



Synthesis, Characterization and Antimicrobial Activities of 1,2,4-Triazole-Coumarin Schiff Bases and their Mn(II), Co(II) Complexes

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Manganese(II) and cobalt(II) metal complexes have been synthesized with newly synthesized Schiff bases derived from 8-formyl-7-hydroxy-4-methylcoumarin and 3-substituted 4-amino-5-mercapto-1,2,4-triazole by microwave irradiation method as well as conventional method. Reaction achieved by microwave irradiation technique, require drastically reduced reaction time and provide high yield with improved selectivity as compared to conventional method. The synthesized compounds were characterized by elemental analysis, spectral studies, magnetic measurements and thermal studies. The elemental analysis were clearly indicated that $ML_2 \cdot 2H_2O$ type complexes have 1:1 stoichiometry (M = metal, L = ligand). All the Mn(II) and Co(II) complexes were stable at room temperature, non-hygroscopic, insoluble in water and all of them were polymeric in nature. The synthesized Schiff bases and their metal complexes screened for antimicrobial activities against selected bacteria and fungi.

Keywords: Microwave irradiation, Schiff bases, 1,2,4-Triazole, Coumarin, Antimicrobial, Complexes.

INTRODUCTION

The chemistry of 1,2,4-triazole and its derivatives is particularly interesting because of their potential applications in medicinal, agricultural and industrial fields¹⁻⁴. Derivatives of 1,2,4-triazoles show variety of biological activities such as antimicrobial⁵, anticonvulsant⁶, anticancer⁷, analgesic⁸, anti HIV⁹ and anti-inflammatory¹⁰ properties. Similarly, coumarins have long been recognized to possess anti-inflammatory¹¹, antioxidant¹², antithrombotic¹³, antiallergic¹⁴, hepatoprotective¹⁴, antiviral¹² and anticarcinogenic¹⁴ activities. The hydroxyl coumarins are typical phenolic compounds and therefore act as potent metal chelators and free radical scavengers. They are powerful chain-breaking antioxidants¹⁵. The coumarins display a remarkable array of biochemical and pharmacological actions¹¹⁻¹⁴. The antitumor effects of coumarin and its major metabolite, 7-hydroxycoumarin were tested in several human tumor cell lines¹⁶. Furthermore, cytotoxic effects of complexes of coumarin derivatives were examined on several neuronal cell lines¹⁷. Some metal complexes derived from coumarin and 1,2,4-triazole Schiff bases have reported to exhibit antimicrobial activities¹⁸. These diverse biological applications of Schiff bases and their precursors have inspired to synthesize a new series of metal [Mn(II), Co(II)] complexes with Schiff bases containing 8-formyl-7-hydroxy-4-methylcoumarin and 3-substituted 4-amino-5-mercapto-1,2,4-triazole.

In recent years microwave assisted reactions have attracted researchers much interest because of simplicity of operation, enhanced reaction rates, high yields, improved selectivity^{19,20} and environmental friendly reaction conditions²¹⁻²³. The reactions, which are not possible under normal conditions can be overcome by high-energy microwave irradiation. Therefore we have made efforts to develop and optimize a new environmentally benign method using microwave irradiation in our laboratory and finally 3-substituted 4-amino-5-mercapto-1,2,4-triazole²⁴ and 8-formyl-7-hydroxy-4-methylcoumarin have been synthesized. These compounds were also prepared by conventional methods^{25,26} to compare their results with new microwave irradiation method. The newly synthesized compounds were characterized by spectral as well as elemental analysis and screened for their biological activities.

EXPERIMENTAL

The melting points of synthesized compounds were determined on open aluminum block and are not corrected. All the metal complexes decomposed above 290 °C. Purity was checked by TLC using Merck Silica gel G-60. Infrared (IR) spectra of all the synthesized compounds recorded using KBr from Shimadzu FTIR, Affinity-1. The NMR spectra has taken by Varian Gemini 400 spectrometer (300MHz) using TMS as an internal standard. The electronic spectra of synthesized

complexes were recorded in DMF on a VARIAN CARY 50-BIO UV-Spectrophotometer. Thermo gravimetric data were obtained by using a PERKIN-ELMER DIAMOND TG/DTG instrument from room temperature to 1000 °C and study of magnetic moments was carried out by Faraday balance. Elemental data obtained from all the synthesized compounds were found satisfactory.

Synthesis of Schiff bases

Conventional method: The equimolar quantity of 3-substituted 4-amino-5-mercapto-1,2,4-triazole (10 mmol) and 8-formyl-7-hydroxy-4-methylcoumarin (10 mmol) containing 3-4 drops concentrated HCl in hot ethanol (45 mL) was refluxed for 5 h on water bath. After completion of reaction as monitored by TLC, the reaction mixture was cooled at room temperature. The solid separated out was filtered and washed with alcohol, dried and recrystallized from ethanol.

Microwave assisted method: A mixture of 3-substituted 4-amino-5-mercapto-1,2,4-triazole (1 mmol) and 8-formyl-7-hydroxy-4-methylcoumarin (1 mmol) in ethanol (10 mL) containing concentrated HCl (0.5 mL) was subjected to microwave irradiation intermittently at 30 s for 4-5 min. After completion of reaction as monitored by TLC, the reaction mixture was cooled at room temperature. The solid separated out was filtered and washed with alcohol, dried and recrystallized from ethanol.

The analytical data for all the synthesized Schiff bases are summarized here. The yield obtained by microwave-assisted method is represented in bracket.

8-[[3-(3-Phenyl-5-mercapto-1,2,4-triazol-4-yl)iminomethyl]-7-hydroxy-4-methyl chromen-2-one (3a): Yield 66 % (87 %); m.p. 240 °C; IR (KBr, ν_{\max} , cm^{-1}): 1697 (>C=O), 1632 (C=N), 3146 (N-H), 2735 (S-H), 1110 (C=S), 1055 (O-C-O), 3264 (H bonded -OH stretching), 1286 (phenolic C-O); $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.20-7.83 (Ar-8H, m), 13.98 (N-H, 1H, s), 8.55 (CH=N, 1H, s), 10.20 (phenolic -OH, 1H, s), 3.55 (S-H, 1H, s); Anal. calcd. (%) for $\text{C}_{19}\text{H}_{14}\text{N}_4\text{O}_3\text{S}$; C: 60.31, H: 3.70, N: 14.81, S: 8.46; Found (%): C: 60.28, H: 3.69, N: 14.76, S: 8.45.

8-[[3-(4-Methoxyphenyl)-5-mercapto-1,2,4-triazol-4-yl]iminomethyl]-7-hydroxy-4-methylchromen-2-one (3b): Yield 61 % (90 %); m.p. 249 °C; IR (KBr, ν_{\max} , cm^{-1}): 1693 (>C=O), 1638 (C=N), 3150 (N-H), 2730 (S-H), 1115 (C=S), 1050 (O-C-O), 3250 (H bonded -OH stretching), 1298 (phenolic C-O); $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.22-7.80 (Ar-7H, m), 13.90 (N-H, 1H, s), 8.51 (CH=N, 1H, s), 10.16 (phenolic -OH, 1H, s), 3.50 (S-H, 1H, s), 3.71 (OCH_3 , 3H, s); Anal. calcd. (%) for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_4\text{S}$; C: 58.82, H: 3.92, N: 13.72, S: 7.84; Found (%): C: 58.80, H: 3.91, N: 13.69, S: 7.85.

8-[[3-(4-Chlorophenyl)-5-mercapto-1,2,4-triazol-4-yl]iminomethyl]-7-hydroxy-4-methylchromen-2-one (3c): Yield 60 % (85 %); m.p. 258 °C; IR (KBr, ν_{\max} , cm^{-1}): 1707 (>C=O), 1633 (C=N), 3142 (N-H), 2728 (S-H), 1101 (C=S), 1061 (O-C-O), 3255 (H bonded -OH stretching), 1290 (phenolic C-O); $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.15-7.70 (Ar-7H, m), 13.95 (N-H, 1H, s), 8.60 (CH=N, 1H, s), 10.26 (phenolic -OH, 1H, s), 3.58 (S-H, 1H, s); Anal. calcd. (%) for $\text{C}_{19}\text{H}_{13}\text{N}_4\text{O}_3\text{S}\text{Cl}$; C: 55.27, H: 3.15, N: 13.57, S: 7.75; Found (%): C: 55.25, H: 3.15, N: 13.56, S: 7.73.

8-[[3-(4-Bromophenyl)-5-mercapto-1,2,4-triazol-4-yl]iminomethyl]-7-hydroxy-4-methylchromen-2-one (3d): Yield 58 % (88 %); m.p. 272 °C; IR (KBr, ν_{\max} , cm^{-1}): 1701 (>C=O), 1630 (C=N), 3139 (N-H), 2736 (S-H), 1118 (C=S), 1064 (O-C-O), 3246 (H bonded -OH stretching), 1285 (phenolic C-O); $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.24-7.90 (Ar-7H, m), 13.95 (N-H, 1H, s), 8.60 (CH=N, 1H, s), 10.26 (phenolic -OH, 1H, s), 3.65 (S-H, 1H, s); Anal. calcd. (%) for $\text{C}_{19}\text{H}_{13}\text{N}_4\text{O}_3\text{SBr}$; C: 49.90, H: 2.84, N: 12.25, S: 7.00; Found (%): C: 49.88, H: 2.83, N: 12.23, S: 7.01.

8-[[3-(4-Nitrophenyl)-5-mercapto-1,2,4-triazol-4-yl]iminomethyl]-7-hydroxy-4-methylchromen-2-one (3e): Yield 65 % (84 %); m.p. 263 °C; IR (KBr, ν_{\max} , cm^{-1}): 1713 (>C=O), 1641 (C=N), 3145 (N-H), 2742 (S-H), 1105 (C=S), 1050 (O-C-O), 3260 (H bonded -OH stretching), 1290 (phenolic C-O); $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.29-7.88 (Ar-7H, m), 14.10 (N-H, 1H, s), 8.66 (CH=N, 1H, s), 10.30 (phenolic -OH, 1H, s), 3.62 (S-H, 1H, s); Anal. calcd. (%) for $\text{C}_{19}\text{H}_{13}\text{N}_5\text{O}_5\text{S}$; C: 52.17, H: 2.97, N: 16.01, S: 7.32; Found (%): C: 52.13, H: 2.96, N: 16.03, S: 7.31.

Synthesis of metal complexes

All the metal complexes were synthesized by both conventional and microwave assisted methods. The latter method provided reproducible results and analytical data related to the products obtained from both methods were found coherent.

Conventional method: An ethanolic solution (20 mL) of Schiff base (1 mmol) was added to an ethanolic solution (20 mL) of the metal chloride (1 mmol) and 2 mmol of sodium acetate and refluxed on steam bath for 4 h. The reaction mixture was cooled at room temperature and the solid separated out was filtered, washed thoroughly with water-ethanol and dried.

Microwave assisted method: An ethanolic solution (7 mL) of Schiff base (1 mmol) was added to an ethanolic solution (7 mL) of the metal chloride (1 mmol) and 2 mmol of sodium acetate and subjected to microwave irradiation intermittently at 30 s for 7-8 min. After completion of the reaction as monitored by TLC, the hot reaction mixture was cooled and the solid separated out was filtered, washed thoroughly with water-ethanol and dried.

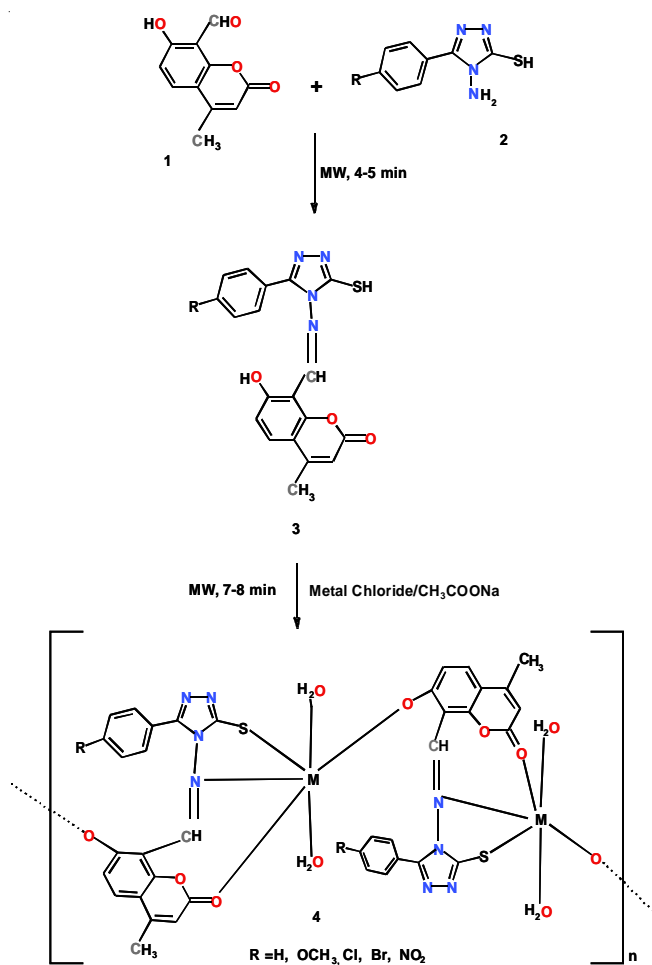
Antimicrobial activity: Antimicrobial activity of synthesized Schiff bases and their metal complexes were evaluated *in vitro* by using agar-plate diffusion technique⁸ by measuring the zone of inhibition in mm. The antibacterial activity was evaluated against five bacterial strains *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella typhi*, *Staphylococcus aureus* and *Bacillus subtilis* at 100 $\mu\text{g}/\text{mL}$ concentration of samples with standard drugs gentamycin. After completion of incubation period (18-24 h at 37 °C), the zone of inhibition of growth in the form of diameter in mm was measured.

Antifungal activities was evaluated against *Aspergillus neiger* and *Candida albicans* at 100 $\mu\text{g}/\text{mL}$ concentration of samples using fluconazole as standard drug. After completion of the incubation period (18-24 h at 37 °C), the zone of inhibition of growth in the form of diameter in mm was measured.

RESULTS AND DISCUSSION

The present work was focused on the synthesis of some new Schiff bases and their Mn(II) and Co(II) complexes by

microwave irradiation (**Scheme-I**). These compounds were also synthesized by conventional method¹⁸. In microwave method, the reaction time reduced from 5 h to 4-5 min (**3a-e**) and from 4 h to 7-8 min (**4a-j**). The yield obtained from microwave method was better as compared to conventional method. All the Mn(II) and Co(II) complexes were stable at room temperature, non-hygroscopic, insoluble in water. The purity of the compounds was checked by TLC. The compounds were characterized with the help of spectral data (IR, ¹H NMR) and elemental analysis. All data were found in accordance with the proposed structures of synthesized compounds.



Scheme-I: Synthetic pathway of compounds

The IR spectroscopic data have indicated the formation of **3a-e** by disappearance of the NH₂ band at 3400 cm⁻¹ (**2a-e**) and appearance of C=N band at about 1641-1630 cm⁻¹ (**3a-e**). The characteristic bands at about 3150-3135 cm⁻¹ and at 2742-2725 cm⁻¹ clearly indicate the presence of N-H and S-H group, respectively²⁷ and another band around at 1118-1101 cm⁻¹ is assigned to ν(C=S)²⁷. These observations indicate that the Schiff bases exhibit thiol-thione tautomerism (Fig. 1). The broad band at about 3265-3245 cm⁻¹, a strong band at 1713-1693 and 1298-1285 cm⁻¹ in the IR spectra of the Schiff bases are assigned to H-bonded OH stretching, ν(C=O) lactonic carbonyl²⁸ and phenolic ν(C-O) vibrations, respectively. A medium band around at 1064-1050 cm⁻¹ is characterized for ν(O-C-O) of coumarin ring.

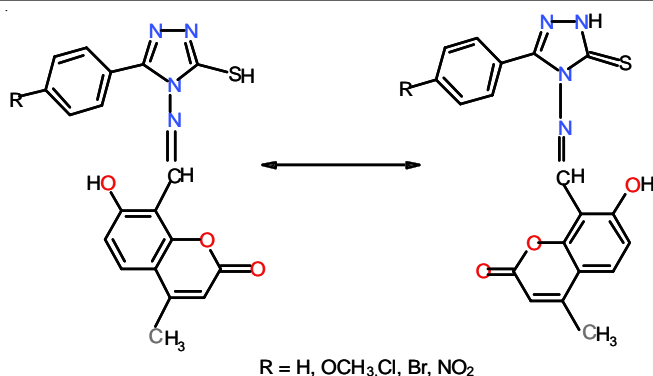


Fig. 1. Tautomeric form of synthesized Schiff base

All the metal complexes exhibited a band for ν(C=N) in the region 1628-1617 cm⁻¹, showing the shift of this band to lower wave numbers, as compared with the spectra of the Schiff bases. This shift indicates that the azomethine nitrogen is coordinated to the metal ion. The new bands in the region of 463-450 cm⁻¹ in the spectra of the metal complexes are assigned to stretching frequencies of (M-N) bonds. The absence of a band around at 2742-2728 cm⁻¹ in all the metal complexes and new band in the region 371-359 cm⁻¹ in far IR-spectra indicate the formation of metal-sulfur bonds. All the metal complexes exhibited high intensity band at about 1360-1342 cm⁻¹ due to phenolic (C-O) which is exhibited by the Schiff bases in the region at 1298-1285 cm⁻¹. These observation indicate the formation of M-O bonds. So the hydrogen bonded -OH group has been replaced by metal ion *via* deprotonation. The band for ν(C=O) in the region 1700-1684 cm⁻¹ in the complexes, showing the shift to lower wave numbers compared with Schiff bases confirms that the lactone oxygen is also coordinated to the metal ion²⁹. This is further supported by downward shift in (O-C-O) of the coumarin ring³⁰. The presence of coordinated water molecules in the metal complexes²⁷ is indicated by a broad band in the region 3466-3245 cm⁻¹ and two weaker bands in the region 807-766 and 723-710 cm⁻¹ due to ν(OH) rocking and wagging mode of vibrations, respectively³¹. The new bands in the region 385-374 cm⁻¹ in all the complexes are assigned to stretching frequencies of (M-O) bonds. All the infrared frequencies of metal complexes are summarized in Table-1. The IR data, taken together with the insolubility of the complexes in water and as all the complexes are fusible at higher temperatures, suggest that they exist in the solid state as polymeric structures with bonding of Mn(II), Co(II) likely to both the lactone carbonyl oxygen and deprotonated phenolic oxygen³²⁻³⁴.

The comparison of ¹H NMR spectroscopic data of Schiff bases and their precursors also indicate the formation of **3a-e** by the appearance of signals of NH protons³⁵ at about 13.90-14.10 ppm and the disappearance of the NH₂ protons in the **2a-e** at about 5.00-5.40 ppm. The ¹H NMR spectra of Schiff bases exhibited singlet at 10.16-10.30, 8.51-8.66 ppm and multiplet at 7.15-7.90 ppm due to phenolic OH, -CH=N³⁶ and aromatic protons, respectively. A sharp singlet at 3.50-3.65 ppm is assigned to SH protons³⁷. The singlet exhibited around 3.71 ppm is due to methoxy protons.

Electronic spectra of all the Mn(II) complexes display weak absorption bands in the region 18595-18671 cm⁻¹ (ν₁),

TABLE-1
CHARACTERISTIC INFRARED VIBRATIONS (cm⁻¹) OF METAL COMPLEXES (4a-j)

Compd. No.	v(C=O)	v(C=N)	v(-OH)	v(C-O)	v(M-S)	v(M-N)	v(M-O)
4a	1685	1620	3426	1350	365	450	375
4b	1691	1626	3431	1346	360	455	381
4c	1695	1622	3428	1352	362	460	385
4d	1696	1620	3430	1350	364	457	379
4e	1690	1625	3440	1356	359	462	377
4f	1684	1623	3428	1348	370	452	378
4g	1697	1625	3420	1342	368	463	380
4h	1690	1618	3435	1345	365	458	382
4i	1698	1617	3438	1353	371	460	376
4j	1700	1628	3436	1360	362	455	374

23640-23732 cm⁻¹ (v₂), 27690-27766 cm⁻¹ (v₃) and 38855-38990 cm⁻¹ (v₄). These transitions correspond to ⁶A_{1g} → ⁴T_{1g}(4G), ⁶A_{1g} → ⁴T_{2g}(4D), ⁶A_{1g} → ⁴T_{1g}(4P), ⁶A_{1g} → ⁴E_g(4G), respectively and are characteristic of octahedral geometry around the Mn(II) ions. The cobalt complexes exhibited two distinct bands in the region 9780-9950 and 18955-20670 cm⁻¹ which may be corresponding to ⁴T_{1g}(F) → ⁴T_{2g}(F) (v₁) and ⁴T_{1g}(F) → ⁴T_{1g}(P) (v₃) transitions, respectively and these indicate octahedral geometry around the cobalt(II) ions^{38,39}. The magnetic moments obtained at room temperature are listed in Table-2. The Mn(II) complexes showed the magnetic moment in the range of 5.76–5.89 BM which suggest the octahedral geometry of these complexes. The magnetic moment, 4.70-4.94 BM for Co(II) complexes also suggest⁴⁰ their octahedral environment.

The thermal behaviour of Mn(II) and Co(II) complexes has been studied as a function of temperature and it is almost the same. Hence, only Mn(II) (4a) and Co(II) (4f) complexes were discussed. The DTG curve of the Mn(C₁₉H₁₂N₄O₃S)·2H₂O complex showed that the two coordinated water molecule, triazole moiety and coumarin moiety were lost in the regions of 205-240, 300-325 and 480-510 °C corresponding to the mass losses of 7.66 % (calc. 7.70 %), 40.38 (calc. 40.47 %) and 39.81 % (calc. 39.83 %). Finally, the formation of metal oxide took place above 520 °C. The complex Co(C₁₉H₁₂N₄O₃S)·2H₂O lost two coordinated water molecule, triazole moiety and coumarin moiety in the regions of 205-240, 300-325 and 480-510 °C corresponding to the mass losses of 7.60 % (calc. 7.64 %), 39.98 (calc. 40.13 %) and 39.43 % (calc. 39.49 %). Finally, the formation of metal oxide took place above 530 °C.

The Schiff bases (3a-e) and their metal complexes (4a-j) along with some standard antibiotics and antifungal drugs were screened for their antimicrobial activities against selected bacteria and fungus. The antimicrobial activity results of the synthesized compounds are summarized in Table-3. All the Schiff bases were found biologically active and their metal complexes show higher antimicrobial activity in comparison to respective Schiff bases against selected bacteria and fungi. The Mn(II), Co(II) metal complexes showed much enhanced activity against *S. typhi*. Both the Schiff-bases and their Mn(II) and Co(II) complexes were found to possess good antifungal activity.

Conclusion

The prepared Schiff bases behave as tetradentate chelating agent with Mn(II), Co(II) metal ions and coordinated with metal ions through N, phenolic oxygen, lactone oxygen and S atoms. All the metal(II) complexes exhibit coordination number six on the basis of magnetic and electronic data. The elemental analysis were clearly indicated that ML·2H₂O type complexes have 1:1 stoichiometry (M = metal, L = ligand). The spectral data, taken together with the insolubility of the complexes in water and as all the complexes are fusible at higher temperatures, suggest that they exist in the solid state as polymeric structures with bonding of metal [Mn(II), Co(II)]. All the Schiff bases and their Mn(II), Co(II) metal complexes were synthesized by microwave irradiation as well as by conventional method to compare analytical data and confirm their structure. The studies revealed that all metal complexes show higher antimicrobial activity in comparison to respective Schiff bases against selected bacteria and fungi. It is also

TABLE-2
PHYSICAL PROPERTIES AND ANALYTICAL DATA OF METAL COMPLEXES (4a-j)

Comp. No.	Formula	R	Yield (%)		Elemental analysis (%): Found (calcd.)				Magnetic moment (BM)
			Conven. method	Micro. method	M	C	N	S	
4a	Mn(C ₁₉ H ₁₂ N ₄ O ₃ S)·2H ₂ O	H	67	80	11.75 (11.76)	48.80 (48.82)	11.96 (11.99)	6.84 (6.85)	5.76
4b	Mn(C ₂₀ H ₁₄ N ₄ O ₄ S)·2H ₂ O	OCH ₃	62	84	11.02 (11.05)	48.27 (48.29)	11.24 (11.26)	6.39 (6.43)	5.84
4c	Mn(C ₁₉ H ₁₁ N ₄ O ₃ SCl)·2H ₂ O	Cl	60	90	10.88 (10.91)	45.26 (45.30)	11.11 (11.12)	6.34 (6.35)	5.89
4d	Mn(C ₁₉ H ₁₁ N ₄ O ₃ SBr)·2H ₂ O	Br	56	81	10.00 (10.02)	41.59 (41.61)	10.20 (10.22)	5.83 (5.84)	5.79
4e	Mn(C ₁₉ H ₁₁ N ₅ O ₅ S)·2H ₂ O	NO ₂	61	88	10.37 (10.40)	43.18 (43.18)	13.23 (13.25)	6.02 (6.06)	5.80
4f	Co(C ₁₉ H ₁₂ N ₄ O ₃ S)·2H ₂ O	H	70	91	12.49 (12.51)	48.40 (48.41)	11.87 (11.89)	6.77 (6.79)	4.70
4g	Co(C ₂₀ H ₁₄ N ₄ O ₄ S)·2H ₂ O	OCH ₃	65	89	11.75 (11.76)	47.89(47.91)	11.15 (11.17)	6.35 (6.38)	4.90
4h	Co(C ₁₉ H ₁₁ N ₄ O ₃ SCl)·2H ₂ O	Cl	65	80	11.59 (11.60)	44.90(44.93)	11.01 (11.03)	6.27 (6.30)	4.87
4i	Co(C ₁₉ H ₁₁ N ₄ O ₃ SBr)·2H ₂ O	Br	59	82	10.66 (10.67)	41.30(41.31)	10.12 (10.14)	5.79 (5.79)	4.94
4j	Co(C ₁₉ H ₁₁ N ₅ O ₅ S)·2H ₂ O	NO ₂	70	85	11.03 (11.07)	42.85(42.86)	13.13 (13.15)	6.00 (6.01)	4.73

TABLE-3
ANTIMICROBIAL ACTIVITIES OF SCHIFF BASES AND THEIR METAL COMPLEXES

Compd. No.	Zone of inhibition (%)						Antifungal activity	
	Antibacterial activity							
	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>S. typhi</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>A. niger</i>	<i>C. albicans</i>	
3a	58.20	55.14	64.73	50.34	46.11	61.54	62.00	
3b	56.33	58.04	69.89	51.13	45.21	66.91	70.31	
3c	63.07	63.00	76.44	50.87	48.85	70.15	65.79	
3d	60.82	66.41	72.96	53.00	44.06	67.98	68.00	
3e	69.67	71.00	78.32	62.02	54.00	72.65	75.12	
4a	61.00	60.56	68.13	55.17	48.91	63.00	65.32	
4b	57.50	62.09	72.00	53.40	44.33	66.50	70.67	
4c	62.61	67.22	79.36	50.00	48.50	73.01	69.56	
4d	65.00	66.83	76.44	56.29	51.70	69.40	73.00	
4e	72.52	75.00	82.05	68.10	58.02	76.09	79.23	
4f	60.31	56.87	65.00	52.05	46.55	60.04	62.33	
4g	56.57	58.99	66.49	51.19	47.00	67.50	71.32	
4h	64.00	63.76	75.66	54.09	50.00	71.00	66.10	
4i	62.77	65.90	72.22	53.67	45.55	67.45	70.00	
4j	70.33	72.50	80.00	65.09	55.25	73.84	77.62	
Standard	100.00	100.00	100.00	100.00	100.00	100.00	100.00	

observed that both the Schiff-bases and their Mn(II) and Co(II) complexes were found to possess good antifungal activity.

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