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Synthesis, physico-chemical characterization and antimicrobial activities of 3-methoxysalicylaldehyde-2-aminobenzoylhydrazone and its transition metal complexes

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ABSTRACT

The transition metal complexes of 3-methoxysalicylaldehyde-2-aminobenzhydrazone (H_2L) were synthesized and characterized by various spectroscopic (IR, NMR, UV–Vis, Mass), thermal and other physicochemical methods. The ligand acts both in monobasic as well as dibasic manner and coordinates in tridentate fashion with carbonyl oxygen, azomethine nitrogen and phenolic oxygen via deprotonation except in Cu(II) complex where the ligand coordinates via enolization and deprotonation of amide proton. An octahedral geometry was assigned for Mn(II), Co(II), Ni(II) and Zn(II) complexes and square planar for Cu(II) complex. The ligand and its metal complexes have been screened for their *in vitro* antimicrobial activities using serial dilution method. Metal complexes in general have exhibited better antibacterial and antifungal activity than the free ligand. The Cu(II) complex exhibited highest antimicrobial activity among the compounds tested.

1. Introduction

The hydrazone compounds along with their metal complexes have been extensively investigated for their versatile coordination modes [1–3] with prospective biological activities [4–6]. The promising antimicrobial activities of hydrazone Schiff bases have been recently reviewed [7]. The hydrazone Schiff bases and their transition metal complexes derived from the salicylaldehyde have attracted much attention in recent years [8–14], on the other hand, the complexes derived from the 3-methoxysalicylaldehyde have rarely been reported and shows promising applications [15]. The facile syntheses of hydrazones have been achieved by the condensation reaction of aldehydes with primary amines of substituted benzhydrazides [16–19].

Many workers have reported [20–22] the chelating behavior of hydrazone Schiff bases obtained by the reaction of aldehydes and 2-aminobenzoylhydrazide [2-ABH]. However recently it has been shown that the condensation of 2-ABH with aromatic and heterocyclic aldehydes yielded 1,2-dihydroquinazolinone instead of the Schiff base product [23–26]. It is remarkable to note that the reactions at room temperature even with a 1:1 equivalent of 2-ABH and aldehyde lead to the formation of 1,2-dihydroquinazolinone. It was suggested that the formation of 1,2-dihydroquinazolinone proceeds through an intermediate hydrazone formation step, hence it is appealing to isolate 2-aminobenzoylhydrazone derived from 2-ABH in which the NH_2 at second position remains free when reacted with aromatic aldehyde.

In our earlier communication, it has been reported that the reaction of 2-ABH and 3-methoxysalicylaldehyde at refluxing temperature yielded 1,2-dihydroquinazolinone [27]. In the present work, we describe a simple temperature controlled condensation of 2-ABH and 3-methoxysalicylaldehyde to yield the title compound 3-methoxysalicylaldehyde-2-aminobenzoylhydrazone (H_2L). The transition metal complexes of H_2L were synthesized, characterized and evaluated for their anti-microbial activities.

2. Experimental details

2.1. Materials and methods

Analytical reagent grade 3-methoxysalicylaldehyde, methyl anthranilate, hydrazine hydrate and metal(II) chlorides are purchased from s.d. Fine chemicals and Spectrochem, India and are used as received. Solvents were distilled before use [28]. Melting points (uncorrected) are determined using the Gallenkamp melting point apparatus. Conductance measurements were made in DMF (10^{-3} M) solution using an ELICO-CM-82 conductivity meter with cell type CC-01 and cell constant 0.53. Metal complexes were analyzed for their metal content after decomposition with a mixture of

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HCl and $HClO_4$. The presence/absence of chlorides in the complexes was tested by reacting them with $AgNO_3$ as precipitating agent after decomposition of complexes with conc. HNO_3. The C, H, and N elemental analyses were recorded on a Thermoquest CHN analyzer. IR spectra were recorded as KBr disks on a Nicolet 170 SX FT-IR spectrometer in the range 4000–400 cm^{-1}. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer operating at 400.23 MHz in DMSO-d_6 solvent. UV–visible spectra were recorded in DMF solutions on a CARY-50 Bio UV–visible spectrophotometer in the range 200–1100 nm. Magnetic susceptibilities were carried out on a Gouy Balance using $Hg[Co(SCN)_4]$ as the calibrant and diamagnetic corrections are calculated using Pascal's constants [29]. Thermogravimetric analyses were carried out using a TGA7 ANALYSER, Perkin–Elmer, US, at a heating rate of 10 °C per min in 25–1000 °C temperature range. The mass spectra were recorded on QTOF (Quadrupole Time-of-Flight) and FAB mass spectrometer.

2.2. Preparation of H_2L

A solution of 3-methoxysalicylaldehyde (1.52 g, 10 mmol) in methanol (10 mL) was added drop wise to a cold (−5 to 0 °C) solution of 2-aminobenzoylhydrazide (1.51 g, 10 mmol) in methanol (20 mL) with constant stirring. The resulting yellow solution was kept stirring at −5 to 0 °C for 4 h. The yellowish product separated was filtered, washed with cold methanol and dried in vacuo. Yield 90%. m.p. 143 °C.

H_2L: ^{1}H NMR (DMSO-d_6, δ ppm): 11.84 (s, 1H, O*H*), 11.24 (s, 1H, N*H*), 8.58 (s, 1H, NC=*H*), 6.43 (s, 2H, NH_2), 7.60–6.67 (m, 7H, Ar-C*H*), 3.81 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6, δ ppm): 163.12 (*C*=O), 154.31 (*C*=N), 149.12 (*C*—OH), 147.51, 134.15, 132.44, 128.15, 121.87, 120.99, 118.95, 117.50, 116.39, 113.62, 111.95, 55.75.

2.3. Preparation of metal (II) complexes

The transition metal complexes were prepared by drop wise addition of hydrated metal chloride salts [Mn(II), Co(II), Ni(II), Cu(II)] (1 mmol) and anhydrous $ZnCl_2$ (1 mmol) in methanol (5 mL) to the methanolic solution (20 mL) of H_2L (1 mmol) with constant stirring at room temperature for 2 h. The precipitated complexes were filtered, washed several times with methanol, ether and dried under vacuo. The isolation of crystals suitable for X-ray diffraction study was unsuccessful. Yield 60–75%.

$[Zn(HL)_2]$: ^{1}H NMR (DMSO-d_6, δ ppm): 12.12 (s, 1H, N*H*), 8.57 (s, 1H, NC=*H*), 6.27 (s, 2H, NH_2), 7.69–6.53 (m, 7H, Ar-C*H*), 3.83 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6, δ ppm): 164.17 (*C*=O), 156.34 (*C*=N), 149.08 (*C*—OH), 147.14, 134.11, 132.46, 128.18, 121.92, 120.93, 118.94, 117.53, 116.41, 113.60, 111.93, 55.74.

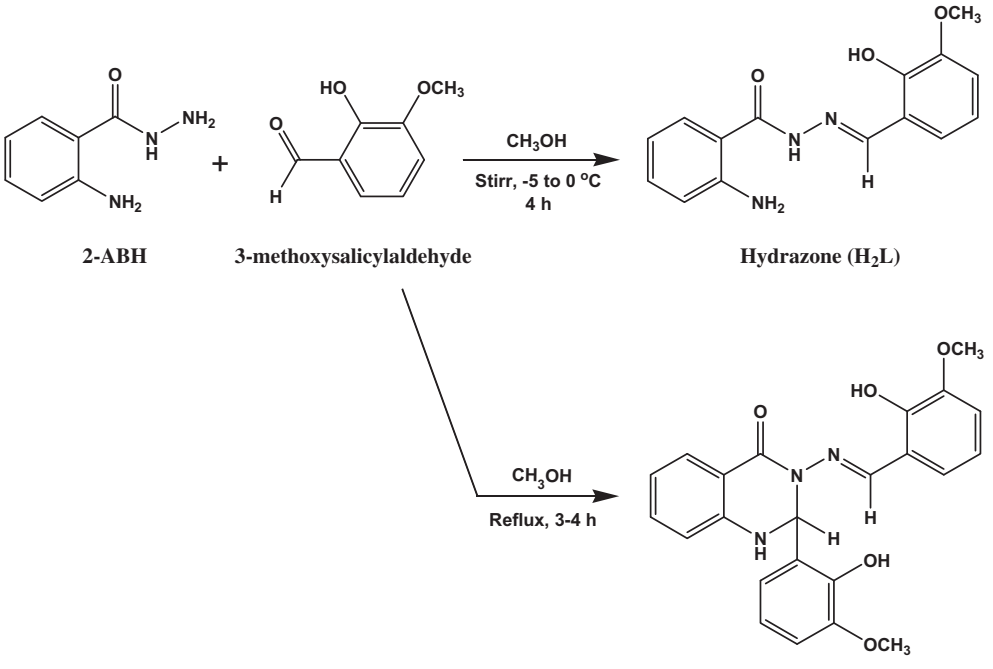
2.4. Antimicrobial studies

Micro-dilution broth susceptibility method was adopted for the evaluation of *in vitro* antimicrobial activity as described in our earlier report [30].

3. Results and discussion

3.1. Synthesis

In our earlier communication, we have reported that the reaction of 2-ABH with 3-methoxysalicylaldehyde leads to the formation of 1,2-dihydroquinazolinone [27] at elevated temperature (Scheme 1). It was assumed that the formation of quinazolinone product proceeds through an intermediate hydrazone formation step. Thus, in the present work, we have adopted the simple methodology for the isolation of hydrazone, H_2L as shown in Scheme 1. The synthesis of H_2L was achieved by the condensation of 1:1 equivalent of 2-ABH and 3-methoxysalicylaldehyde at −5 to 0 °C. To validate the utility of this methodology the reaction was also performed with different stoichiometric ratios of the reactants. It is momentous to note that the reactions at −5 to 0 °C even with 1:2 equivalent of 2-ABH and 3-methoxysalicylaldehyde lead to the formation of H_2L rather than 1,2-dihydroquinazolinone product.



2-ABH 3-methoxysalicylaldehyde Hydrazone (H_2L)

1,2-dihydroquinazolinone [Ref. 27]

Scheme 1.

Transition metal complexes of H_2L ligand were prepared by treating methanolic solution of the ligand and an equimolar amount of $MCl_2{\cdot}nH_2O$. The complexes are stable and soluble in DMF and DMSO solvents. Molar conductance values (Table 1) of the complexes measured in DMF (10^{-3} M solutions) adequately confirm the non-electrolytic nature of the complexes.

3.2. Infrared spectral studies

The infrared spectrum of the ligand H_2L is consistent with the formation of hydrazone (Table 2). The band at 1645 cm^{-1} is due to amide carbonyl and a sharp band at 1612 cm^{-1} corresponds to an azomethine stretching frequency. This suggests the existence of ligand in keto form in the solid state. The phenolic —OH and —NH stretching vibrations appear as a strong envelope in the range 3413–3273 cm^{-1}. The O—H bending and C—O stretching vibrations are found around 1352 and 1249 cm^{-1}, respectively. The absence of —OH stretching bands in IR spectra of all complexes, clearly indicates the coordination of ligand in its deprotonated form. The decrease in ν(C=O) stretching band vibrations upon coordination with Mn(II), Co(II), Ni(II), Zn(II) complexes in the range 1631–1638 cm^{-1} clearly indicates its coordination in keto form. This band is absent in Cu(II) complex and the appearance of new band around 1589 cm^{-1}, assigned to —C=N—N=C— stretching vibration indicates that the ligand coordinates to Cu(II) metal ion via enolization and deprotonation. The other non ligand band $\delta(OH)_{Water}$ appeared around 811 cm^{-1} in Cu(II) complex suggests the coordination of water molecule to the metal ion. Strong bands in the range 1577–1598 cm^{-1} for complexes are assigned to ν(C=N) stretching which is low as compared with the ligand revealing its coordination to the metal ion. The bands due to $\nu(NH_2)$ remain unchanged at 3400 cm^{-1} (asymmetric) and 3310 cm^{-1} (symmetric) in the ligand and complexes, showing its non-participation in the coordination. The stretching vibrations for —OCH_3 groups appear at 2927–2838 cm^{-1}. The above assignments suggest that, in Mn(II), Co(II), Ni(II), Zn(II) complexes the ligand has coordinated through carbonyl oxygen, azomethine nitrogen and phenolic oxygen via deprotonation. For Cu(II) complex, imino nitrogen and deprotonated enolic oxygens are the coordinating sites. Thus, the IR spectral data clearly reveals that the ligand acts in both monobasic and dibasic tridentate nature.

3.3. NMR spectral studies

In order to validate the formation of H_2L and to correlate the chemical shifts of directly attached protons and carbon, we have undertaken C—H COSY (HMQC) NMR spectral studies (Fig. 1). The absence of contour around 65–75 ppm in the C—H COSY (HMQC) NMR spectrum, which is characteristic for the sp^3 hybridized carbon confirms the ligand to be a hydrazone product rather than the cyclized 1,2-dihydroquinazolinone. ^{1}H NMR spectrum of H_2L shows D_2O exchangeable broad singlet's at 11.84, 11.24 ppm integrating for one proton each and 6.43 ppm integrating for two protons assigned to OH, NH and NH_2 respectively. Appearance of NH_2 protons, downfield to TMS, may be due to the presence of intra molecular hydrogen bonding between NH_2 proton and carbonyl oxygen. Aromatic protons appear between 7.60–6.67 ppm integrating for seven protons. The protons due to —OCH_3 and —N=C*H* have appeared as singlets at 3.81 and 8.58 ppm respectively. The ^{13}C NMR spectrum of H_2L shows fifteen signals corresponding to the total number of carbon atoms present in H_2L. Carbon signals due to carbonyl carbon, azomethine carbon, methoxy carbon and carbon attached to hydroxy group are observed at 163.12, 154.31, 55.75 and 149.12 ppm respectively. Thus, the ^{1}H, ^{13}C and C—H COSY (HMQC) NMR prove the formation of ligand. The ^{1}H and ^{13}C NMR spectra of H_2L are given in Supplementary material as S-1 and S-2 respectively.

The absence of OH resonance in ^{1}H NMR spectrum of Zn(II) complex indicates the coordination of H_2L via deprotonation of phenolic OH. The resonance due to NH_2 protons has shifted up field, indicating the breakdown of intra molecular bonding between NH_2 proton and carbonyl oxygen on complexation. Absence of these NH_2 protons after the D_2O exchange in ^{1}H NMR spectrum of Zn(II) complex confirms the noninvolvement of NH_2 protons in coordination. In the ^{13}C NMR spectrum of Zn(II) complex, signals corresponding to carbonyl carbon and azomethine carbon have shifted downfield by 1.05 and 2.03 ppm and thus confirms the coordination of carbonyl oxygen and azomethine nitrogen to metal ion.

Table 1
Analytical and physicochemical data of H_2L and its metal complexes.

Compound (empirical formula)	M.W	Elemental analysis (%) found (calculated)				λ_{max} (nm)	μ_{eff} (BM)	(Λ_M[a])
		C	H	N	M			
H_2L ($C_{15}H_{15}N_3O_3$)	285.11	63.23 (63.15)	5.27 (5.30)	14.71 (14.73)	–	398, 690	–	–
$[Mn(HL)_2]$ ($C_{30}H_{28}MnN_6O_6$)	623.14	57.73 (57.79)	4.57 (4.53)	13.54 (13.48)	8.78 (8.81)	343	5.89	1.61
$[Co(HL)_2]$ ($C_{30}H_{28}CoN_6O_6$)	627.14	57.28 (57.42)	4.46 (4.50)	13.43 (13.39)	9.37 (9.39)	364, 435, 538, 466	4.78	0.35
$[Ni(HL)_2]$ ($C_{30}H_{28}N_6NiO_6$)	626.14	57.41 (57.44)	4.42 (4.50)	13.46 (13.40)	9.31 (9.36)	373, 447, 789, 634	2.89	2.48
$[Cu(L)H_2O]$ ($C_{15}H_{15}CuN_3O_4$)	364.03	49.33 (49.38)	4.09 (4.14)	11.54 (11.52)	17.37 (17.42)	380, 463, 600–840	1.66	3.63
$[Zn(HL)_2]$ ($C_{30}H_{28}N_6O_6Zn$)	632.13	56.83 (56.84)	4.42 (4.45)	13.30 (13.26)	10.37 (10.31)	468	–	0.55

[a] Ω^{-1} cm^2 mol^{-1}.

Table 2
Diagnostic IR bands (cm^{-1}) in H_2L and its metal complexes.

Compound	$\nu(NH_2)$	ν(NH)	ν(OH)	$\nu(OCH_3)$	ν(C=O)	ν(C=N)	ν(C—O)	$\delta(OH)_{Water}$	ν(—C=N—N=C—)
H_2L	3403–3305s	3273w	3413s	2927–2838s	1645s	1612sh	1249s	–	–
$[Mn(HL)_2]$	3407–3304sh	3225w	–	2931–2840w	1631s	1587sh	1243s	–	–
$[Co(HL)_2]$	3410b	n.o.	–	2937–2842s	1634s	1590w	1253w	–	–
$[Ni(HL)_2]$	3408–3305w	3213b	–	2925–2833s	1638s	1598sh	1257s	–	–
$[Cu(L)H_2O]$	3400–3306w	3185b	–	2928–2849w	–	1592w	1251s	811w	1589sh
$[Zn(HL)_2]$	3401–3310sh	3228b	–	2939–2845w	1637s	1577sh	1259s	–	–

b = broad, sh = sharp, s = strong, w = weak, n.o. = not observed.

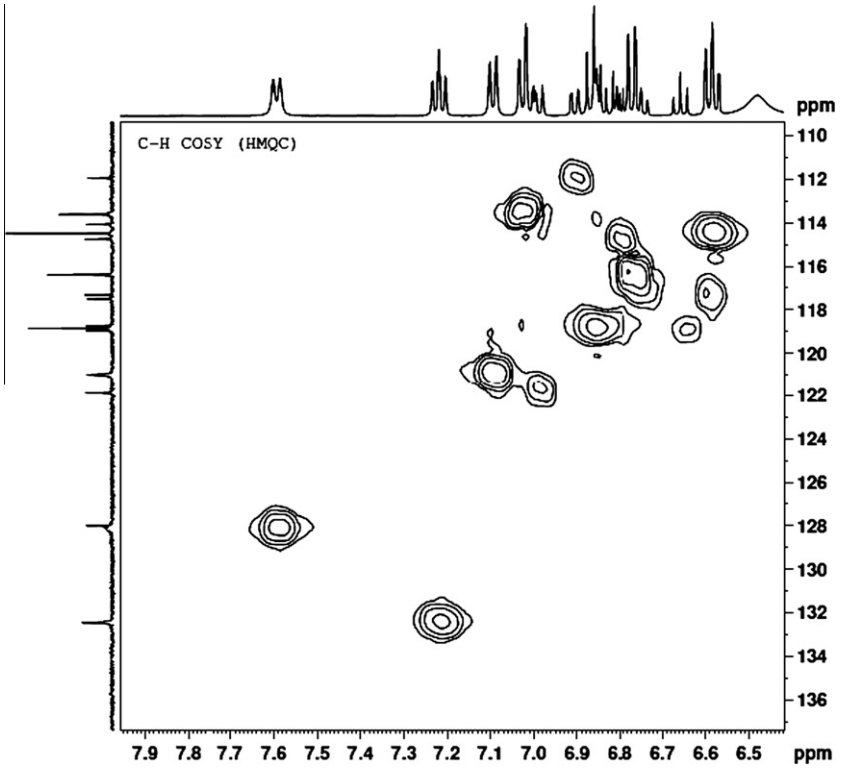


Fig. 1. C—H COSY (HMQC) NMR spectrum of H_2L.

3.4. Electronic spectral and magnetic moment studies

Electronic spectrum of the ligand shows two prominent absorptions at 398 and 690 nm. The band at 398 nm correspond to the azomethine group and a broad band at 690 nm corresponds to the $n \rightarrow \pi^*$ transition [31,32]. All the complexes show $\pi \rightarrow \pi^*$ transition in the range 343–380 nm. In addition, they also display bands at 435, 447, 463 and 468 nm in case of Co(II), Ni(II), Cu(II) and Zn(II) complexes respectively and were assigned to charge transfer transitions. A broad band around 600–840 nm appearing as an envelope in the Cu(II) complex, was assigned to $E_{2g} \rightarrow T_{2g}$ transition. This may be due to the compression of the tetrahedron towards square planar geometry [33]. Ni(II) complex exhibits two bands at 789 and 634 nm and are due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ transitions indicating an octahedral geometry [34]. The two distinct bands in regions 538 and 466 for the Co(II) complex are assignable to spin allowed transitions and are consistent with an octahedral geometry [31].

Magnetic moments of paramagnetic complexes were recorded in order to obtain the structural information of these complexes. The magnetic moment value observed for Co(II) complex is 4.78 BM indicating that it has three unpaired electrons reveals an high-spin octahedral geometry around Co(II) metal center. Higher magnetic moment value observed for octahedral Co(II) complexes, may be due to large orbital contribution of ^{4}Tg ground term and exhibit μ_{eff} value in the range 4.6–5.6 BM [35,36]. The μ_{eff} value of 2.89 BM for Ni(II) complex also suggest an octahedral geometry around the metal ion [37]. The magnetic moment value for Cu(II) complex (1.66 BM) is well within the range corresponding to spin-only value for one unpaired electron with a square planar geometry. An effective magnetic moment of 5.89 was observed for Mn(II) complex and is within the range for high spin octahedral complexes [37].

3.5. Mass spectral studies

The molecular ion peak, m/z = 308 ($M + Na^+$) corresponds to the molecular weight of the ligand H_2L (Fig. 2). The FAB mass spectra of Mn(II) and Cu(II) complex show molecular ion peaks with m/z values 623 and 364 corresponding to the molecular weight of the respective complexes. These values are in good agreement with the proposed composition for the complexes. Representative FAB mass spectra of Cu(II) and Mn(II) complexes are shown in Figs. 3 and 4.

3.6. Thermal studies

Thermal studies of complexes have been undertaken to know the presence/absence of coordinated/lattice held water molecules and to confirm the composition as well. The thermogram of Cu(II) complex show a weight loss of 4.93% (Calc. 4.95%) between the temperature 50 and 250 °C indicating the presence of one coordinated water molecule. Weight loss of 77.71% (Calc. 77.76%) around 250–510 °C corresponds to the loss of a ligand molecule. The plateau obtained after heating above 510 °C corresponds to the formation of stable metal oxide, and the metal content calculated from this residue (17.28%) tallies with the metal analysis (17.37%). In case of Mn(II), Co(II), Ni(II) and Zn(II) complexes, no weight loss was observed up to the temperature 260 °C and indicates the absence of any lattice held/coordinated solvent molecules. The weight loss of 91.13%, 90.57%, 90.63% and 89.81% (Calc. 91.18%, 90.60%, 90.74% and 89.88%) respectively around 360–390 °C correspond to the loss of two ligand molecules. Weight of the residue obtained after heating the complex above 390 °C corresponds to the formation of stable metal oxides. Thus, thermal studies support the suggested composition for the complexes. As representatives, thermograms of Cu(II) and Ni(II) complexes are given in Figs. 5 and 6 respectively.

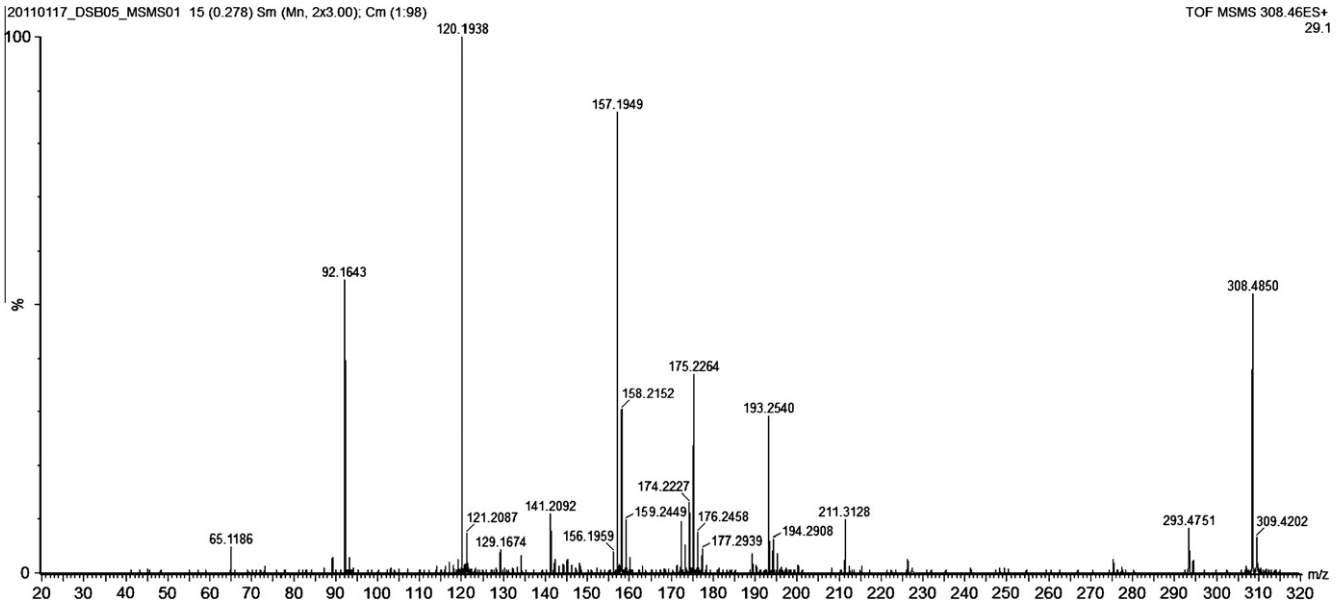


Fig. 2. Mass spectrum of H_2L.

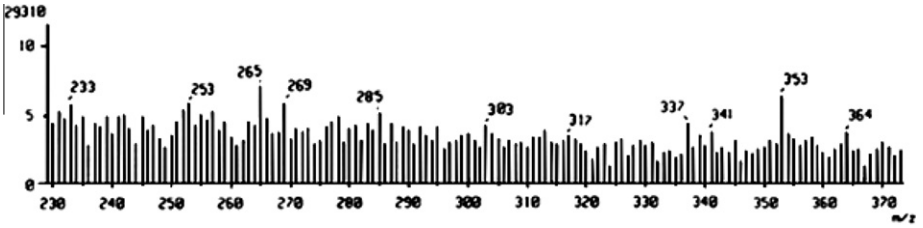


Fig. 3. FAB Mass spectrum of Cu(II) complex.

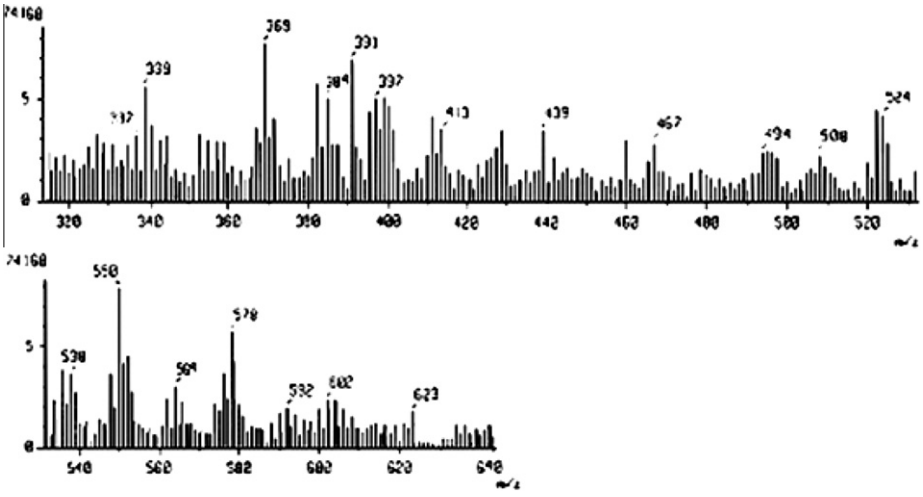


Fig. 4. FAB Mass spectrum of Mn(II) complex.

3.7. EPR Spectral studies

The EPR spectra of the Cu(II) complex show a broad absorption band, both at 300 and 77 K, which is isotropic due to the tumbling motion of the molecules. The 'g_{iso}' values at 300 and 77 K are 2.016 and 2.012 respectively.

3.8. Antimicrobial studies

The *in vitro* antimicrobial activity of synthesized derivatives was measured in comparison with ciprofloxacin and Fluconozole (Table 3) as standards to reveal the potency of synthesized derivatives. All the selected strains of bacteria and fungi namely

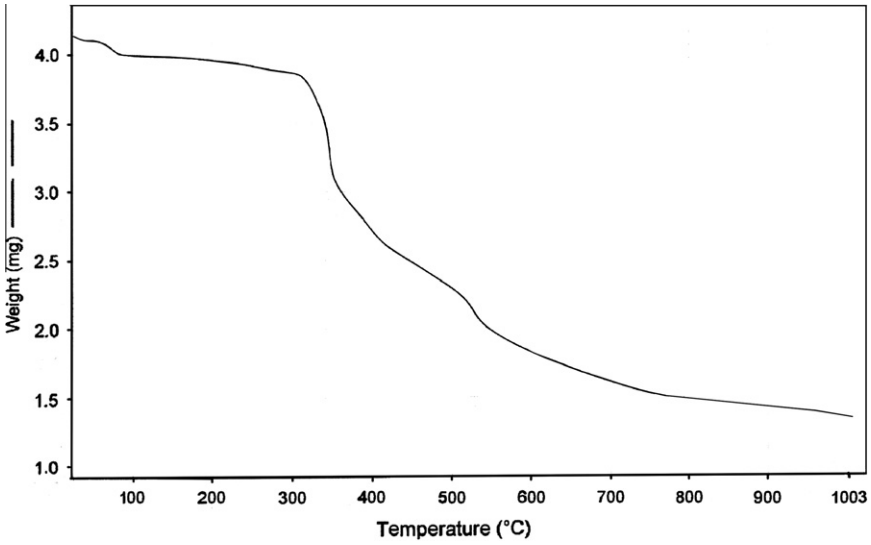


Fig. 5. Thermogram of Cu(II) complex.

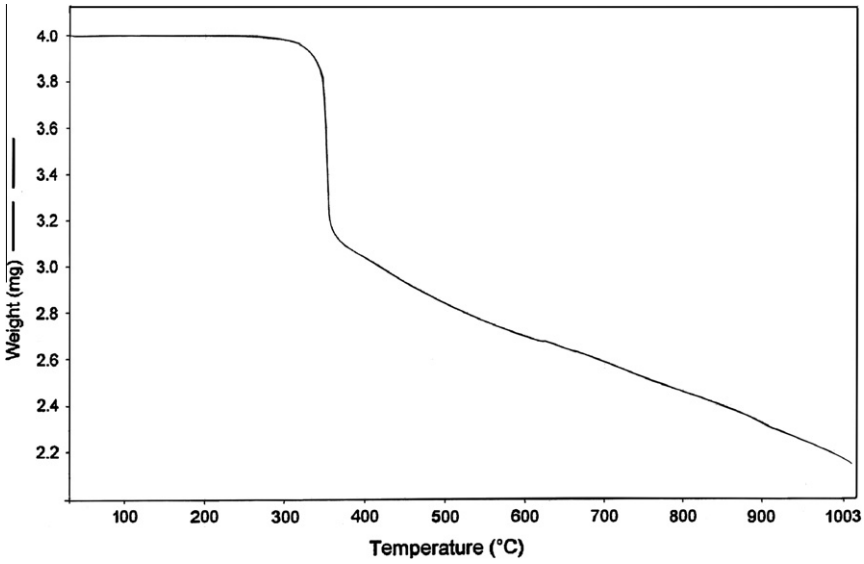


Fig. 6. Thermogram of Ni(II) complex.

Table 3
In vitro antimicrobial activities of H_2L and its metal complexes (MIC in μg/mL).

Compound	Bacteria				Fungi	
	Gram positive		Gram negative			
	SA	*EF*	*EC*	*SM*	*CA*	*AN*
H_2L	50	100	25	50	25	12.5
$[Mn(HL)_2]$	25	50	25	12.5	6.25	3.125
$[Co(HL)_2]$	12.5	25	12.5	25	3.125	12.5
$[Ni(HL)_2]$	12.5	25	6.25	3.125	12.5	6.25
$[Cu(L)H_2O]$	6.25	3.125	3.125	12.5	1.6	1.6
$[Zn(HL)_2]$	25	12.5	3.125	6.25	12.5	6.25
Ciprofloxacin	0.006	0.006	0.0125	0.0125	–	–
Fluconozole	–	–	–	–	0.05	0.006

SA – Staphylococcus aureus; *EF – Enterococcus faecalis*; *EC – Escherichia coli*; *SM – Streptococcus mutans*; *CA – Candida albicans*; *AN – Aspergillus niger*.

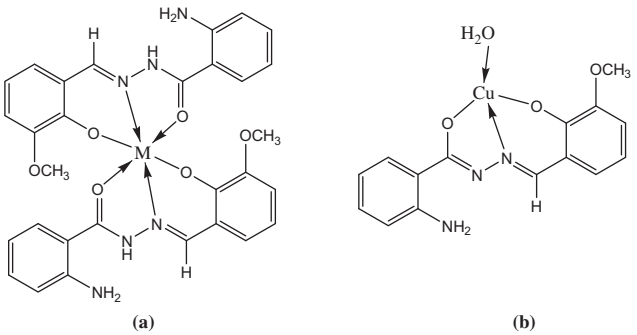


Fig. 7. Tentative structures for complexes.

Staphylococcus aureus (*SA*), *Enterococcus faecalis* (*EF*) (Gram positive), *Escherichia coli* (*EC*), *Streptococcus mutans* (*SM*) (Gram negative) and the fungal strains *Candida albicans* (*CA*) and *Aspergillus niger* (*AN*) showed sensitivity to all the derivatives comparatively at lower concentration (MIC 1.6–100 μg/mL). Among the prepared compounds, complexes (MIC 1.6–50 μg/mL) have shown enhanced

activity compared to the ligand (MIC 12.5–100 μg/mL) and are quite comparable with standard drugs used.

In general, the activity shown by the compounds against all the strains varies in the order *CA, AN* > *EC*, *SM* > *SA*, *EF* strains. Among the complexes, Cu(II) complex has shown the maximum activity against the tested bacterial strains and significant activity against fungal strains (*CA* and *AN*) with an MIC value of 1.6 μg/mL. For the other complexes, the activity is in the following order Ni > Co > Zn > Mn complexes.

The Mn(II) complex exhibits significant activity against *AN* with an MIC of 3.125 μg/mL. Similarly Ni(II), Co(II) and Zn(II) complexes have shown highest activity against *SM*, *CA* and *EC* strains respectively (Table 3). The antifungal potency of complexes is noteworthy against all fungal strains. The increased lipophilic nature of the complexes may have a pronounced effect on antimicrobial activity.

4. Conclusion

Methoxysalicylaldehyde-2-aminobenzoylhydrazone (H_2L) was isolated by the condensation of 2-ABH and 3-methoxysalicylaldehyde at −5 to 0 °C. The structure of H_2L was confirmed by various spectroscopic techniques. The coordination mode of H_2L is well established from elemental analysis, molar conductivity, IR, NMR, mass, electronic spectral and thermal studies. These studies indicate that the ligand essentially coordinates in tridentate fashion with carbonyl oxygen, azomethine nitrogen and phenolic oxygen via deprotonation except in Cu(II) complex where the ligand coordinates via enolization and deprotonation of amide proton. The octahedral geometry was assigned for Mn(II), Co(II), Ni(II) and Zn(II) complexes and square planar for Cu(II) complex. Thus, the ligand acts both in monobasic as well as dibasic manner. The tentative structures for complexes are depicted in Fig. 7a and b.

The H_2L and their complexes have been screened for their *in vitro* antimicrobial activities. The activity of ligand was enhanced on complexation. The increase in activity of the metal complexes was probably due to the greater lipophilic nature of the complexes. Among the complexes Cu(II) complex has shown highest activity. The difference in activity among the tested compounds may be attributed to the electrostatic nature of ligand and central metal ion.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2012.02.062.

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