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# Complexes of some 3d-metals with a Schiff base derived from 5-acetamido-1,3,4-thiadiazole-2-sulphonamide and their biological activity

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*Abstract*: Using a bidentate ligand, a Schiff base of 5-acetamido-1,3,4-thiadiazole--2-sulphonamide, complexes of transition metals having the general formula $ML_2$, where M = Mn(II), Fe(II), Ni(II) and Cu(II), were synthesized. The complexes were characterized by elemental analysis, molar conductivity, magnetic moment, electronic, ESR and IR spectroscopy, and particle size analysis. The conductivity data of the complexes suggests their non-electrolytic nature. The stability constants and free energy change for the complexes were calculated. Spectral studies and magnetic susceptibility measurements revealed an octahedral geometry for all the complexes. The ligand and its complexes were screened for their fungicidal activity against *Aspergillus niger* and *A. flavus*.

*Keywords*: Schiff base; conductivity; non-electrolytic; stability constant; fungicidal activity.

## INTRODUCTION

5-Acetamido-1,3,4-thiadiazole-2-sulphonamide (acetazolamide) is a diuretic drug. Diuretics are described as medicines that help to reduce the amount of water in the body. In the present day scenario, diseases such as high blood pressure, renal failure, diabetes, *etc*. have become very common. Hence, diuretic drugs were chosen for the present study. Schiff base metal complexes played a central role in the development of coordination chemistry. Schiff bases are widely applicable because of their industrial and biological importance and hence were well studied in the past.[1–4] It was established that the biological activity of a Schiff base is altered many fold on its coordination with suitable metal ions.[5–7] The introduction of nitrogen atoms into the structure of organic compounds often resulted in important changes in their behaviour towards metal ions. Many investigations

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were undertaken of the interaction of metal ions with ligands containing oxygen and nitrogen as donor atoms.[8,9] In the present study, metal complexes of Mn(II), Fe(II), Ni(II) and Cu(II) with a Schiff base derived from 5-acetamido-1,3,4-thiadiazole-2-sulphonamide (acetazolamide) and salicylaldehyde were synthesized and characterized in view of their importance in biological systems.[10–12]

## EXPERIMENTAL

All the chemicals used in this work were of analytical reagent grade (anhydrous) and purchased from Merck (USA).

*Synthesis of Schiff base*

Equimolar (0.01 M) solutions of pure drug (3.26 g) (provided by Shalaks' Pharmaceuticals, Mumbai, India) and salicylaldehyde (1.04 ml) were separately dissolved in a methanol––water mixture (1:1). The mixture was refluxed for four hours and kept for a day. Pale yellow crystals of acetazolamide Schiff base formed in the reaction mixture (Fig. 1), which were filtered and washed thoroughly with 50 % methanol–water mixture, dried under vacuum and weighed. The colour of the solid product was pale yellow (yield 54 %). Melting point of the Schiff base was recorded.

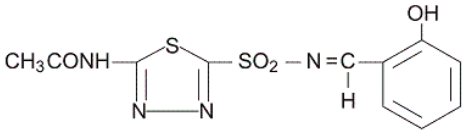


Fig. 1. The structure of the Schiff base.

*Synthesis of complexes*

For the synthesis of the complexes, 0.02 mol acetazolamide–salicylaldimine ligand solution (AZM–SA) was prepared in 60 % acetone–water solvent and then the required metal salt (0.01mol) was added. The resulting solution was refluxed for 4–5 h. The refluxed solutions were kept for some days whereby solid crystalline compounds appeared in the solution, which were filtered, washed with 60 % acetone–water mixture, dried and weighed. The melting points of the complexes were recorded.

*Methods and apparatus applied*

Elemental analyses were performed on a model 240 Perkin–Elmer elemental analyzer (USA) at CDRI Lucknow, India. The metal contents were determined gravimetrically.[13] Magnetic susceptibility measurements of the complexes in the solid state were determined on a vibrating sample magnetometer (PAR, model 155, USA) at room temperature. Molar conductance measurements were realized in anhydrous DMF on a Systronics model 305 (India) conductivity bridge. The electronic spectra of the metal complexes in dimethylformamide (DMF) were recorded on a Shimadzu UV-160A UV–Vis (USA) spectrophotometer (5815–32573 $cm^{-1}$). The infrared spectra were measured on a Nicolet 400 D FT-IR (USA) spectrophotometer in the wave number range 4000–400 $cm^{-1}$ using KBr pellets. The electron spin resonance (ESR) spectra were recorded on a Bruker DRX-300 (Germany) spectrophotometer and an X-E-4 bands spectrometer (Bruker, Germany) at LNT (liquid nitrogen temperature) and RT (room temperature), respectively. Particle size analysis was performed at Sicart, Gujarat (India) using a laser diffraction particle size analyzer (Cilas, model 1064 L/D, France). The melting points of the ligand and complexes were recorded in open capillaries on a capillary melting point apparatus (EI, model 934, IndiaLine no. 60, India).



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*Antifungal activity*

The antifungal activities of the newly synthesized compounds and ligand were evaluated by the agar growth food poison technique[14] at 500 and 1000 ppm concentrations against *Aspergillus niger* and *A. flavus*. The disc diffusion method was used for the standard drug netamycin against *A. niger* and *A. flavus* using Czapek's agar medium. The fungi were grown at 25±1 °C on dextrose agar medium. All the microbial plates were incubated for 48 h at 35 °C. The antifungal activity of all the synthesized compounds was evaluated by percentage zone of growth inhibition. Three replicates were performed for each dilution of the test compounds from the screening results. All the fungal species were procured from the Microbial Type Collection and Gene Bank, Institute of Microbial Technology (IMTECH), Chandigarh, India.

## RESULTS AND DISCUSSION

Based on the physicochemical characteristics (Table I), it was found that all the complexes were non-hygroscopic, stable at room temperature and insoluble in water but fairly soluble in dimethyl sulfoxide (DMSO). The magnetic moment data indicated all the complexes to be paramagnetic in nature. The molar conductance values for the complexes were found between 13–17 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ in DMSO, which indicates their non-electrolytic nature.[15] The elemental analysis data, formula weights and melting points are given in Table II.

TABLE I. Synthesis and physico–chemical characteristics of the complexes

| Ligand/complex | Ligand–metal ratio | Colour | Yield % | Stability constant log $K$ L mol$^{-1}$ | $\Delta F$ kJ mol$^{-1}$ | $\Lambda_m$[a] $\Omega^{-1}$ cm$^2$ mol$^{-1}$ | $\mu_{eff}$ $\mu_B$ |
|---|---|---|---|---|---|---|---|
| AZM-SA | – | Pale yellow | 54 | – | – | – | – |
| $[Mn(AZM\text{-}SA)_2(H_2O)_2]$ | 2:1 | Brown | 35 | 11.16 | –64.58 | 15.3 | 5.38 |
| $[Fe(AZM\text{-}SA)_2(H_2O)_2]$ | 2:1 | Black | 69 | 11.15 | –64.62 | 16.4 | 5.78 |
| $[Ni(AZM\text{-}SA)_2(H_2O)_2]$ | 2:1 | Pale green | 65 | 10.84 | –65.12 | 13.0 | 3.18 |
| $[Cu(AZM\text{-}SA)_2(H_2O)_2]$ | 2:1 | Dark green | 42 | 12.08 | –71.26 | 14.6 | 1.83 |

[a]$10^{-3}$ M solution in DMSO

TABLE II. Analytical data of the ligand and complexes

| Ligand/complex | Elemental analysis, found (calcd.), % | | | | | M.p., °C |
|---|---|---|---|---|---|---|
| | C | H | N | S | Metal | |
| $C_{11}H_{10}N_4O_4S_2$ | 39.01 (40.46) | 4.08 (3.06) | 18.21 (17.26) | 19.50 (19.61) | – | 242 |
| $(C_{11}H_9N_4O_4S_2)_2Mn{\cdot}2H_2O$ | 38.46 (37.13) | 2.63 (2.53) | 15.69 (15.75) | 18.10 (18.00) | 3.38 (3.52) | 355 |
| $(C_{11}H_9N_4O_4S_2)_2Fe{\cdot}2H_2O$ | 37.36 (37.00) | 2.53 (2.91) | 15.53 (15.67) | 18.18 (18.50) | 6.88 (7.91) | 360 |



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TABLE II. Continued

| Ligand/complex | Elemental analysis, found (calcd.), % | | | | | M.p., °C |
|---|---|---|---|---|---|---|
| | C | H | N | S | Metal | |
| $(C_{11}H_9N_4O_4S_2)_2Ni{\cdot}2H_2O$ | 35.00 | 2.80 | 14.93 | 17.14 | 7.96 | 260 |
| | (35.45) | (2.41) | (15.03) | (17.18) | (7.91) | |
| $(C_{11}H_9N_4O_4S_2)_2Cu{\cdot}2H_2O$ | 36.98 | 2.50 | 15.69 | 17.93 | 8.86 | 199 |
| | (36.00) | (2.91) | (16.67) | (17.50) | (8.91) | |

*Magnetic measurements*

The magnetic moment data are presented in Table I. The Mn(II) complex showed a value of 5.38 $\mu_B$, which is slightly lower than the spin only value of 5.92 $\mu_B$ for high spin octahedral Mn(II) complexes.[16] The magnetic moment of the Fe(II) complex was 5.78 $\mu_B$, which supports its high spin octahedral geometry.[17] The observed magnetic value of Ni(II) complex was 3.18 $\mu_B$, which is in good agreement with a spin free octahedral geometry.[18] The Cu(II) complex exhibited a value of 1.83 $\mu_B$, which suggests an octahedral geometry[19] around the central metal ion.

*Electronic spectra*

The electronic spectra of the complexes were recorded in the solution state. The energies of the observed spin allowed bands in all the complexes agreed with the octahedral geometry. The electronic spectrum of Mn(II) complex shows four weak bands at bands at 16000, 19810, 20746 and 26740 $cm^{-1}$, which can be assigned to $^6A_{1g} \rightarrow {}^6T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$, $^6A_{1g} \rightarrow {}^4E_g$ and $^6A_{1g} \rightarrow {}^4T_{1g}$, respectively, for an Mn(II) ion in an octahedral field.[20] The electronic spectrum of the Fe(II) complex showed two bands. The band at 10820 $cm^{-1}$ may be assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition[21] and the other at 20490 $cm^{-1}$ to charge transfer.[22] Similar types of transitions were reported for octahedral Fe(II) complexes.[23] The electronic spectrum of the Ni(II) complex displayed three bands at 12500, 18900 and 26400 $cm^{-1}$, assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ transitions, respectively, which indicate octahedral geometry[24] of the Ni(II) complex. The electronic spectrum of the Cu(II) complex showed two ligand field bands at 13700 and 18000 $cm^{-1}$, assigned to the transitions $^2E_g \rightarrow {}^2T_{2g}$ and charge transfer, respectively. The electronic spectrum of the Cu(II) complex suggests an octahedral geometry.[25]

*Infrared spectra*

The IR spectrum of the Schiff base showed a sharp band near 1610 $cm^{-1}$, which may be due to the azomethine linkage,[26–28] which was shifted to lower frequencies in the metal complexes, indicating coordination of the metal ions through the azomethine linkage.[29] The ligand showed a strong band at 3410 $cm^{-1}$ due to the phenolic –OH group.[30] This band was absent in the spectra of all the



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metal complexes, indicating involvement of this group in the formation of the complexes.[31] The bands observed at 1176, 1174, 1178, 1175 and 1173 $cm^{-1}$ are characteristics of $SO_2$–N linkages in the Schiff base and the Mn(II), Fe(II), Ni(II) and Cu(II) complexes, respectively.[32] The appearance of the M–N bands at 411, 409, 412 and 415 $cm^{-1}$ and the M–O bands at 505, 508, 511 and 550 $cm^{-1}$ in the complexes indicate that AZM-SA was coordinated through an O and a N atom.[33,34] The absorption bands at 3410, 3592, 3621 and 3547 $cm^{-1}$ show the presence of coordination water in the complexes.[35] The weak bands observed at 1280, 1286, 1282, 1288 and 1290 $cm^{-1}$ are characteristics of $\nu_{C-O}$ (phenolic)[36] in the Schiff base and the metal complexes, respectively. The medium frequencies observed in the region 674 $cm^{-1}$ in the ligand and the respective metal complexes are assigned to $\nu_{C-S}$.[37] The IR spectral data and their tentative assignments are given in Table III.

TABLE III. Infrared spectral data ($cm^{-1}$) and their tentative assignments (*vs* – very strong, *s* – strong, *m* – medium, *w* – weak)

| Ligand/complex | $\nu$(HC=N) | $\nu(SO_2N)$ | $\nu$(N–H) | $\nu$(M–N) | $\nu$(M–O) | $\nu(H_2O)$ |
|---|---|---|---|---|---|---|
| AZM-SA | 1610 *vs* | 1176 *vs* | 3301 *s* | – | – | – |
| $[Mn(AZM\text{-}SA)_2(H_2O)_2]$ | 1578 *s* | 1174 *vs* | 3300 *s* | 505 *m* | 411 *s* | 3410 *vs* |
| $[Fe(AZM\text{-}SA)_2(H_2O)_2]$ | 1581 *s* | 1178 *s* | 3304 *s* | 508 *s* | 409 *w* | 3592 *vs* |
| $[Ni(AZM\text{-}SA)_2(H_2O)_2]$ | 1590 *s* | 1175 *vs* | 3300 *s* | 511 *m* | 412 *s* | 3621 *vs* |
| $[Cu(AZM\text{-}SA)_2(H_2O)_2]$ | 1593 *s* | 1173.5 *s* | 3300 *s* | 550 *s* | 415 *w* | 3547 *vs* |

*ESR spectra*

The ESR spectra of the Fe(II) and Cu(II) complexes were recorded in DMSO at LNT (liquid nitrogen temperature) and RT (room temperature). The spectrum of the Cu complex at RT shows one intense absorption band in the high field. At LNT, the Cu(II) complex shows four well-resolved peaks in the low field region. The $g_{\parallel}$ and $g_{\perp}$ components were calculated respectively from the low and high intensity envelopes. The values obtained for Cu(II) complex were $g_{\parallel} > g_{\perp} > 2$, indicating that the Cu(II) lies predominantly in the $d_{x^2-y^2}$ orbital.[38] The observed values of $\alpha^2$, $\beta^2$ and $\gamma^2$ of the Cu(II) complex are less than unity, which indicates that the complex has some covalent character in the ligand environment.[39] The ESR spectrum of the Fe(II) complex at both RT and LNT, consisted of a single broad peak of high intensity, explaining its paramagnetic character that is also supported by the value of the magnetic moment (Table I). The values of $g_{\parallel} = g_{\perp}$ and $g_{av}$ were less than two, which predicts the presence of vacant energy shells in Fe(II) ion to accept an electron pair from the ligand.[40]

*Particle size analysis*

The pure acetazolamide drug (5-acetamido-1,3,4-thiadiazole-2-sulphonamide), its Schiff base and the Mn(II) and Cu(II) complexes derived from the Schiff



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base were evaluated for their particle size distribution and average particle diameter using the laser diffraction method. The average particle size of the Mn(II) and Cu(II) complexes were found to be 2.93 and 2.76 μm, respectively, which is smaller than that of the Schiff base (AZM-SA) with an average diameter of 4.01 μm and that of the pure drug with an average diameter of 4.16 μm. The smaller particle size of the complexes results in an enhanced solubility of the drug.[41]

*Fungicidal activity*

Above synthesized compounds and the ligand (Schiff base) were screened against *A. niger* and *A. flavus* by the agar growth food poison technique to assess their potentials as fungicidal agents. The disc diffusion method was used for the standard drug gentamycin against *A. niger* and *A. flavus* using Sabouraud agar medium. The percentage growth by an inhibitor at different dilutions is determined as $100(C - T)/C$ (where $C$ is the diameter of the fungus colony in the control plate and $T$ is the diameter of fungus colony in the test plate). The zone of inhibition based on the size around the disc was measured. The inhibition zone percentages are recorded in Table IV. From the results, it can be observed that the complexes showed greater activity as compared to the Schiff base. The improved activities of some of the metal complexes as compared to the ligand can be explained by the chelation theory. This theory explains that a decrease in the polarizability of the metal could enhance the lipophilicity of the complexes, which leads to a breakdown of the permeability of the cells, resulting in interference with normal cell processes.[42] This indicates that chelation increases the fungicidal activity.[43]

TABLE IV. Antifungal activity (inhibition zone, %) of Schiff base and complexes; medium: Czapek's agar; time: 5 days; temperature: 25±1 °C, dose = 500 ppm

| Compound | *A. niger* | *A. flavus* |
|---|---|---|
| AZM-SA | 51.23 | 59.47 |
| $(AZM\text{-}SA)_2Mn$ | 66.38 | 71.23 |
| $(AZM\text{-}SA)_2Fe$ | 72.25 | 81.78 |
| $(AZM\text{-}SA)_2Ni$ | 81.46 | 95.67 |
| $(AZM\text{-}SA)_2Cu$ | 81.45 | 98.55 |
| Netamycin | 55.23 | 45.53 |

## CONCLUSIONS

Based on elemental analysis, magnetic moment data, conductivity measurements and spectral studies, an octahedral structure for the complexes is proposed (Fig. 2.). All the synthesized metal complexes showed biological activities against the tested pathogenic fungal species by the well agar method. To counter increased fungal disease to their rapid growth in the population, investigation of the fungicidal activities of ligands and their metal complexes would be very use-



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ful to control this harmful disease. The present work will be extended to the synthesis of other metal complexes and their biological activities.

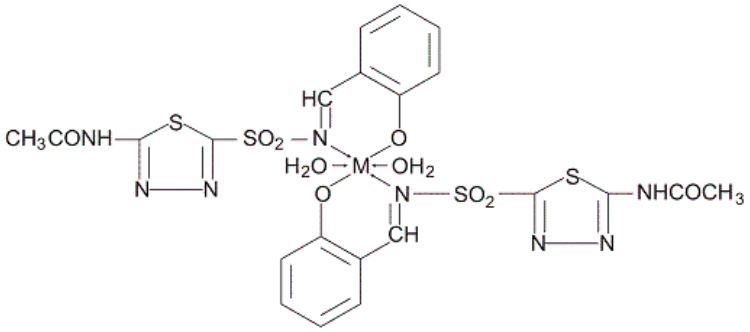


Fig. 2. The proposed structure of the complexes: M = Mn(II), Fe(II), Ni(II), Cu(II).

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ИЗВОД

## КОМПЛЕКСИ НЕКИХ 3d-МЕТАЛА СА ШИФОВИМ БАЗАМА КОЈЕ СУ ДОБИЈЕНЕ ИЗ 5-АЦЕТАМИДО-1,3,4-ТИЈАДИАЗОЛ-2-СУЛФОНАМИДА И ЊИХОВА БИОЛОШКА АКТИВНОСТ

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Полазећи од бидентатног лиганда, Шифове базе 5-ацетамидо-1,3,4-тијадиазол-2-сулфонамида, синтетизовани су комплекси неких прелазних метала, опште формуле $ML_2$ (где је M = Mn(II), Fe(II), Ni(II) и Cu(II)). За карактеризацију комплекса употребљени су елементална микроанализа, мерења моларне проводљивости и магнетног момента, електронска, ESR и IR спетроскопија, као и метода анализе прахова. На основу мерења моларне проводљивости претпостављено је да су испитивани комплекси електронеутрални. Израчунате су вредности константи стабилности, као и вредности промене слободне енергије. На основу измерених вредности магнетних момената за све испитиване комплексе претпостављена је октаедарска геометрија. Испитивана је антифунгална активност за лиганд и одговарајуће комплексе на сојевима *Aspergillus niger* и *A. flavus.*

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