylamine hydrochloride, metal salts were obtained from Sigma Aldrich or BDH extra pureE. Merck.

Physical Measurements

The percentage (%) of Co, Ni and Cu were determined by EDTA complexometric titration. The elemental analysis (C, H and N) data was obtained using 2400 CHN Perkin-Elmer elemental analyzer. The molar conductivity of the complexes in DMF solution (10^{-3}M) were measured by using DI-909 digital conductivity meter. The IR spectra of the ligand and metal complexes were recorded on Shimadzu FTIR spectrophotometer using KBr disc. The magnetic susceptibility data were measured By Gouy method using Hg [Co $(SCN)_4$] as a calibrant. The electronic spectra of the complexes were recorded by using Shimadzu model UV-1601 spectrophotometer in DMSO solution.

Synthesis of Schiff base Ligand

The Schiff base ligand 2,3-bis (α-imino acetohydroxamic acid) butane was prepared by adding 0.01 molof butane-2,3-dione in 25 ml ethanol and 0.02 mol of α-imino acetohydroxamic in 25 ml ethanol. The reaction mixture was refluxed for 2-3 h. On cooling the reaction mixture, the crystalline solid was formed. The precipitate is washed with cold ethanol and dried over KOH placed in a desiccator to obtain the required Schiff base. The compound was further analysed and found to the molecular formula $C_8H_{14}O_4N_4$.

Synthesis of Metal Complexes

The metal complexes were prepared by mixing (50 ml) ethanolic solution of $CoCl_2.6H_2O$ / $NiCl_2.6H_2O$ / $CuCl_2.2H_2O$ with the (50 ml) ethanolic solution of Schiff base in a metal-ligand ratio 1:1. The resulting mixture was refluxed on water bath for 2-3 h. The complex obtained in each time was cooled, filtered and washed with ether and recrystallized with ethanol and dried over KOH in a desiccators.

Results and Discussion

All the metal complexes are colored, solid and stable at room temperature. They decompose on heating at high temperature. The analytical data of the metal complexes are presented in Table 1-3. The metal ligand ratio in all the metal complexes have 1:1.Schiff base acts as tetradentate ligand. The molar conductivities in DMF solution show that all metal complexes are non-electrolytic nature.

Table-1 Analytical data of Co(II) complexes

Compounds	Elemental analysis Found (Calcd) %			
	C	H	N	Metal(M)
$[Co(C_8H_{14}O_4N_4)\ (H_2O)_2]$	29.60(29.73)	4.98(4.95)	17.41(17.34)	18.10(18.25)
$[Co(C_8H_{14}O_4N_4)\ (NH_3)_2]$	29.78(29.91)	5.65(5.60)	26.25(26.17)	18.21(18.35)
$[Co(C_8H_{14}O_4N_4)\ (C_9H_7N)_2]$	57.12(57.25)	4.80(4.77)	15.46(15.41)	10.64(10.80)
$[Co(C_8H_{14}O_4N_4)\ (C_6H_5NC)_2]$	53.40(53.56)	4.50(4.46)	17.10(17.04)	11.76(11.94)
$Co(C_8H_{14}O_4N_4)\ (C_5H_5N)_2]$	48.38(48.55)	4.98(4.95)	18.96(18.88)	13.08(13.23)

Table-2 Analytical data of Ni(II) complexes

Compounds	Elemental analysis Found (Calcd) %			
	C	H	N	Metal(M)
$[Ni(C_8H_{14}O_4N_4)\ (H_2O)_2]$	29.60(29.74)	4.98(4.95)	17.42(17.36)	18.10(18.19)
$[Ni(C_8H_{14}O_4N_4)\ (NH_3)_2]$	29.80(29.94)	5.66(5.62)	26.24(26.19)	18.20(18.31)
$[Ni(C_8H_{14}O_4N_4)\ (C_9H_7N)_2]$	57.15(57.27)	4.82(4.77)	15.48(15.42)	10.62(10.77)
$[Ni(C_8H_{14}O_4N_4)\ (C_6H_5NC)_2]$	53.40(53.56)	4.50(4.46)	17.10(17.04)	11.81(11.94)
$[Ni(C_8H_{14}O_4N_4)\ (C_5H_5N)_2]$	48.42(48.57)	4.98(4.94)	18.96(18.88)	13.08(13.19)

Table-3 Analytical data of Cu(II) complexes

Compounds	Elemental analysis Found (Calcd) %			
	C	H	N	Metal(M)
$[Cu(C_8H_{14}O_4N_4)\ (H_2O)_2]$	29.20(29.31)	4.90(4.87)	17.20(17.08)	19.22(19.39)
$[Cu(C_8H_{14}O_4N_4)\ (NH_3)_2]$	29.32(29.49)	5.54(5.52)	25.92(25.80)	19.36(19.51)
$[Cu(C_8H_{14}O_4N_4)\ (C_9H_7N)_2]$	56.60(56.77)	4.76(4.72)	15.40(15.31)	11.42(11.57)
$[Cu(C_8H_{14}O_4N_4)\ (C_6H_5NC)_2]$	52.90(53.06)	4.47(4.42)	16.96(16.88)	12.61(12.76)
$[Cu(C_8H_{14}O_4N_4)\ (C_5H_5N)_2]$	47.95(48.04)	4.92(4.89)	18.76(18.68)	14.08(14.13)

Table-4 Electrical conductance and magnetic moment data of Co(II) complexes

Complexes	Colour	Molar conductivity $(\Omega^{-1}\ cm^2\ mol^{-1})$	Solvent	Magnetic moment (B.M)	Nature
$[Co(C_8H_{14}O_4N_4)\ (H_2O)_2]$	Brown	18	DMF	4.96	Paramagnetic
$[Co(C_8H_{14}O_4N_4)\ (NH_3)_2]$	Brown	24	DMF	4.90	Paramagnetic
$Co(C_8H_{14}O_4N_4)\ (C_9H_7N)_2]$	Light brown	12	DMF	4.98	Paramagnetic
$[Co(C_8H_{14}O_4N_4)(C_6H_5NC)_2]$	Light brown	10	DMF	4.80	Paramagnetic
$[Co(C_8H_{14}O_4N_4)\ (C_5H_5N)_2]$	Pale brown	08	DMF	4.86	Paramagnetic

Table-5 Electrical conductance and magnetic moment data of Ni(II) complexes

Complexes	Colour	Molar conductivity $(\Omega^{-1}\ cm^2\ mol^{-1})$	Solvent	Magnetic moment (B.M)	Nature
$[Ni(C_8H_{14}O_4N_4)\ (H_2O)_2]$	Light green	24	DMF	2.96	Paramagnetic
$[Ni(C_8H_{14}O_4N_4)\ (NH_3)_2]$	Greenish white	16	DMF	3.00	Paramagnetic
$[Ni(C_8H_{14}O_4N_4)\ (C_9H_7N)_2]$	Green	18	DMF	2.96	Paramagnetic
$[Ni(C_8H_{14}O_4N_4)(C_6H_5NC)_2]$	Pale green	14	DMF	2.90	Paramagnetic
$[Ni(C_8H_{14}O_4N_4)\ (C_5H_5N)_2]$	Light green	16	DMF	2.96	Paramagnetic

Table-6 Electrical conductance and magnetic moment data of Cu(II) complexes

Complexes	Colour	Molar conductivity $(\Omega^{-1}\ cm^2\ mol^{-1})$	Solvent	Magnetic moment (B.M)	Nature
$[Cu(C_8H_{14}O_4N_4)\ (H_2O)_2]$	Deep green	26	DMF	2.10	Paramagnetic
$[Cu(C_8H_{14}O_4N_4)\ (NH_3)_2]$	Light green	24	DMF	2.00	Paramagnetic
$[Cu(C_8H_{14}O_4N_4)\ (C_9H_7N)_2]$	Green	28	DMF	1.94	Paramagnetic
$[Cu(C_8H_{14}O_4N_4)(C_6H_5NC)_2]$	Green	18	DMF	1.96	Paramagnetic
$[Cu(C_8H_{14}O_4N_4)\ (C_5H_5N)_2]$	Light green	20	DMF	1.92	Paramagnetic

IR Spectra

The important infrared spectral bands of the Schiff base and its metal complexes are listed in Table 7-8. The coordination sites in chelate compounds are determined by the IR spectra of free ligand compared with that of complexes. The IR spectrum of the synthesized Schiff base ligand showed absorption band at 1650 $cm^{-1}$is characteristic of azomethine (>C=N) group present in the Schiff base ligand. This band was shifted to lower regions (1590 cm^{-1}) in the metal complexes, which indicates the bonding of the metal to the azomethine nitrogen. A sharp and strong band at 1080 cm^{-1} due to vibration of ν(N-O) present in hydroxamic acid moiety of the ligand. Deprotonation of hydroxamic acid to form dinegative ion.

The Schiff base ligand act as dianionic tetradentate which coordinate through two imine nitrogen atoms and two oxime nitrogen atoms with the metal ions. The broad and strong band due to vibrations of ν(N-H) and $\nu(O-H)$ of the ligand at 3160 cm^{-1} disappears in all the metal complexes and a new band appears at 3320 cm^{-1} which confirming the presence of one free -OH group in the complexes. A new band appearing in the low frequency range 450 cm^{-1} are indicate the formation of M-N bond in the complexes.

Table-7 I.R spectral data of Schiff base

I.R band (cm^{-1})	Nature	**Assigns**
3160	Strong /broad	$\nu(O-H)+\nu(N-H)$
2970	Broad / weak	$\nu(C-H)$
1850	Broad / strong	$\nu(C-CH3)$
1650	Broad / strong	$\nu(C=N)$
1440	Broad / weak	$\nu(C-N)$
1080	Broad / strong	$\nu(N-O)$

Table-8 I.R spectral data of metal complexes

I.R band (cm^{-1})	Nature	**Assigns**
3320	Strong /broad	$\nu(O-H)$
2940	Broad / weak	$\nu(C-H)$
2180	Broad / weak	$\nu(Phenyl\ isocyanide)$
1590	Broad / strong	$\nu(C=N)$
1420	Broad / strong	$\nu(C-M)$
1130	Broad / strong	$\nu(N-O)$

Magnetic moment and electronic spectra

The electronic spectrum of Co (II) complexes, the absorption bands at 248 nm and 396 nm assigned to intra ligand charge transfer and $^3T_{1g} \rightarrow {}^3T_{2g}$ transitions. The magnetic moment values for [Co(L)(X)$_2$]complexes have been found in the range of 4.80-4.96 B.M, which suggest high spin octahedral geometry. The electronic spectrum of Ni (II) complexes showed three bands at 228 nm, 330 nm and 432 nm corresponds to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(p)$ transitions. The magnetic moment values for [Ni(L)(X)$_2$] complexes have been found in the range of 2.90-3.00 B.M, which suggest octahedral geometry. The Cu(II) complexes show one broad and unsymmetrical band at 450 nm has been obtained due to $^2E_g \rightarrow {}^2T_{2g}$ transition. The magnetic moment values for [Cu(L)(X)$_2$] complexes have been found in the range of 1.92 -2.10 B.M, which suggest high spin octahedral geometry around Cu(II) ions.

Antimicrobial activity

The synthesized ligand and its complexes were screened for their in vitro antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* and antifungal activity against *Aspergillus niger* and *Candida albicans* by minimum inhibitory concentration method. The minimum inhibitory concentration profiles of all the compounds against bacteria and fungi are presented in Table 9. The MIC values indicated that all the complexes show more activity compared to the free ligand against microorganisms, and this activity is found to be enhanced on coordination with the metal ions.

This also can be explained on the basis of Tweedy's chelation theory and the effect of the metal ion on the normal cell processes. It was further noted that the delocalization of electrons over the whole chelate ring enhanced the lipophilicity of the complexes. This increased lipophilicity enhanced the penetration of the complexes into lipid membrane and blocking the metal sites on enzymes of microorganisms.

Table-9 Antimicrobial data of ligand and metal complexes

Compounds	Minimum inhibition concentration (mg /ml)			
	E. coli	*S. aureus*	*A. niger*	*C. albicans*
Schiff base	12	10	10	13
$[Co(L)(py)_2]$	14	13	12	15
$[Ni(L)(py)_2]$	15	14	11	14
$[Cu(L)(py)_2]$	18	16	13	16
Gentamicin	20	18	-	-
Clotrimazole	-	-	18	21

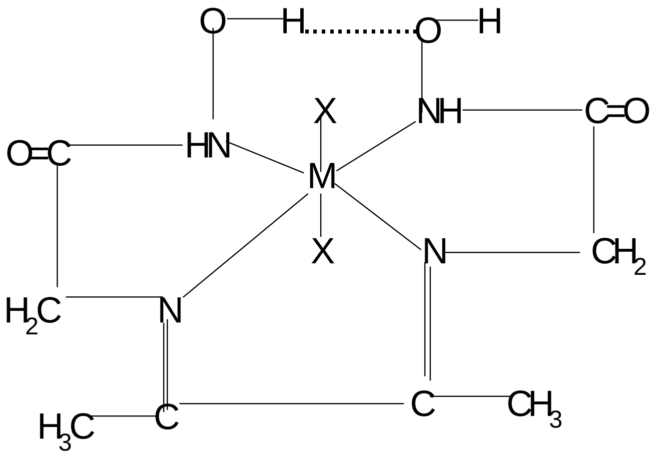

Fig 1. Proposed structure of metal complexes
X= Water, ammonia, pyridine, quinoline and phenyl isocyanide
M =Co (II), Ni (II) and Cu (II)

Conclusion

A new Schiff base has been prepared by the condensation of α- amino acetohydroxamic acid and Butane-2,3- dione. The metal complexes of Co (II), Ni (II) and Cu (II) were synthesized and characterized by analytical and spectroscopic techniques.The elemental analysis of the transition metal complexes indicate that the metal complexes are monomeric in nature. The metal complexes have general formula $[M(L)(X)_2]$, where X=water, ammonia, quinoline, phenyl isocyanide and pyridine. The lower molar conductance values of these metal complexes show their non-electrolytic in nature. The broad and strong band due to vibrations of ν(OH) and ν(N-H) of Schiff base located at 3160 cm^{-1} which disappears in all the metal complexes and a new broad band appears at 3320 cm^{-1} confirming the presence of at least one free -OH group with a very weak H-bonding even in the complexes. The band position due to ν(C=N) and ν(C-N) located at 1650 cm^{-1} and 1440 cm^{-1} in the ligand is also shifting to lower frequency in the complexes, which suggest the coordination of the two imine nitrogen atoms of the ligand in the complexes. The two nitrogen atoms of hydroxamic acid and two nitrogen atoms of azomethine group are the bonding sites of ligand. On the basis of elemental analysis, magnetic moment and spectral data indicates distorted high spin octahedral structure for metal complexes. The synthesized Schiff base complexes exhibit higher antimicrobial activity than the free Schiff base ligand due to chelation.

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