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Synthesis, Characterization and Biological Studies of *Bis*{μ-2,2'-[N,N'-diyl*bis*(nitrilomethylidyne)]diphenolato}dicobalt(II) Using Triple Component Solvent System

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The crystal structure of compound $[Co_2(C_{14}H_{12}N_2O_2)_2]$ showed dimeric complex. Two nitrogen atoms and two oxygen atoms of the [N,N-*bis*(salicylidine)diamine] formed distorted square pyramidal geometry in the region of Co(II) and one oxygen atom from each ligand acting as bridge between two ligand molecules which are distorted in parallel path among each other. The titled complex showed amorphous crystalline structure in toluene solvent but to get more clear X-ray crystallographic data three component solvent system (ethanol, toluene, ethyl acetate) was used. The ligand was synthesized and characterized by FTIR, Mass spectrometry, NMR while the titled complex was characterized by FTIR and X-ray crystallography. The ligand and complex were screened for their antibacterial activity against bacterial species *Escheria coli*, *Staphylococcus aureus* and *Bacillus subtilis* and antifungal activity against *A. flavus*, *A. alternate* and *A. niger*. The activity data shows that the metal complex has more antibacterial and antifungal activities than the synthesized ligand against bacterial strains.

Key Words: Triple component solvent system, Schiff bases, Cobalt(II) complex, Salicylaldehyde, Hydrazine.

INTRODUCTION

The imine group (-CH=N) containing compounds are known as Schiff Bases[1]. These are formed by condensation reaction of carbonyl compounds with amines and play important role in revelation of mechanism and in different biological systems[1]. Aromatic aldehyde Schiff bases have a valuable conjugation system and are stable while aliphatic aldehydes on other hand are unstable and are readily polymerizable. There are numerous applications of Schiff bases formed by condensation with aldehydes and ketones such as purification of carbonyl and amino compounds and purification of these groups during sensitive reactions[2]. Detection, identification and determination of aldehydes and ketones also include in these applications. Schiff bases form stable complexes with transition metals[3-11]. The high affinity for metal ion chelation with Schiff bases is used in the synthesis of their complexes. Schiff base derived from condensation reaction of hydrazine and salicaldehyde acts as neutral ligand and form stable complex with Co(II). The ligand and complex are usually characterized by FTIR, ^{1}H NMR, ^{13}C NMR, mass spectrometry and X-ray crystallography and also employed for antibacterial and antifungal activities against different bacterial strains.

EXPERIMENTAL

All the chemicals and solvents including salicaldehyde, hydrazine, cobalt acetate, ethanol, toluene, acetic acid, ethyl acetate were of analytical regent grade and were purchased from Sigma-Aldrich.

Synthesis of ligand: Ligand was synthesized by condensation reaction of equimolar of salicaldehyde (12.2 g, 0.01 mol) and hydrazine (6 g 0.01 mol). Toluene and ethanol were stirred over night. The mixture was stirred at room temperature and then refluxed for 4 h[6].

Synthesis of complex: The complex was prepared by mixing ethanolic solution of the ligand with that containing the required amount of cobalt(II) acetate. The mixture was stirred over night at room temperature and then refluxed

TABLE-1
CHARACTERISTICS IR ABSORPTION FREQUENCIES (cm^{-1}) OF BENDING VIBRATIONS FOR IMINE AND PHENOLIC OH GROUPS

Bending vibrations	Ligand		Complex	
	Observed value	Standard value	Observed value	Standard value
Imine group	1617	1575-1630	1599	1575-1630
Phenolic OH group	1384 and 1197	Sharp at 1410-1310 and *ca.* 1200	1374 and 1194	Sharp at 1410-1310 and *ca.* 1200

continuously on water bath for 12 h. These solutions were filtered and washed with appropriate solvents. The reaction mixture was left for crystallization by using three component solvent system *i.e.*, ethanol, toluene, ethyl acetate. A fine crystalline product obtained was washed with solvent and dried.

The compound was analyzed for spectroscopic measurements by using different spectroscopic techniques. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer FTIR and Thermo FTIR Nicolet IS 10. Mass spectra of ligand was recorded at 70 eV by electron ionization technique on Perkin Elmer Clarus 680 GC-MS instrument in the R & D section of Zeta Chemical Company (PVT) Ltd., Lahore, Pakistan. ^{1}H and ^{13}C NMR were recorded by using 400 MHz JNM-ECX400 FT NMR System. X-Ray crystallography of complex was taken on the single crystal X-ray diffraction.

Antibacterial activity: Antibacterial activity was tested by using different strains. The selected strains were *Escheria coli*, *Staphylococcus aureus* and *Bacillus subtilis*[4]. Disc diffusion method CLSI, 2007 was used for antimicrobial activity of metal complex and ligand. Nutrient agar was mixed in distilled water and dispersed homogenously. Sterilization of the medium was carried out by means of autoclave at 121 ºC for 20 min. Medium was treated with Inoculums before it is transferred to Petri plates. Hereafter, filter paper discs were placed parallel on growth medium which contains 100 µL (10 %) of complex and ligand. The incubation of Petri plates was done for 24 h at 37 ºC for bacterial growth. The complex and ligand full of antibacterial activity inhibited the growth of bacteria and formed clear zones. Zone reader was employed to measure the inhibition zones in millimeters[12]. Rifamipicin was used as standard drug.

Antifungal activity: Different fungal strains were used to test the antifungal activity. The selected strains were *A. flavus*, *A. alternate* and *A. niger*[4]. The growth medium was synthesized, sterilized and then transferred to the Petri plates. Petri dishes were incubated for 48 h at 28 ºC for fungus growth. Filter paper discs were sited on growth medium having growth of fungus. The complex and ligand were applied up to 100 µL (10 %) on each disc and then incubated. The metal complex and ligand showed antifungal activities inhibited the growth of fungus and clear zones were produced[12]. The standard drug used was fluconazol[13].

RESULTS AND DISCUSSION

Crystallization in three solvent systems: Crystallization of the cobalt(II) complex was checked by using three independent solvents. However, no single solvent was sufficient to dissolve the obtained complex thus weigh down the crystallization of the complex. With 0.5 g complex dissolved in three different solvents. Solubility of complex in DMSO, $CHCl_3$ and ETOH was 1.1, 0.6 and 0.2 %, respectively. On the basis of earlier reported results[5,14-16], we successfully adopted a three component solvent system to significantly enhance the solubility. Results were impressive as solubility of the complex was up to 09 % for 0.5 g of the complex dissolved. Reason was probably due to the strong intermolecular bridging of the solvent molecules.

Characterization of ligand

Infrared spectroscopic analysis: The structure of the synthesize ligand was confirmed by FTIR. On the basis of previously reported work the IR spectra of the ligand were recorded in the range of 4000-400 cm^{-1} as KBr pallets[17]. In IR spectra of the ligand, bending vibrations for CH=N group was observed at 1617 cm^{-1}. Ligand show bending vibrations for phenolic OH group at 1384 and 1197 cm^{-1}. IR vibrations attached as Table-1.

^{1}H NMR: NMR spectra were taken on -ECX400 FT NMR (400 MHz) by using $CDCl_3$ as solvent and TMS as reference standard. Ethylene protons were observed at 3.95 ppm as a singlet peak. There were four protons on each aryl group in the molecule. All these four protons have different environments and these labeled as C_1-C_4. In order to understand the positions of the protons attached to the carbon atoms these are labeled as shown in the Table-2. C_1 is at *ortho* position of hydroxyl group. Protons of C_1, C_2, C_3 and C_4 were observed as doublet, triplet, triplet and doublet at 7.02, 7.52, 7.08 and 7.66, respectively. The proton of CH=N (Imine) was observed at 8.40 as singlet and other side proton of CH=N (Imine) was observed at 8.48 as singlet. These were deshielded due to π electrons of C=N and were observed at high ppm value. Phenolic protons were observed as singlet at 11.26 ppm due to strong deshielding effect of oxygen atom.

TABLE-2
CHARACTERISTICS ^{1}H NMR AND ^{13}C NMR DATA OF LIGAND

NMR type	Position of protons	Type of peak	Value (ppm)
^{1}H NMR	C_1	Doublet	7.02
	C_2	Triplet	7.52
	C_3	Triplet	7.08
	C_4	Doublet	7.66
	Position of carbon	Observed value (ppm)	Peak area equivalent to No. of carbon
^{13}C NMR	1 and 1'	157.3	Two
	2 and 2'	118.5	Two
	3 and 3'	161.1	Two
	4 and 4'	117.8	Two
	5 and 5'	132.4	Two
	6 and 6'	121.4	Two
	7 and 7'	132.1	Two

^{13}C NMR: The ^{13}C NMR spectrum of the ligand was found easy due to the simplicity and identical environment of the atoms in the molecule. In the spectra attached as Table-2, each peak corresponds to two carbon atoms in the molecule. The observed value for (CH=N) carbon was 157.3 while sp^2 hybridized CH carbon generally found at 140 ppm (not terminal) with value 118.5 (found value). This deviation of the observed value for this carbon can be correlated with the presence of more electronegative nitrogen atom. The carbon atoms of the aromatic system are generally observed near 130 ppm while in this case the peak observed at 161.1 pm corresponds to two phenolic carbon atoms in the molecule. This downfield shift could be attributed towards the presence of highly electronegative oxygen atom bonded to this carbon. Similarly the comparative up field shift of carbon atom present at *ortho* and *para* positions of the phenolic carbon can be correlated with the mesomeric effect of the lone pair of oxygen atom while the carbon atoms at meta position to this phenolic carbon are almost unchanged as shown in the Table-2.

Mass spectrometry: Mass spectrometry analysis of ligand was performed and elucidated on the basis of earlier reported results[7]. Molecular ion peak of ligand was observed at 240 which is also a base peak. The molecular ion fragment was disintegrated by the cleavage of OH group resulting in the fragment peak at 223. The fragment pattern of the molecules observed also by the cleavage of nitrogen-nitrogen bond and two fragments were observed one with molecular mass 147 and other 120. Isotopic peak for the molecule was observed at 241 with intensity of *ca.* 1 % of the molecular ion peak.

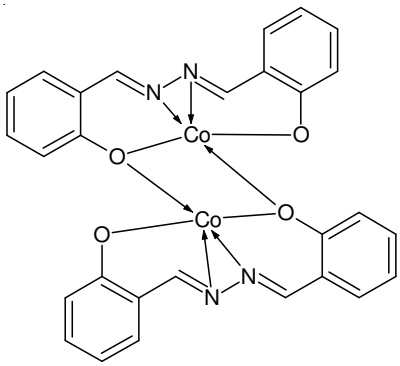

Fig. 1. Structure of complex

Characterizations of complex

Infrared spectroscopy: The functional groups of the complex were confirmed by FTIR. On the basis of earlier reported work[9] the IR spectra of complex were recorded in the range of 4000-400 cm^{-1} as KBr pallets. The CH=N group showed bending vibrations at 1599 cm^{-1} in the IR spectra of metal complex. Bending vibrations for phenolic OH group was observed at 1374 and 1194 cm^{-1}. IR vibrations are shown in Table-1.

XRD: The structure of the complex ($Co_2(C_{14}H_{10}N_2O_2)_2$ (Fig. 1) was confirmed by X-ray crystallography. The crystallographic data and atom numbering scheme of the structure 1, is shown in Table-3. The molecular structure, selected bond lengths and bond angles are shown in Fig. 2 and Table-4. The crystal structure justify that the present complex is dimeric[18] in nature containing two cobalt metals Co (19) and Co (38). Each cobalt atom is bonded to two nitrogen atoms and two oxygen atoms of the Schiff base ligand (L) and one oxygen

TABLE-3
CRYSTAL DATA FOR **I**

Formula	$C_{28}H_{20}N_4O_4Co_2$
f.w.	594.3
Crystal class	Monoclinic
Space group C	2/c
a	26.632(5)
b	6.9755(10)
c	14.708(2)
β	97.271(5)
Colour	Light Pink
Shape	Needle
Volume	2759.0(7)
Z	4
Radiation type	MoK'$_\alpha$
θ_{max}	28.92
H_{min}, H_{max}	-35 35
K_{min}, K_{max}	-8, 8
L_{min}, L_{max}	-19, 19
R-factor	0.05
Max shift/su	0.0003
Weighted R-factor	0.08
$\Delta\rho_{min}$	-1.69
$\Delta\rho_{max}$	2.92
Reflections used	3328
Sigma (I) limit	-10.00
Number of parameters	191
Goodness of fit	1.096

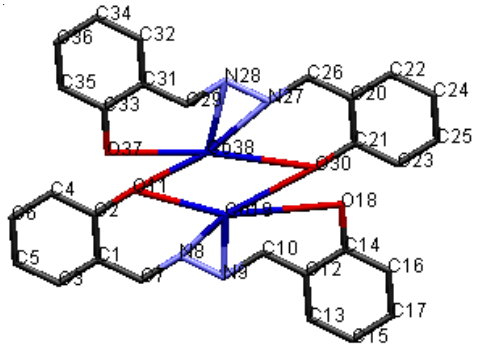

Fig. 2. View of atomic numbering scheme of the structure (I) at 50 % probability level of ellipsoid displacement

TABLE-4
SELECTED BOND LENGTHS (nm) AND ANGLES (º) FOR PRESENT COMPLEX

Co(19)-N(8)	2.0040(8)
Co(19)-O(11)	2.6125(6)
Co(19)-O(30)	2.8332(7)
Co(19)-N(9)	2.0040(8)
Co(19)-O(18)	3.2093(7)
N(8)-Co(19)-O(11)	58.09(3)º
O(11)-Co(19)-O(18)	169.47(3)º
N(8)-Co(19)-N(9)	37.57(3)º
O(11)-Co(19)-N(9)	95.66(3)º
N(8)-Co(19)-O(30)	153.21(3)º.
O(11)-Co(19)-O(30)	148.70(3)º
N(9)-Co(19)-O(30)	115.64(3)º
O(18)-Co(19)-N(8)	132.44(3)º
Co(19)-O(11)-Co(38)	32.19(3)º
N(28)-Co(38)-N(27)	70.38(3)º

atom of the adjacent ligand (Lº) to form a distorted square pyramidal geometry. The bond distances of Co(19)-O(11) and Co(19)-O(18) are 2.6125 (6) nm and 3.2093 (7) nm, respectively. The bond length of Co(19)-O(18) is longer than Co(19)-O(11) with a difference of 1.0468 nm which indicate that Co(19)-O(18) is coordinate and Co(19)-O(11) is covalent one. The bond distance of Co(19)-O(30) is 2.8332 (7) nm which is shorter than Co(19)-O(18) but longer than Co(19)-O(11) indicating that Co(19)-O(30) is a covalent bond and this difference in both covalent bond lengths is due to the co-ordinate covalent bonds of Co(38)-O(11) and Co(19)-O(18). Furthermore the both bond distances of Co(19)-N(8) and Co(19)-N(9) are same *i.e*., 2.0040 (8) nm which indicates that both are coordinate covalent bonds. The bond angles involving ligand and Co center for N (8)-Co (19)-O (11), O (11)-Co(19)-O(18), N(8)-Co(19)-N(9), O(11)-Co(19)-N(9), N(8)-Co(19)-O(30), O(11)-Co(19)-O(30), N(9)-Co(19)-O(30), O(18)-Co(19)-N(8), Co(19)-O(11)-Co(38) and N(28)-Co(38)-N(27) are 58.09(3)º, 169.47(3)º, 37.57(3)º, 95.66(3)º, 153.21(3)º, 148.70(3)º, 115.64(3)º, 132.44(3)º, 32.19(3)º and 70.38(3)º, respectively.

Biological activity: Different types of organisms were used to check the biological activity in order to enhance the ability to detect the antibacterial and antifungal potentional of the synthesized compounds. Disc diffusion method was used to test the antibacterial and anti fungal activity. Different strains (bacterial and fungal strains) were engaged to check the anti-bacterial and antifungal activity[19].

Antibacterial activity: The complex and ligand were tested for their antibacterial activity against different bacteria via disc diffusion method. The selected strains to test the anti-bacterial activities were *Escheria coli*, *Staphylococcus aureus* and *Bacillus subtilis*[1,2,19]. On the basis of previous reported work of the given references the ligand had shown less anti bacterial activity than the metal complex with the bacterial strains *B. subtilis*, *E. coli* and *S. aureus*. The ligand showed less activity as compared to metal complex. The highest activity was shown by ligand against *S. aureus* with zone 6 mm. The activity against *B. subtilis*, *E. coli* and were negligible with zone 4.25 and 4 mm, respectively. The maximum antibacterial activity was shown by complex against *E. coli* with zone 9 mm. The antibacterial activities of metal complex against *B. subtilis* and *S. aureus* were with zone 8 and 5.25 mm, respectively.

Antifungal activity: Disc diffusion method was engaged to test the antifungal activity of complex and ligand against different fungus by using different fungal strains. The strains used were *A. flavis*, *A. alternate* and *A. niger*[1,2,19]. According to the earlier reported work the metal complex showed high antifungal activity than the parent synthesized ligand. The complex showed more significant activity than ligand. The maximum antifungal activity showed by ligand against *A. flavis* with zone 4.25 mm. The activity showed by *A. niger* was nill and *A. alternata* was 4 mm. The highest antifungal activity showed by metal complex against *A. alternata* with zone 12.25 mm and aginst *A. niger* and *A. flavis* were with zones 7.75 mm and 4 mm, respectively.

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