

SYNTHESES, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF COORDINATION COMPOUNDS OF SCHIFF BASE POSSESSING SEMICARBAZONE MOIETY

D. Kumar*, N. Sharma and S. Chadda

Department of Chemistry, National Institute of Technology,
Kurukshetra-136119, Haryana (India)

*E-mail : dkumar_nitk@yahoo.com

ABSTRACT

Salicylaldehyde and *o*-hydroxyphenylsemicarbazide (OHPSC) react in 1:1 molar ratio in EtOH and produce the Schiff base, LH₄ (**1**). On refluxing a MeOH solution of **1** with divalent Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Zr(OH)₂(IV), MoO₂(VI) and UO₂(VI) ions in 1:1 molar ratio, produces the corresponding non-electrolytic ($\Lambda_M = 2.9-10.2 \text{ mho cm}^2 \text{ mol}^{-1}$ in DMSO) dimeric coordination compounds, [Mn(LH₂)(H₂O)]₂ (**2**), [Co(LH₂)(H₂O)]₂ (**3**), [Ni(LH₂)(H₂O)]₂ (**4**), [Cu(LH₂)(H₂O)]₂ (**5**), [Zn(LH₂)(H₂O)]₂ (**6**), [Cd(LH₂)(H₂O)]₂ (**7**), [Zr(OH)₂(LH₂)(H₂O)]₂ (**8**), [MoO₂(LH₂)(H₂O)]₂ (**9**) and [UO₂(LH₂)(H₂O)]₂ (**10**) respectively. The various studies like elemental analyses, molar conductance, spectral (IR, reflectance, ¹H NMR), TGA and magnetic susceptibility measurements have been used for the characterization of the above synthesized coordination compounds. The Schiff base behaves as a dibasic pentadentate (ONONO donor) ligand and the comparative IR spectral studies of the Schiff base and its coordination compounds suggest the involvement of phenolic O (aldehydic moiety), azomethine N, carbonyl O, semicarbazidic N and phenolic O (aminophenolic moiety) atoms towards coordination. The molecular structures of the Schiff base and its coordination compounds have been optimized by molecular modelling calculations. The Schiff base and all the coordination compounds are good growth retarder for Gram-positive bacteria (*S. aureus*, *B. subtilis*), Gram-negative bacteria (*E. coli*, *P. aeruginosa*) and yeast (*S. cerevisiae*, *C. albicans*). A distorted octahedral structure has been suggested for the coordination compounds.

Keywords: Coordination compounds, distorted octahedral structure, molecular modelling, semicarbazide and spectral studies.

© RASAYAN. All rights reserved

INTRODUCTION

The compounds possessing semicarbazone skeleton are known to exhibit a number of activities namely, anthelmintic, antibacterial, anticonvulsant, antimalarial, antinociceptive, antitubercular, antitumor, fungicidal, lathyrogenic and teratogenic properties.¹⁻⁴ An exhaustive literature survey indicates that comparatively much work has been carried out on the transition metal coordination compounds of Schiff bases containing salicylaldehyde moiety⁵ on the other hand, no work seems to be reported on the coordination compounds of Schiff base derived from salicylaldehyde and OHPSC. Keeping in view, the above mentioned importance of semicarbazide and its derivatives, it was thought worthwhile to synthesize and characterize the Schiff base, LH₄ (**1**) and [Mn(LH₂)(H₂O)]₂ (**2**), [Co(LH₂)(H₂O)]₂ (**3**), [Ni(LH₂)(H₂O)]₂ (**4**), [Cu(LH₂)(H₂O)]₂ (**5**), [Zn(LH₂)(H₂O)]₂ (**6**), [Cd(LH₂)(H₂O)]₂ (**7**), [Zr(OH)₂(LH₂)(H₂O)]₂ (**8**), [MoO₂(LH₂)(H₂O)]₂ (**9**) and [UO₂(LH₂)(H₂O)]₂ (**10**).

EXPERIMENTAL

Material and Methods

All reagents and solvents used were of analytical grade. Hexadecaaqua octahydroxotetrazirconium(IV) acetate and bis(acetylacetonato)dioxomolybdenum(VI) were synthesized according to literature procedures⁶. All the microbial cultures were procured from microbial type culture collection (MTCC), IMTECH, Chandigarh (India). The bacteria were sub-cultured on nutrient agar, whereas the yeasts on

malt agar. The molecular structures of the compounds were optimized by CS Chem 3D Pro-14 program package. The methods reported elsewhere, for the estimation of metal contents, spectral studies (IR, reflectance, ^1H NMR) and the magnetic susceptibility measurements have been used.⁷ The melting points of compounds were determined on digital melting point apparatus Stuart SMP-40. The molecular weights of the coordination compounds were determined by Rast method using diphenyl as solvent⁸. The molar conductances of coordination compounds in DMSO were carried out using a Toshniwal Conductivity Bridge (Model CL01-02A) and a dip type cell calibrated with KCl solution. Elemental analyses were carried out using FLASH EA 1112 CHNS (O) analyzer. The IR spectra were recorded in KBr (4000-250 cm^{-1}) on a Fourier Transform Infrared Spectrometer Model RZX (Perkin Elmer). The reflectance spectra were recorded on a Hitachi-330 UV-vis-NIR spectrophotometer. ^1H NMR spectra were recorded on an Avance-II (Bruker) FT NMR spectrometer at 400 MHz, using DMSO as a solvent. The mass spectra were recorded on Waters Micromass Q-ToF Micro-mass spectrometer. The magnetic measurements were carried out at room temperature by Lakeshore VSM 7410 instrument. The TGA was carried out in inert atmosphere, using limiting temperature of 1000 $^{\circ}\text{C}$ and heating rate of 10 $^{\circ}\text{C}/\text{min}$. The Agar well diffusion method was used to perform the antimicrobial studies of the ligand (**1**) and the coordination compounds (**2-10**) by measuring the MIC and zone of growth inhibition against the test organisms with zone reader (Hi Antibiotic zone scale)⁹. DMSO was used as a negative control, whereas Ciprofloxacin and Amphotericin-B were used as positive and negative control for bacteria and yeast respectively.

General procedure

Synthesis of OHPSC

To synthesize OHPSC, *o*-aminophenol (5.45 g, 50 mmol) was dissolved in 20 mL of 1:1 HCl. To this solution, semicarbazide hydrochloride (22.30 g, 200 mmol) in small quantity was added with constant stirring followed by the addition of distilled water (30 mL), glacial acetic acid (1 mL) and concentrated HCl (1 mL). The brick red colored solution obtained was boiled under reflux on a water bath for 1 h. The white crystalline product obtained, was suction filtered, washed with and recrystallized from EtOH and dried over silica gel *in vacuo*. Yield = 85%, M.p. = 167 $^{\circ}\text{C}$; anal. [$\text{C}_7\text{H}_9\text{N}_3\text{O}_2$; found (calcd.) % C = 50.94 (50.30), H = 5.47 (5.39), N = 25.04 (25.15); IR bands (cm^{-1}): 3309 $\nu(\text{O-H})$ (intramolecular H-bond), 2871 $\nu(\text{N-H})$ (intramolecular H-bond), 1687 $\nu(\text{C=O})$ (carbonyl), 1582 $\delta(\text{NH}_2)$ and 1212 $\nu(\text{C-O})$ (enolic-OH); ^1H NMR (400 MHz; DMSO- d_6 ; δ ppm): (4H, -ArH, 6.63-7.25), (1H, phenolic-OH, 7.76), (2H, -NH₂, 5.26), (2H, -NH, 6.42).

Synthesis of 1

To synthesize Sal-OHPSC, salicylaldehyde (0.61 g, 5 mmol) and OHPSC (0.84 g, 5 mmol) were refluxed in EtOH (50 mL) on water bath for 2 h. The cream colored compound was separated out during refluxion. It was suction filtered, washed with and recrystallized from EtOH and then dried as mentioned above. Yield = 90%, M.p. = 201 $^{\circ}\text{C}$.

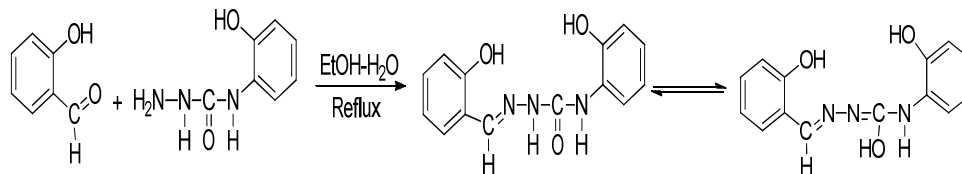
Synthesis of 2

To synthesize coordination compounds (**2**), a MeOH solution (~ 30 mL) of appropriate metal acetate/compound (5 mmol) and a MeOH solution (~ 50 mL) of LH₄ (0.54 g, 5 mmol) were boiled under reflux on a water bath for 3-4 h. The amorphous solids obtained during refluxion were suction filtered, washed with MeOH and then dried as mentioned above. Yield = 75-90%.

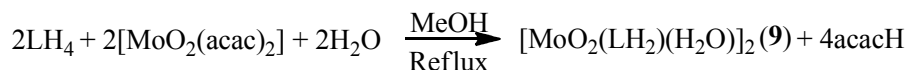
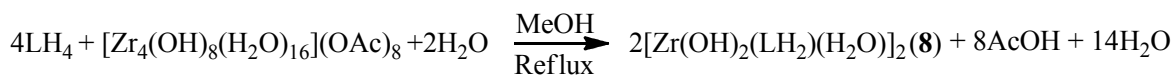
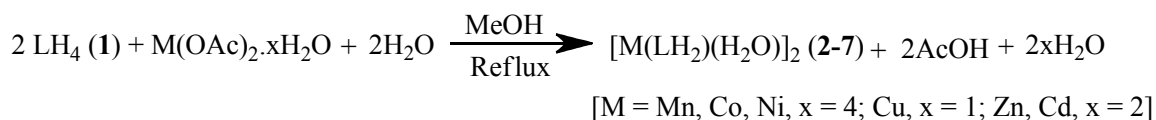
RESULTS AND DISCUSSION

The cream colored Schiff base, LH₄ (**1**) (Scheme-1) is formed when an EtOH solution of salicylaldehyde and OHPSC in 1:1 molar ratio is boiled under reflux for 2 h. A MeOH solution of **1** reacts with MeOH solution of divalent Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Zr(OH)₂(IV), MoO₂(VI) and UO₂(VI) ions in 1:1 molar ratio and produces the dimeric coordination compounds, [Mn(LH₂)(H₂O)]₂ (**2**), [Co(LH₂)(H₂O)]₂ (**3**), [Ni(LH₂)(H₂O)]₂ (**4**), [Cu(LH₂)(H₂O)]₂ (**5**), [Zn(LH₂)(H₂O)]₂ (**6**), [Cd(LH₂)(H₂O)]₂ (**7**), [Zr(OH)₂(LH₂)(H₂O)]₂ (**8**), [MoO₂(LH₂)(H₂O)]₂ (**9**) and [UO₂(LH₂)(H₂O)]₂ (**10**) respectively

(Scheme-2). The coordination compounds are stable towards air and moisture. They get decomposed above 200 °C. The molecular weight measurements in diphenyl indicate their dimeric nature⁸. They are fairly soluble in DMSO but sparingly soluble in DMF, H₂O, MeOH and EtOH. Their molar conductance data (Table-1) reveal their non-electrolytic nature.¹⁰



Scheme-1: Synthesis of Schiff base (1)



Scheme-2: Synthesis of coordination compounds (2-10)

Table-1: Analytical, color, molar conductance (mho cm² mol⁻¹), mass spectral and molecular weight data of Schiff base (1) and its coordination compounds (2-10)

S.No.	Molecular Formula	Color	Λ_M	M. Wt Obs. (Cald.)	Found (Calcd) (%)			
					M	C	H	N
1.	C ₁₄ H ₁₃ N ₃ O ₃ (1)	Cream	-	271 ^a (271)	-	61.81 (61.99)	4.72 (4.80)	15.29 (15.50)
2.	Mn ₂ C ₂₈ H ₂₆ N ₆ O ₈ (2)	Brown	7.4	699 ^b (683.8)	15.95 (16.06)	49.28 (49.14)	3.70 (3.80)	12.43 (12.28)
3.	Co ₂ C ₂₈ H ₂₆ N ₆ O ₈ (3)	Brick Red	4.9	687 ^b (691.8)	17.20 (17.03)	48.73 (48.57)	3.63 (3.76)	12.26 (12.14)
4.	Ni ₂ C ₂₈ H ₂₆ N ₆ O ₈ (4)	Green	5.2	695 ^b (691.4)	17.05 (16.98)	48.34 (48.60)	3.69 (3.76)	12.02 (12.15)
5.	Cu ₂ C ₂₈ H ₂₆ N ₆ O ₈ (5)	Dirty Green	4.8	732 ^b (701)	18.05 (18.12)	47.98 (47.93)	3.65 (3.71)	12.03 (11.98)
6.	Zn ₂ C ₂₈ H ₂₆ N ₆ O ₈ (6)	Cream	10.2	704.8 ^a (704.8)	18.72 (18.56)	47.75 (47.67)	3.80 (3.69)	11.75 (11.92)
7.	Cd ₂ C ₂₈ H ₂₆ N ₆ O ₈ (7)	Cream	6.3	698 ^b (798.8)	28.38 (28.14)	42.28 (42.06)	3.35 (3.25)	10.65 (10.52)
8.	Zr ₂ C ₂₈ H ₃₀ N ₆ O ₁₂ (8)	Brown	4.1	812.1 ^b	22.46	40.65	3.58	10.28

				(824.4)	(22.12)	(40.83)	(3.64)	(10.19)
9.	Mo ₂ C ₂₈ H ₂₆ N ₆ O ₁₂ (9)	Dirty Brown	3.4	843.2 ^b (829.8)	23.46 (23.11)	40.36 (40.56)	3.22 (3.13)	10.56 (10.26)
10.	U ₂ C ₂₈ H ₂₆ N ₆ O ₁₂ (10)	Orange	2.9	1158 ^b (1114)	43.58 (43.99)	30.13 (30.16)	2.45 (2.33)	7.69 (7.54)

Abbreviations: ^aMass spectral data and ^bRast method data

Infrared spectra

The important IR spectral peaks (cm⁻¹) of the Schiff base (**1**) and its coordination compounds (**2-10**), recorded in KBr are shown in Table-2. The Schiff base (**1**) exhibits the $\nu(\text{O-H})$ (intramolecular H-bond), $\nu(\text{N-H})$ (intramolecular H-bond), $\nu(\text{C=O})$ (carbonyl), $\nu(\text{C=N})$ (azomethine), $\nu(\text{C-O})_{\text{phenolic}}$ and $\nu(\text{C-O})_{\text{enolic}}$ stretches at 3278, 3154, 1695, 1622, 1520 and 1200 cm⁻¹, respectively. The $\nu(\text{C-O})_{\text{phenolic}}$ stretch of **1** is expected to occur at higher energy as compared to the $\nu(\text{C-O})_{\text{enolic}}$ stretch.¹¹ This is due to the delocalization of π -electrons towards the benzene ring. The $\nu(\text{C-O})_{\text{phenolic}}$ stretch of **1** occurs at 1520 cm⁻¹. This band shifts to higher energy by 25-37 cm⁻¹ in **2-10**, supporting the involvement of phenolic O atom towards coordination.¹² The magnitude of the high positive shift of the $\nu(\text{C-O})_{\text{phenolic}}$ stretch indicates the dimeric nature of all coordination compounds¹³. The $\nu(\text{C=N})$ azomethine stretch of **1** occurring at 1622 cm⁻¹ undergoes a negative shift by 20-35 cm⁻¹ in **2-10**, indicating the involvement of azomethine N atom towards coordination¹⁴. This downward shift is expected due to the reduction in electron density in azomethine link on compound formation.¹³

The appearance of a band at 1695 cm⁻¹ and another band at 1200 cm⁻¹ due to the $\nu(\text{C=O})$ (carbonyl) and $\nu(\text{C-O})_{\text{enolic}}$ stretches, respectively in **1** evinces the occurrence of both keto and enol forms in it. The $\nu(\text{C=O})$ (carbonyl) stretch of **1** decreases by 13-52 cm⁻¹ in the coordination compounds, indicating the involvement of carbonyl O atom towards coordination¹⁵. Interestingly, the $\nu(\text{C-O})_{\text{enolic}}$ as well as the $\nu(\text{N-H})$ stretches remain at the same energies in **1** and **2-10** suggesting the non-involvement of enolic O and hydrazidic N atoms towards coordination.¹⁶

All the coordination compounds exhibit a broad band in the region 3279-3340 cm⁻¹ indicating the presence of coordinated water molecule.¹⁷ The appearance of new non-ligand bands between 535-556 cm⁻¹ and 462-481 cm⁻¹ due to the $\nu(\text{M-O})$ and $\nu(\text{M-N})$ stretches, respectively in **2-10** supports the involvement of phenolic O and azomethine N atoms towards coordination.¹⁸ Thus, as discussed above it is suggested that Schiff base act as a dibasic pentadentate ONONO donor.

Table-2: IR spectral data (cm⁻¹) of the Schiff base (**1**) and its coordination compounds (**2-10**)

S.No.	Compound	$\nu(\text{C=O})$ (carbonyl)	$\nu(\text{C=N})$ (azomethine)	$\nu(\text{C-O})$ (phenolic)	$\nu(\text{H}_2\text{O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
1.	1	1695	1622	1520	–	–	–
2.	2 (M = Mn)	1667	1597	1557	3295	535	470
3.	3 (M = Co)	1668	1602	1546	3334	535	481
4.	4 (M = Ni)	1682	1592	1545	3279	556	462
5.	5 (M = Cu)	1680	1588	1548	3288	550	477
6.	6 (M = Zn)	1643	1587	1552	3340	545	465
7.	7 (M = Cd)	1667	1596	1557	3294	538	467
8.	8 (M = Zr)	1652	1598	1554	3296	542	479
9.	9 (M = Mo)	1665	1602	1557	3318	552	480
10.	10 (M = U)	1646	1589	1547	3325	548	476

Reflectance spectral studies

[Mn(LH₂)(H₂O)]₂ shows three absorption bands at 15875, 21332 and 25828 cm⁻¹ assigned to the ⁶A_{1g} → ⁴T_{1g}(G)(ν_1), ⁶A_{1g} → ⁴T_{2g}(G)(ν_2) and ⁶A_{1g} → ⁴A_{1g}(G)(ν_3) transitions, respectively.¹⁹ The absorption bands

occurring in $[\text{Co}(\text{LH}_2)(\text{H}_2\text{O})]_2$ at 9118, 13333 and 19417 cm^{-1} are due to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions, respectively.²⁰ $[\text{Ni}(\text{LH}_2)(\text{H}_2\text{O})]_2$ shows absorption bands at 9180, 16600 and 25594 cm^{-1} due to the ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions, respectively.²⁰ $[\text{Cu}(\text{LH}_2)(\text{H}_2\text{O})]_2$ shows bands at 15586 cm^{-1} and 28188 cm^{-1} , respectively corresponding to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition. No spectral bands were found below 10000 cm^{-1} which supports octahedral geometry.²¹

Mass spectra

The prominent fragmentation peaks in **1** observed at $m/z = 271, 254, 237, 151, 135, 104$ and 91 are tentatively assigned to $[\text{M}]^{+}$, $[\text{M}-\text{OH}]^{+}$, $[\text{M}-2\text{OH}]^{+}$, $[\text{M}-\text{C}_7\text{H}_6\text{NO}]^{+}$, $[\text{M}-\text{C}_7\text{H}_6\text{NO}_2]^{+}$, $[\text{M}-\text{C}_7\text{H}_7\text{N}_2\text{O}_3]^{+}$ and $[\text{M}-\text{C}_8\text{H}_8\text{N}_2\text{O}_3]^{+}$ respectively. The prominent fragmentation peaks in $[\text{Zn}(\text{LH}_2)(\text{H}_2\text{O})]_2$ (**6**) observed at $m/z = 704.8, 689.8, 668.8, 648.8, 592.8, 576.8, 511.4, 475.4$ and 448.8 are tentatively assigned to $[\text{M}]^{+}$, $[\text{M}-\text{CH}_3]^{+}$, $[\text{M}-2\text{H}_2\text{O}]^{+}$, $[\text{M}-\text{C}_3\text{H}_4\text{O}]^{+}$, $[\text{M}-\text{C}_5\text{H}_8\text{N}_2\text{O}]^{+}$, $[\text{M}-\text{C}_5\text{H}_8\text{N}_2\text{O}_2]^{+}$, $[\text{M}-\text{ZnC}_5\text{H}_8\text{N}_2\text{O}_2]^{+}$, $[\text{M}-\text{ZnC}_5\text{H}_{12}\text{N}_2\text{O}_4]^{+}$ and $[\text{M}-\text{C}_{10}\text{H}_{16}\text{N}_4\text{O}_4]^{+}$ respectively.

${}^1\text{H}$ NMR spectra

The ${}^1\text{H}$ NMR spectra of **1** and $[\text{M}(\text{LH}_2)(\text{H}_2\text{O})]_2$ [$\text{M} = \text{Zn, Cd, Zr}(\text{OH})_2, \text{MoO}_2, \text{UO}_2$] were recorded in $\text{DMSO}-d_6$. The chemical shifts (δ) are expressed in ppm downfield from TMS.²² The Schiff base (**1**) exhibits a multiplet between $\delta 6.6-7.5$ ppm due to the aromatic protons, a broad band at $\delta 7.70$ ppm due to phenolic proton, a singlet at $\delta 8.14$ ppm due to the azomethine protons and a doublet at $\delta 6.3$ ppm due to the two N-H protons. The absence of the resonance signals due to the phenolic protons in the compounds indicates the deprotonation of their OH groups followed by involvement in coordination. The appearance of signals due to the enolic proton and N-H protons in **1** at same δ values indicates non-involvement of these groups towards coordination. The new signal appearing between $\delta 3.44-3.49$ ppm is tentatively assigned to the protons of coordinated H_2O molecules.²³

Thermal analysis

$[\text{Cd}(\text{LH}_2)(\text{H}_2\text{O})]_2$ loses its coordinated H_2O molecules between 135-143 $^\circ\text{C}$. The organic skeleton is lost around 320 $^\circ\text{C}$. CdO , the final product is obtained above 400 $^\circ\text{C}$.

Magnetic susceptibility measurements

The value of magnetic moments of **2, 3, 4, 5** coordination compounds at room temperature are 5.68, 4.53, 3.65 and 1.46 B.M. respectively, suggesting their octahedral behavior²⁴ (Figure-1). The comparative lower values of the magnetic moments indicate that antiferromagnetic exchange is involved in present cases.

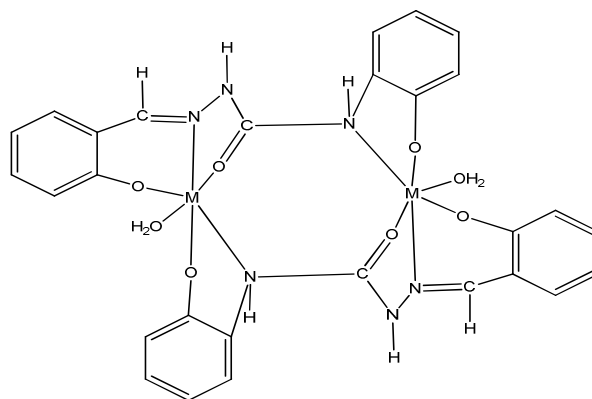


Fig.-1 : Proposed structure of **2-10** ($\text{M} = \text{Mn, Co, Ni, Cu, Zn, Cd, Zr}(\text{OH})_2, \text{MoO}_2, \text{UO}_2$)

Molecular modelling

The 3D molecular modelling of **1** and **2-10** were performed by using MM2 programme contained under CS Chem 3D Pro-14 program package. The 3D optimized geometrical structures of Schiff base and its

coordination compound are presented in Figures-2 and 3. The [C(11)=O(12) (carbonyl) bond length, 1.197 Å] and [C(7)=N(8) (azomethine) bond length, 1.261 Å] in **1** indicate the double bond character between C and O atoms and C and N atoms, respectively.²⁵ In coordination compounds, these bond lengths undergo elongation by 0.011-0.089 Å and 0.012-0.102 Å respectively. On the other hand, [C(19)-O(20) (phenolic, salicylaldehyde moiety) bond length, 1.365 Å] and C(5)-O(9) (phenolic, aminophenolic moiety) bond length, 1.361 Å] of **1** undergo shortening by 0.010-0.085 Å and 0.013-0.062 Å, respectively (Table-3). The above changes in the respective bond lengths in Schiff base and its coordination compounds are indicative of the coordination of phenolic O (aldehydic moiety), azomethine N, carbonyl O, semicarbazidic N and O (aminophenolic moiety) atoms.²⁶ The various bond angles in coordination compounds are indicative of a distorted octahedral geometry.²⁶

Antibacterial activities

Antimicrobial activities of the Schiff base (**1**) and its corresponding coordination compounds (**2-10**) were performed against gram-positive bacteria (*S. aureus*, *B. subtilis*), gram-negative bacteria (*E. coli*, *P. aeruginosa*) and fungi (*S. cerevisiae*, *C. albicans*). Inhibition zone observed around compounds were measured and thus their activities were evaluated.²⁷ Positive and negative controls produced significantly sized inhibition zones against the above mentioned bacteria and fungi. The results indicate that all the coordination compounds have higher activity than the Schiff base. [Cd(LH₂)(H₂O)]₂ was the most effective against Gram-positive, Gram-negative bacteria and fungi.

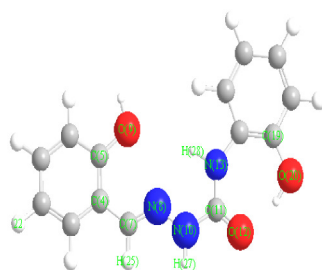


Fig.-2: Energy Optimized structure of Schiff base (**1**)

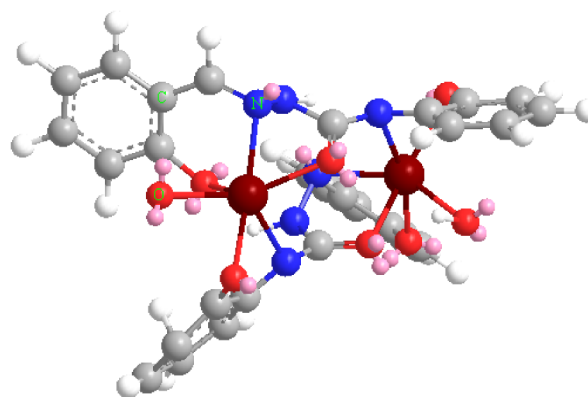


Fig.-3: Energy Optimized structure of **2-10** (M = Mn, Co, Ni, Cu, Zn, Cd, Zr(OH)₂, MoO₂, UO₂)

Table-3: Bond length (Å) and bond angle (°) of the Schiff base (**1**) and its coordination compounds (**2-10**)

S.No.	Compound	v(C=O) (carbonyl) (Å)	v(C=N) (azomethine) (Å)	v(C-O) (phenolic) sal moiety (Å)	v(C-O) (phenolic) aminophenolic moiety (Å)	Bond angle (°)
1.	1	1.197	1.261	1.365	1.361	-
2.	2 (M =Mn)	1.278	1.363	1.289	1.333	O _{phenolic} MnO _{carbonyl} = 101.49° O _{H2O} MnO _{phenolic} = 86.35° N _{azomethine} MnO _{carbonyl} = 89.12°
3.	3 (M = Co)	1.239	1.291	1.287	1.299	O _{phenolic} CoO _{carbonyl} = 88.40° O _{H2O} CoO _{phenolic} = 87.15° N _{azomethine} CoO _{carbonyl} = 81.21°
4.	4 (M = Ni)	1.253	1.320	1.281	1.303	O _{phenolic} NiO _{carbonyl} = 90.49° O _{H2O} NiO _{phenolic} = 76.35° N _{azomethine} NiO _{carbonyl} = 86.19°

5.	5 (M = Cu)	1.263	1.355	1.280	1.321	O ^{phenolic} CuO _{carbonyl} = 91.40° O _{H2O} CuO ^{phenolic} = 99.01° NazomethineCuO _{carbonyl} = 94.21°
6.	6 (M = Zn)	1.208	1.351	1.355	1.333	O ^{phenolic} ZnO _{carbonyl} = 91.53° O _{H2O} ZnO ^{phenolic} = 85.30° NazomethineZnO _{carbonyl} = 88.12°
7.	7 (M = Cd)	1.226	1.273	1.355	1.348	O ^{phenolic} CdO _{carbonyl} = 91.49° O _{H2O} CdO ^{phenolic} = 86.35° NazomethineCdO _{carbonyl} = 86.13°
8.	8 (M = Zr)	1.286	1.291	1.321	1.313	O ^{phenolic} ZrO _{carbonyl} = 85.44° O _{H2O} ZrO ^{phenolic} = 88.57° NazomethineZrO _{carbonyl} = 90.37°
9.	9 (M = Mo)	1.265	1.340	1.340	1.317	O ^{phenolic} MoO _{carbonyl} = 103.52° O _{H2O} MoO ^{phenolic} = 99.36° NazomethineMoO _{carbonyl} = 101.46°
10.	10 (M = U)	1.267	1.316	1.333	1.315	O ^{phenolic} CoO _{carbonyl} = 101.43° O _{H2O} CoO ^{phenolic} = 86.68° NazomethineCoO _{carbonyl} = 98.90°

CONCLUSION

It is suggested that **1** behaves as the dibasic pentadentate ONONO donor ligand in **2-10** coordinating through its phenolic O (aldehydic moiety), azomethine N, carbonyl O, semicarbazidic N and phenolic O (aminophenolic moiety) atoms. A distorted octahedral structure for **2-10** is proposed. The coordination compounds show significant increased antimicrobial activities as compared to the free Schiff base. Thus, present Schiff base and the corresponding coordination compounds have great potential as antimicrobial agent.

REFERENCES

1. A.K. Gadad, M.N. Noolvi and R.V. Karpoornath, *Bioorg. Med. Chem.*, **12**, 5651(2004).
2. J. Slawinski and M. Gdaniek, *Eur. J. Med. Chem.*, **40**, 377(2005).
3. M. Pitucha, Z. Rzaczyńska and L. Mazur, *X ray Structure Analysis Online*, **25**, 67(2009).
4. N.K. Sharma, Sapna, M. Agarwal, S. Kohli, B. Tiwari, J.N. Gurtu and B. Agarwal, *Orient J. Chem.*, **26**, 103(2010).
5. T.P. Devi and R.K. Hemakumar Singh, *Rasayan J. Chem.*, **3**, 266(2010); J. R. Anaconda, J. Calvo, O.A. Almanza, *Int. J. Inorg. Chem.*, 108740(2013).
6. D. Kumar, P.K. Gupta and A. Syamal, *Indian J. Chem.*, **41**, 2494(2002).
7. D. Kumar, A. Syamal, A. Gupta, M. Rani and P.K. Gupta, *J. Indian Chem. Soc.*, **87**, 1185 (2010).
8. G. Mann, B. C. Saunders, "Practical Organic Chemistry", Longmans, 435, 1961.
9. I. Ahmad and A.Z. Beg, *J. Ethnopharm.*, **74**, 113(2001); J.M. Andrews, *J. Antimicrob. Chemother.*, **48**, 5(2001); O.H.S. Al-Obaidi, *Int. J. Chem. Res.*, **3**, 1(2012).
10. W.G. Geary, *Coord. Chem. Rev.*, **7**, 81(1971).
11. A. Syamal, O.P. Singhal, *Transition Met. Chem.*, **4**, 179(1979); D. Kumar, N. Sharma, S. Chadda *J. Indian Chem. Soc.*, **93**, 1343(2016).
12. R.K. Dubey, U.K. Dubey and C.M. Mishra, *Indian J. Chem.*, **47A**, 1208(2008).
13. A. Syamal, *J. Indian Chem. Soc.*, **85**, 231(2008).
14. D. Kumar, J. Sharma, S. Chadda and A. Syamal, *J. Indian Chem. Soc.*, **91**, 185(2014).
15. J.E. Covacic, *Spectrochim. Acta*, **23A**, 183(1967); B.B. Mahapatra and B.K. Mahapatra, *J. Inorg. Nucl. Chem.*, **39**, 2291(1977).
16. A.P. Mishra and M. Soni, *Metal-Based Drugs*, Article ID 875410, **1**(2008).
17. D. Kumar, A. Syamal, A. Gupta, V. Pandey and M. Rani, *J. Indian Chem. Soc.*, **89**, 745 (2012).

18. A. Sharma and M. Shah, *J. Appl. Chem.*, **3**, 62(2013); D. Kumar, J. Sharma, S. Chadda and A. Syamal, *J. Indian Chem. Soc.*, **90**, 1077(2013).
19. D. Kumar, S. Chadda, J. Sharma and P. Surain, *Bioinorg. Chem. Appl.*, Article ID 981764, **1**(2013).
20. A.B.P. Lever, *Electronic Spectra of Ions in Inorganic Electronic Spectroscopy*, 2nd Ed, Elsevier, Amsterdam, 1984; S. Chandra and U. Kumar, *Spectrochim. Acta Part A*, **61**, 219 (2005); V. Phillip, V. Suni, M.R.P. Kurup and M. Nethaji, *Spectrochim. Acta Part A*, **64**, 171(2006).
21. A. Mumtaz, T. Mahmud and M.R. Elsegood, G.W. Weaver, *J. Nucl. Med. Radiat. Ther.*, **7** (2016).
22. R.M. Silverstein and G.C. Bassler, 2nd ed., Wiley Interscience, New York, 1967.
23. O.B. Ibrahim, M.A. Mohamed and M.S. Refat, *Canad. Chem. Trans.*, **2**, 108(2014).
24. R.L. De, M. Mandal, L. Roy, J. Mukherjee, R. Bhawal and K. Maiti, *Indian J. Chem.*, **47**, 1480(2008).
25. T.M. Ismail, M.A. EL Gharmy, S.M.A. EL-Wafa and D.F. Sallam, *Modern Chemistry.*, **3**, 18(2015).
26. K. Siddappa, S.B. Mane and D. Manikprabhu, *The Scient. Wor. J.*, Article ID 817365, **1** (2014).
27. K.R. Aneja, C. Sharma and R. Joshi, *J. Microbio.*, **4**, 175(2011).

[RJC-1643/2017]