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RESEARCH ARTICLE

Synthesis, Spectral and Antibacterial Studies of Metal Complexes Derived from 2-[1-(2-Aminobenzylimino)-ethyl]phenol

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Abstract: A novel Schiff base ligand is derived from ortho-hydroxy acetophenone and 2-substituted amine and its transition metal complexes with Cu(II), Ni(II), VO(IV), Cd(II) have been synthesized and characterized by analytical data, conductance and magnetic susceptibility measurements, UV Visible near IR, Mass, IR spectra and ^{1}H NMR spectral data. The results are indicating that the ligand coordinates through azomethine nitrogen, amine nitrogen and phenolic oxygen to the metal ions. The spectral data indicate that the ligand is behaving as a monobasic terdentate ligand. The mass spectral data and ^{1}H NMR spectral data confirmed the proposed structure of the ligand.

Keywords: 2-Aminobenzylimine, Antibacterial activity, Complexes

Introduction

Schiff bases and their metal complexes have been found to possess important biological and catalytic activities[1,2]. Due to their great flexibility and diverse structural aspects, a wide range of Schiff bases have been synthesized and their complexation behaviour was studied[3]. Schiff bases are typical in connection with a diverse range of applications such as in organic synthesis[4-7], as liquid crystals[8] and as heterogeneous catalysts[9]. We report here the synthesis of Schiff base ligands (HL) and its Cu(II), Ni(II), Cd(II) and VO(IV) complexes.

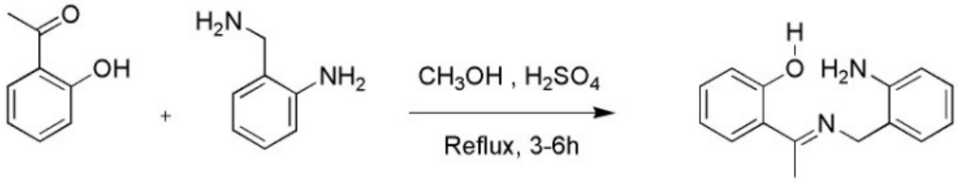
Experimental

All the chemicals used were of AR grade. All the solvents were purified by reported methods before use[10]. Double distilled water has been used where ever necessary. Copper(II) and Vanadium(II) as sulphates, Cadmium(II) and Nickel(II) as chloride salts were purchased from Merck.

Melting Points were determined with Bock Monoscope Wreck NR instrument. Electrical conductivity of the metal complexes was studied at room temperature with freshly prepared 1×10^{-3} M solutions in DMSO using Digisun Conductometer Model DI 909. UV Visible spectra were recorded on a UV Visible near IR Varian Cary 5E instrument. IR spectra (KBr discs) were recorded on a Bruker IFS-66V FT IR spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 300 MHz spectrometer using TMS as standard. ESI mass spectrum was recorded on LC MSD Trap SL mass spectrometer. The elemental analyses (C, H and N) of the complexes were carried out on Perkin-Elmer 240 C (USA) elemental analyzer. Metal estimations were carried out using a Varian Spectra AA 20 atomic absorption spectrometer. The magnetic susceptibility measurements were carried out on a Faraday Balance at room temperature using Hg [Co $(SCN)_4$] as calibrant.

Preparation of the ligand

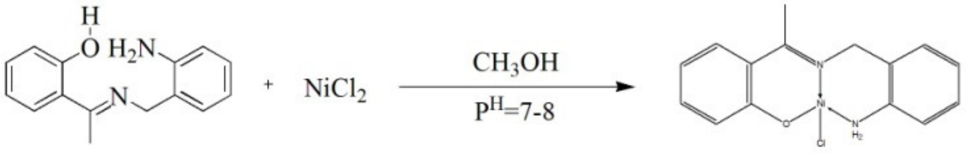
The ligand was prepared by taking ortho-hydroxy acetophenone and 2-amino benzyl amine in methanol in 1:1 molar ratio and refluxing for 3- 6 hours. Then 1-2 drops of sulphuric acid was added. Upon cooling, a yellow coloured solid separates out was filtered and dried (Scheme 1).



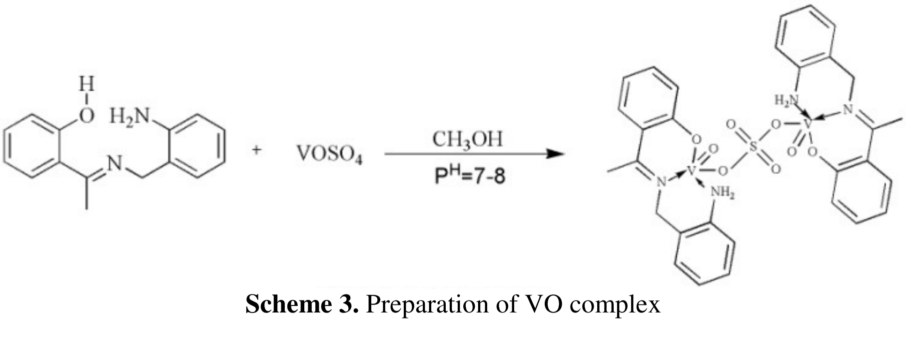
Scheme 1. Preparation of 2-[1-(2-aminobenzylimino)ethyl]phenol ligand

Synthesis of metal complexes

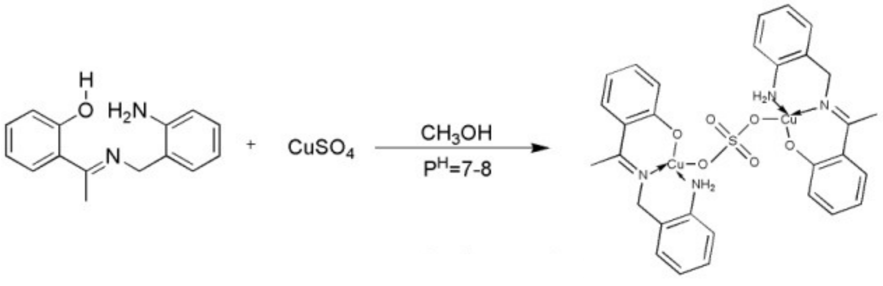
Metal(II) chloride / sulphate hexahydrate (1 mmol) in MeOH was added gradually and with constant stirring to a solution of ligand, the stoichiometry of the metal ion to ligand was 1:1. The solution was heated for some time. The pH of the reaction mixture was adjusted to 7-8 using ammonia solution. Upon cooling overnight the metal chelates were separates out. These were filtered by suction, washed with methanol followed by petroleum ether and dried in vacuum at 60-80 °C (Scheme 2-5).



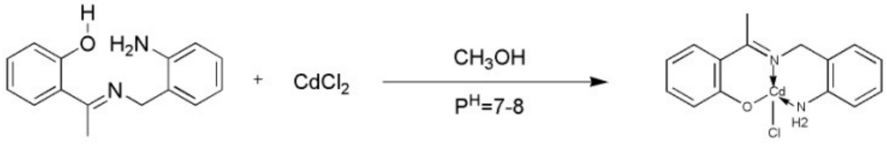
Scheme 2. Preparation of Ni complex



Scheme 3. Preparation of VO complex



Scheme 4. Preparation of Cu complex



Scheme 5. Preparation of Cd complex

Biological activity

Media and culture conditions

2.4% MH media (Muller Hinton media) was used for culturing the microorganisms. The prepared plates with microorganisms were incubated at 37 °C for overnight.

Preparation of agar plates

2.4 g of M H media was weighed and dissolved in 100 mL of distilled H_2O, then autoclaved. The media was cooled to 45 ^oC then it was poured into five sterile boiling test tubes 20 mL each. For each tube different cultures were used (20 µL), then these cultures were poured in to sterile Petri plates and they were allowed to solidify. Standardization of antibiotic property of the samples was to different concentrations (100-250 µg).

Testing of samples

The solidified MH agar plates were taken and made grooves with borer. Then samples of transition metal complexes with Cu(II), Ni(II), VO(IV) and Cd(II) were added in sterile conditions to the grooves and the plates were cooled to room temperature then kept in incubator at 37 ^oC for overnight. Then the activity of samples was measured in diameter of zone of inhibition.

Results and Discussion

The analytical data of the ligand and their metal complexes are given in the Table 1. This is in agreement with the proposed structures of the ligand and its complexes. All the metal chelates are coloured. They are stable to air and moisture. The complexes decompose around 250-300 °C. They are insoluble in water. But they are soluble in organic solvents like ethanol, DMF, DMSO and dioxane. Molar conductance measurements in DMSO solution indicate that they are non electrolytic in nature[11].

Characterization of ligand and metal complexes

IR spectral data

The reaction of Schiff base, HL with VO(IV), Ni(II), Cu(II) and Cd(II) metal ions produce a new series of binuclear and mononuclear metal complexes. The analytical and physical data of the ligand and metal complexes are listed in Table 1.

Table 1. Analytical data and physical properties of the ligand and complexes

Composition of Ligand/Complex	Colour	Melting point	% Found (Calcd.)			
			Carbon	Hydrogen	Nitrogen	Metal
$C_{15}H_{16}ON_2$	Yellow	115 °C	75.10 (75.00)	6.52 (6.67)	11.01 (11.66)	- -
$[VO(C_{15}H_{15}ON_2)]_2\ SO_4$	Greenish blue	>300 °C	69.50 (69.40)	5.20 (5.18)	10.19 (10.33)	17.30 (17.42)
$[Ni(C_{15}H_{15}ON_2)Cl]$	Brown	>300 °C	66.50 (66.46)	5.63 (5.70)	10.10 (10.07)	19.52 (19.60)
$[Cu(C_{15}H_{15}ON_2)]_2SO_4$	Dark green	>300 °C	69.00 (69.30)	5.16 (5.18)	10.31 (10.33)	21.00 (21.13)
$[Cd(C_{15}H_{15}ON_2)Cl]$	White	>300 °C	64.61 (64.69)	5.79 (5.85)	9.90 (9.91)	32.08 (32.28)

Solubility: Ligand in Methanol and complexes in DMSO

The characteristic IR bands of the ligand and its complexes listed in Table 2. In the IR spectrum of the ligand (HL), ν(N-H), ν(O-H) (phenolic), ν(C=N) and ν(C=O) stretching vibrations were observed at 3600, 3362, 1608 and 1304 cm^{-1} respectively. Figure 1 shows the azomethine vibration of the ligand at 1608 cm^{-1} was shifted to lower frequencies after complexation, appearing at 1603, 1601, 1598 and 1571 cm^{-1} for Copper(II), Nickel(II), Vanadium(IV) and Cadmium(II) complexes respectively, indicating the participation of azomethine nitrogen of ν(C=N) in complexation[12]. The ν(N-H) vibration of the ligand at 3610 cm^{-1} was shifted to lower frequencies after complexation, appearing at 3410, 3580, 3450 and 3505, cm^{-1} for Copper(II), Nickel(II), Vanadium(IV) and Cadmium(II), complexes respectively, indicating the participation of amine nitrogen of ν(N-H) in complexation[12]. On the other hand, the ν(C-O) (phenolic) band at 1304 cm^{-1} in the free ligand was moved to a higher frequency by 20-50 cm^{-1} after complexation indicates the participation of phenolic oxygen of C-O in complex formation[13,14]. The IR frequencies observed for metal complexes in the region of 515-755 and 410-578 cm^{-1} are attributed to ν(M-N) and ν(M-O) IR stretching frequencies. On the basis of IR spectral data it is inferred that the ligand is behaving as a monobasic terdentate ligand with O:N:N donor sequence.

^{1}H NMR spectral data

The ^{1}H NMR spectrum of the ligand 2-[1-(2-Aminobenzylimino)ethyl]phenol was recorded in DMSO-d_6. The spectrum shows characteristic signals of the ligand in δ (ppm). Signals are observed at δ 12.0 (s, H_7, -OH), δ 4.6 (s, 2-H_{10}, CH_2 of benzyl), δ 7.8-6.64 (arom-H) and δ3.4 (s, 3H_{17}) respectively and the NH hydrogen appears as broad singlet at δ 11.07. All the signals correlate very well with the proposed structure of the ligand[15].

Table 2. FT- IR spectral data Schiff Base and its various metal complexes

Ligand/Complex	ν(N-H)	ν (O-H)	ν(C=N)	ν(C-N)	ν(C-O) Phenolic	ν(M-N)	ν(M-O)	ν (SO_4)	UV-Vis, nm
$C_{15}H_{16}ON_2$	3610	3362	1608	1216	1304	-	-	-	258
$[VO(C_{15}H_{15}ON_2)]_2\ SO_4$	3450	3350	1598	1183	1333	519	442	1133	630-800
$[Ni(C_{15}H_{15}ON_2)Cl]$	3580	3318	1601	1190	1329	536	480	-	450-630
$[Cu(C_{15}H_{15}ON_2)]_2SO_4$	3410	3290	1603	1201	1338	618	441	1116	450-850
$[Cd(C_{15}H_{15}ON_2)Cl]$	4305	3339	1571	1205	1383	555	412	-	450-630

FT-IR spectra recorded on KBr disc and units are cm^{-1}

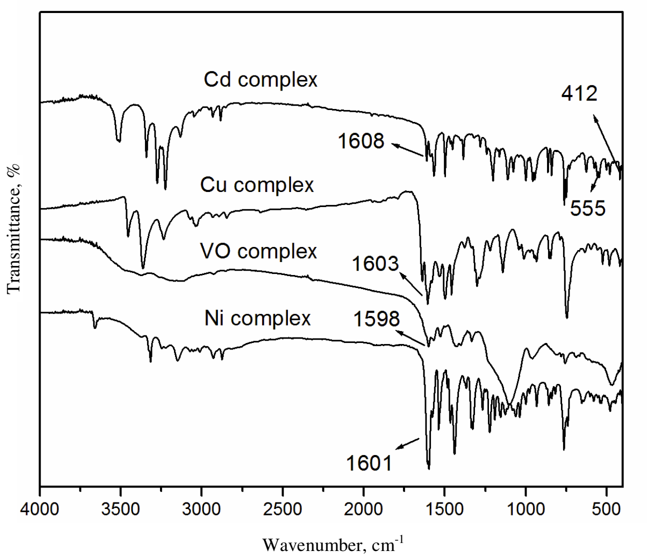


Figure 1. FT-IR Spectra of metal complexes

Mass spectral Data

ESI mass spectrum of the ligand shows a base peak at *m/z* 240, 241 (M^++1). It shows various fragments at *m/z* 224 and *m/z* 200, confirming the same molecular weight, which is same as the calculated M^+ values.

Electronic spectra of metal complexes

The electronic spectrum of the ligands and all the complexes were recorded in DMSO at room temperature, the electronic spectrum of the VO(IV) complex shows three absorption bands at 11363, 15265 and 22222 cm^{-1}. These are assigned to $^2B_2 \leftarrow {}^2E$; $^2A_1 \leftarrow {}^2E$ and $^2B_2 \leftarrow {}^2E$ transitions. Square pyramidal geometry can be assigned to the complex.

The electronic spectrum of the Ni(II) complex shows absorption bands at 15873 and 20000 cm^{-1}. These are interpreted to $^1A_{1g} \leftarrow {}^1E_g$ and $^1B_{1g} \leftarrow {}^1E_g$. Based on these assignments a square planar geometry has been proposed to the complex. The UV Visible spectrum of the Cu(II) complex shows broad absorption bands in the region 12500 cm^{-1} and 15873 cm^{-1}, based on this it has been assigned to $^2B_2 \leftarrow {}^2E$; $^2A_1 \leftarrow {}^2E$ and $^2B_1 \leftarrow {}^2E$ transitions. The electronic absorption spectrum suggests a square pyramidal geometry with a metal- metal bonding in the solid state[16].

Magnetic spectral data

The magnetic susceptibility measurements of the complexes have been carried out at room temperature. The VO (IV) complex exhibits a magnetic moment of 1.90 B. M. This value is in correlation with the single unpaired electron in the complex with square pyramidal disposition.

The Ni(II) complex is diamagnetic and red in colour. So a square planar disposition has been assigned to the complex. The Cu(II) complex exhibits a magnetic moment of 1.04 B.M. The value is according to the single unpaired electron present in the complex. But the lower magnetic moment is due to the antiferromagnetic interaction between the two Cu(II) metal centres. The Cu(II) complex may be assigned a dimeric square planar structure.

The ligand and its various complexes formed from VO(IV), Ni(II), Cd(II) and Cu(II) have been tested. Clear inhibition was noticed with the ligand and complexes. It was noticed that the vanadium complex has shown the highest inhibition followed by other complexes and the ligand shown in the Table 3. The biological evaluations of the simple ligand in comparison to their metal complexes have been determined against bacterial strain[17]. Generally, it is suggested that the chelated complexes deactivate various cellular enzymes, which play a vital role in various metabolic pathways of these micro organisms[18-22].

Table 3. Biological activity of the ligand and metal complexes

Microbial species	Ligand	NiL	CuL	VL
Salmonella typhimurium	+++	_	++	+++
Staphylococcus aureus	++	_	++	+++
Staphylococcus epidermidis	++	_	++	+++
Klebsiella pnuemoniae	++	_	++	+++
Eschirichia coli	++	_	++	+++
Bacillus subtilis	+++	_	++	++
Listeria monocytogenes	+++	_	+++	++
MRSA-I [c]	+++	_	++	+++
MRSA-II	+++	_	++	+++
MRSA-IIII	++	_	++	++

*Inhibition zone diameter (mm) = +~ = 6-10, ++~ = 10-13, +++~ = 14-16; - = No zone of inhibition, Concentration of all compounds = 100-250 µg

Conclusion

The synthesis of novel ligand from ortho-hydroxy acetophenone and 2-substituted amine and its metal complexes with Cu(II), Ni(II), VO(IV), Cd(II) and their biological activity have been demonstrated. Their structures were characterized by analytical data, conductance and magnetic susceptibility measurements and UV Visible, FT-IR, Mass and ^{1}H NMR spectral data. The results indicate that the ligands coordinate through azomethine nitrogen, amine nitrogen and phenolic oxygen to the metal ions.

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