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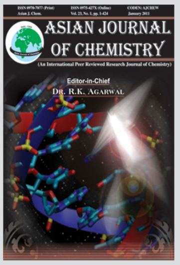

Synthesis, Spectroscopic, Electrochemical and Biological Studies of Co(II), Ni(II) and Cu(II) Complexes of 2-Hydroxybenzylidene-2'-hydroxyaniline

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In this paper, the synthesis, spectroscopic and electrochemical studies of cobalt(II), nickel(II) and copper(II) complexes of 2-hydroxybenzylidine-2'-hydroxyaniline (SAP) are reported. The antibacterial and antifungal activity of 2-hydroxybenzylidine-2'-hydroxyaniline and its Co(II), Ni(II) and Cu(II) complexes have been evaluated against the bacterial strains *E. coli*, *Staphylococcus aures*, *Salmonella typi* and the fungal strains *Aspergillus niger* by the disc diffusion method using agar as the nutrient medium. Co(II), Ni(II) and Cu(II) metal complexes were found to have more antibacterial activity than 2-hydroxybenzylidine-2'-hydroxyaniline.

Key Words: Synthesis, Co(II), Ni(II), Cu(II) Complexes, Schiff base, 2-Hydroxybenzylidene-2'-hydroxyaniline.

INTRODUCTION

Schiff bases and their metal complexes continue to play a significant role in inorganic, bioinorganic and coordination chemistry. Complex formation studies involving Schiff bases derived from salicylaldehyde with amines and amino phenols have been studied extensively[1-4]. Many 'salen' based complexes have shown catalytic properties[5-9]. Copper(II) complexes containing various Schiff bases and their derivatives are of great interest, since they exhibit various biological activities such as anticancer, antitumor, antibacterial, antifilarial and antiviral. Nickel(II) and copper(II) complexes having long chain pendant arms show liquid crystalline or mesogenic behaviour. Cobalt(II) complexes were found to be more biologically active. Cyclic voltammetric studies[10-13] can be undertaken to find out if a reaction is diffusion controlled, reversible, irreversible and number of electrons involved. Hence we report the synthesis, spectroscopic and electrochemical studies of Co(II), Ni(II) and Cu(II) complexes of 2-hydroxybenzylidene-2'-hydroxyaniline

EXPERIMENTAL

Copper(II) sulphate, nickel ammonium sulphate and cobalt acetate tetrahydrate were purchased and used as such. Salicylaldehyde and 2-aminophenol were distilled and used. Melting points of the compounds were determined with a Rider apparatus. Conductivity studies were carried out by an Elico conductivity CM 185 bridge and Elico conductivity cell. C, H, N analysis were performed by using CHNSO elemental analyser. IR spectra were obtained with ModelX99 IR spectrometer and UV studies were carried out by using Microprocessor UV/VIS spectrometer model 1371. CV studies were carried out by using 'Electrochemical analyzer C H instruments INC' with a Platinum working electrode, Platinum wire counter electrode and Ag/AgCl reference electrode.

Synthesis of 2-hydroxybenzylidene-2'-hydroxyaniline (SAP): Salicylaldehyde (1.2 g, 0.01 mol), 2-aminophenol (1 g, 0.01 mol) and alcohol (10 mL) were refluxed for 6 h with constant stirring. The contents poured into crushed ice, filtered, washed with water and diethyl ether sucessively and dried. Purified by recrystallization from alcohol. Red orange crystals. m.p. 175 ºC, Yield (60 %). IR (KBr, ν_{max}, cm^{-1}): 1631 (C=N), 1274 (C-O). UV-VIS (nm): λ_{max}: 250, 420.

Synthesis of [Co(SAP)$_2$(H$_2$O)$_2$]: Aqueous solution of cobalt acetate tetrahydrate (0.6 g, 0.02 mol) and SAP (1 g, 0.05 mol) in alcohol (10 mL)were refluxed for 4 h. Pourd the contents into crushed ice, washed with water, ether and dried. Recrystallized from alcohol. m.p. 220 ºC. Yield (60 %), IR (KBr, ν_{max}, cm^{-1}): 1604 (C=N), 1604 (C-O). UV-VIS (nm): λ_{max}: 250, 420, 550, 590, 850.

Synthesis of [Ni(SAP)$_2$]: Aqueous solution of nickel ammonium sulphate (1 g, 0.0025 mol) and SAP (1 g, 0.005 mol) in alcohol (10 mL) were refluxed for 6 h with continuous stirring. The brown precipitate formed was filtered, washed with water, ether and dried. Recrystallized from alcohol, m.p. 295 ºC. Yield (50 %). UV-Vis (nm): λ_{max}: 260, 330, 420, 700-720, 820-910.

Synthesis of [Cu(SAP)$_2$]: Neutral aqueous solution of copper sulphate (0.6 g, 0.024 mol) and SAP (1 g, 0.005 mol) in alcohol (10 mL)were refluxed for 6 h with continuous stirring. The green precipitate formed was filtered, washed with water, ether and dried. Recrystallized from alcohol. m.p. 300 ºC. Yield (65 %); UV-Vis (nm): λ_{max}: 250, 420, 550, 590.

RESULTS AND DISCUSSION

Hydroxyl Schiff base ligands derived from the reaction between salicylaldehyde and 2-aminophenol have been studied extensively in complex forming reactions.

Metal(II) complexes of [2-hydroxybenzylidine-2'-hydroxyaniline]: Mixture of 2-aminophenol, salicylaldehyde and rectified sprit were refluxed to get 2-hydroxybenzylidine-2'-hydroxyaniline. Alcoholic solution of this compound was refluxed with neutral solution of cobalt(II), nickel(II) and copper(II) in the molar ratio 2:1 to get the complex. It was purified by repeated recrystallization. The purity was checked by TLC. It was characterized through qualitative tests, functional group analysis, uv and ir spectral studies. Electrochemical properties and biological activity of the complexes are also studied. The colour and the melting point of metal(II) complexes are found to be different from the ligand SAP. Molar conductance of complexes are in the ranged from 5.22, 64.2 and 70.4 mhos cm^{-1} for M=Co, Ni and Cu, respectively. Metal(II) complexes do not show the usual reactions of the metal. However, after strong evaporation of the complex with concentrated nitric acid it gives the usual reactions of metal ions. The presence of nitrogen in the complex was confirmed by Lassaign's test. Elemental composition of ligand and complexes are in accordance with the formula proposed for them.

Spectral studies

Infrared: Various important infrared frequencies observed for the sap and the cobalt(II), nickel(II) and copper(II) complex are given in Table-1.

TABLE-1
KEY IR BANDS (cm^{-1}) OF 2-HYDROXYBENZYLIDENE 2'-HYDROXYANILINE (SAP) AND ITS METAL COMPLEXES

Group	SAP	[Co(SAP)$_2$(H$_2$O)$_2$]	[Ni(SAP)$_2$]	[Cu(SAP)$_2$]
C=N	1613	1604	1620	1614
=C-O	1275	1291	1294	1293
M-N	–	586	583	573
M-O	–	491, 444	431	447
O-H	3400-3500	3600	–	–

IR spectra of cobalt(II), nickel(II) and copper(II) complexes show a decrease of C=N stretch indicative of nitrogen co-ordination to the metal ion. In the cobalt(II), nickel(II) and copper(II) complexes of SAP the shift of phenolic CO stretch to higher frequency shows the oxygen coordination to the metal ion. From the IR spectral data, it is inferred that the N of C=N group and O of phenolic group are coordinated to the metal ion.

The electronic spectrum of the Schiff base shows absorption at 300 nm (33333) and 475 nm (21053). This can be assigned to >C=N moiety and phenolic -OH group, respectively. The transitions observed for the SAP complexes of Co(II), Ni(II) and Cu(II) around 40000 (250 nm), 33333 (300 nm) and 40000 (250 nm), respectively may be attributed to >C=N group and the transitions observed for same Schiff base complexes of Co(II), Ni(II) and Cu(II) around 23809 (480 nm), 22222 (450 nm) and 23529 (425 nm) respectively may be assigned to the phenolic group. Hence an octahedral geometry may be suggested for the complexes. Cobalt(II) complex of SAP gave rise to absorption 1-18518 bands in the region 10309 cm^{-1} (970 nm), 23809 cm^{-1} (420 nm) and 18181 cm^{-1} (510-540 nm). Hence an octahedral geometry may be suggested for the complex. From the elemental analysis it can be suggested that two molecules of SAP are co-ordinated as bidentate ligands through 'N' of azomethine group and 'O' of phenolic group and two water molecules are also coordinated. In the UV spectra of nickel(II) complex of SAP absorptions are observed at 23809 cm^{-1} (420 nm), 13888 cm^{-1} (720-700 nm) and a broad band at 10989-12195 cm^{-1} (910-820 nm). An octahedral geometry may be assigned for the complex. The electronic absorption spectrum of copper(II) complex shows an unsymmetrical band around 18181-16949 cm^{-1} (550-590 nm).

A copper(II) d^9 ion is characterized by large distortions from octahedral symmetry and therefore the band is broad and unsymmetrical. Hence a distorted octahedral geometry can be assigned to the copper(II) complex.

It is observed that the reaction of [Co(SAP)$_2$(H$_2$O)$_2$] involves two step process. There is not much deviation in E_P with scan rate (Table-2). The ratio between I_{Pa}/I_{Pc} is not equal to one. So the reaction may be quasi reversible.

Cyclic voltammogram of [Ni(SAP)$_2$] show E_P and ΔE_P changing with scan rate (Table-3). Peak current is propotional to the scan rate. I_{Pa}/I_{Pc} is not equal to one.

In [Cu(SAP)$_2$], peak current is propotional to square root of scan rate. E_P is found to be dependent on scan rate (υ). The anodic and cathodic peak current ratio is not equal to one. That is $I_{Pa}/I_{Pc} \neq 1$. Hence the reaction is irreversible. It can be concluded that the electrochemical reduction of SAP and the metal complexes is irreversible. The reduction of Ni(II) and Cu(II) complex is a one step process. But that of Co(II) complex is a two step process.

TABLE-2
CYCLIC VOLTAMMETRIC DATA FOR COBALT(II) COMPLEX OF 2-HYDROXYBENZYLIDENE-2'-HYDROXYANILINE

Scan rate (mV s^{-1})	E_{Pc} (mV)	E_{Pa} (mV)	I_{Pc} (μA)	I_{Pa} (μA)	E° (mV)	ΔE_P	I_{Pa}/I_{Pc}
150	24 -691	683	4.942×10^{-6} 1.926×10^{-6}	-1.265×10^{-6}	329.5	659	-0.25
250	-81 -503	486	3.541×10^{-6} 8.129×10^{-6}	-2.156×10^{-6}	202.5	405	-0.6
250	67 -583	593	3.943×10^{-6} 1.510×10^{-6}	-1.044×10^{-6}	263	526	-0.26
300	80 -522	564	3.275×10^{-6} 1.064×10^{-6}	-1.237×10^{-6}	484	484	-0.37

TABLE-3
CYCLIC VOLTAMMETRIC DATA FOR NICKEL(II) COMPLEX OF 2-HYDROXYBENZYLIDENE-2'-HYDROXYANILINE

Scan rate (mV s^{-1})	E_{Pc} (mV)	E_{Pa} (mV)	I_{Pc} (μA)	I_{Pa} (μA)	E° (mV)	ΔE_P	I_{Pa}/I_{Pc}
50	16	885	1.209×10^{-6}	-3.393×10^{-6}	450.5	869	-2.81
100	-351	788	2.544×10^{-6}	-2.505×10^{-6}	218.5	1139	-0.98
250	-600	637	1.001×10^{-6}	-1.144×10^{6}	18.5	1237	-1.14

Antibacterial activity: The antibacterial and antifungal activity of SAP and their Co(II), Ni(II) and Cu(II) complexes have been evaluated against the bacterial strains *E. coli*, *Staphylcoccus aureus* and *Salmonella typi* and the fungal strains *Aspergillus niger* by disc diffusion method using agar as the nutrient medium. Gentamicin and itracomazole were used as a standard for antibacterial and anti fungal activity, respectively. Cu(II), Ni(II) and Co(II) metal complexes were found to be have more antibacterial activity than SAP. But, anti fungal activity is less than SAP. In general metal complexes are more active than their ligands because the metal complexes may serve as a vehicle for activation of ligandsas the biological cytotoxic agents.

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