



Synthesis of 4-{(E)-[(3-methyl-5-sulphanyl-4H-1,2,4-triazol-4-yl)imino]methyl} benzaldehyde and its complexes with Ag(I), Hg(II), Zn(II), Co(II), Ni(II) ions and its characterisation

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A novel Schiff base 4-{(E)-[(3-methyl-5-sulphanyl-4H-1,2,4-triazol-4-yl)imino]methyl}benzaldehyde (MSTB) and its complexes with Ag(I), Hg(II), Cu(II), Ni(II) and Co(II) have been prepared. MSTB is prepared by the condensation reaction between triazole and terephthaldehyde. In complexes, MSTB molecules are found to link with the metal ion, through thiol sulphur after deprotonation and the nitrogen of the azomethine group. The composition of the complexes are found to be ML where M = Ag, ML₂ where M = Zn, Hg and ML₂(H₂O)₂ where M = Co, Ni. Linear polymeric structure is proposed for Ag(I) complex, tetrahedral structure is proposed for Zn(II) and Hg(II) complexes and octahedral structure is proposed for Co(II) and Ni(II) complexes.

Keywords: MSTB, Ag(I), Hg(II), Cu(II), Ni(II), Co(II) complex, ML₂(H₂O)₂, Terephthaldehyde

Study of Schiff bases and their complexes have been done for their important and interesting properties like, ability to form complexes with some toxic metals, hydrogenation of olefins, catalytic activity and transfer of an amino group^{1,2}. The condensation reactions of aldehydes or ketones with 3-substituted-4-amino-5-mercapto-1,2,4-triazoles results in imine products known as Schiff bases². Two ring nitrogen atoms at 1 and 2 in the triazole ring system, the tertiary nitrogen of the triazole ring, sulphur of mercapto group and nitrogen of azomethine group are potential coordinating sites in the structure of Schiff base. Therefore Schiff bases easily form complexes with metal ions. Many complexes of transition metals with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazoles have been synthesized and characterized³⁻¹⁵. From the literature survey it was confirmed that very little efforts have done yet for the synthesis of 4-{(E)-[(3-methyl-5-sulphanyl-4H-1,2,4-triazol-4-yl)imino]methyl}benzaldehyde (MSTB) and its metal complexes. So, here in this paper, we have reported the synthesis and characterization of the ligand MSTB and its complexes with Ag(I), Zn(II), Hg(II), Co(II) and Ni(II) metal salts. The structures of the ligand and metal complexes were determined by spectral analysis, CHNSO analysis, magnetic susceptibility

measurements, conductivity measurements and thermal analysis. Schiff base complexes have broad biological and non-biological applications. There is a significant scope for carrying out forthcoming investigation to identify and synthesise new non-toxic, eco-friendly reagents for the metal ions and anions to obtain pollution free environment and healthy life.

Materials and Methods

AR grade reagents were used throughout the study. C, H, N, S and O content of MSTB and its complexes were analysed on microscale using Thermo Scientific (Flash 2000) –CHNS-O analyser. Using Guoy's balance the magnetic susceptibilities of all the complexes were analysed at room temperature. Thermogravimetric analysis (TGA) of the sample was carried out. The UV-visible absorption spectra were measured using Agilent Cary Win UV software based spectrophotometer. The molar conductivities of the complexes in 1×10⁻³ mol dm⁻³ DMSO solution were measured using Equiptronics: EQ-660A-conductivity meter. IR spectra of MSTB and its complexes were recorded using Jasco Model IR spectrophotometer.

Synthesis of MSTB (ligand)

The ligand was prepared by refluxing a mixture of 0.03 mol of 4-amino-5-methyl-4H-1,2,4-triazole-3-

thiol and 0.03 mol of terephthaldehyde in 50 mL of absolute alcohol containing three drops of dilute HCl for about 3 h. Then the reaction mixture was cooled, followed by filtration and thorough washing with ether. Yellow crystals obtained were air dried and then recrystallized using ethanol containing 2-3 drops of dilute HCl. The drying of yellow crystals was done properly. Elemental analysis (%), calculated (found) for $C_{11}H_{10}N_4SO$: C, 53.63 (53.66); H, 4.09 (4.07); N, 22.75 (22.76); O, 6.51 (6.50); S, 13.04 (13.00); melting point: 235-237 °C, solubility: DMSO.

Preparation of 4-{(E)-[(3-methyl-5-sulphanyl-4H-1,2,4-triazol-4-yl)imino]methyl}benzaldehyde silver(I) complex

Ammoniacal silver nitrate solution (2 mM) was heated and to this hot solution, preheated MSTB (2 mM) in 30 mL of absolute alcohol was added dropwise with mixing and the blend was refluxed for about 1 h. The product obtained was cooled and filtered. Washing of the residue was done using hot water, absolute alcohol and then with ether. Finally the orange colour complex was dried at 110-120 °C. Elemental analysis (%), calculated (found) for $Ag(C_{11}H_9N_4SO)$: C, 35.00 (37.00); H, 2.74 (2.60); N, 18.71 (18.69); O, 6.84 (5.00); S, 9.07 (10.00); Ag, 30.53 (30.56); melting point: 212-214 °C, solubility: DMF and DMSO.

Preparation of 4-{(E)-[(3-methyl-5-sulphanyl-4H-1,2,4-triazol-4-yl)imino]methyl}benzaldehyde cobalt(II) complex

To a hot solution of cobalt(II) chloride hexahydrate solution (4 mM) in 30 mL of double distilled water was heated and one gram of ammonium chloride and sufficient ammonium hydroxide to make the solution ammoniacal. Hot solution of MSTB (8 mM) in double distilled water was added dropwise to ammoniacal cobalt(II) chloride hexahydrate solution with stirring followed by refluxing the mixture for about an hour. The resulting dark green colour complex was filtered. Washing of the residue was done using hot water, absolute alcohol and at last with ether. The resulting compound was dried at 110-120 °C. Elemental analysis (%), calculated (found) for $Co(C_{11}H_9N_4SO)_2 \cdot 2H_2O$: C, 45.17 (45.13); H, 3.59 (3.76); N, 20.56 (19.15); O, 10.90 (10.94); S, 9.38 (10.01); Co, 10.64 (10.08); melting point: 240-242 °C, solubility: DMF and DMSO.

Preparation of 4-{(E)-[(3-methyl-5-sulphanyl-4H-1,2,4-triazol-4-yl)imino]methyl}benzaldehyde nickel(II) complex

To the hot solution of nickel chloride hexahydrate (4 mM) in 30 mL of double distilled water containing

1 g of ammonium chloride and enough amount of ammonium chloride to make the solution ammoniacal, preheated MSTB (8 mM) in 50 mL of absolute alcohol was added which is then refluxed for about an hour. The parrot green colour solution containing complex was filtered and washed with hot water, absolute alcohol and with ether. Then the residue was dried. Elemental analysis (%), calculated (found) For $Ni(C_{11}H_9N_4SO)_2 \cdot 2H_2O$: C, 45.11 (45.15); H, 3.66 (3.76); N, 19.14 (19.16); O, 10.90 (10.94); S, 10.91 (10.95); Ni, 10.01 (10.04); melting point: 252-254 °C, solubility: DMF and DMSO.

Preparation of 4-{(E)-[(3-methyl-5-sulphanyl-4H-1,2,4-triazol-4-yl)imino]methyl}benzaldehyde Zinc(II) complex

Hot solution of zinc(II)acetate dehydrate (2 mM) in 50 mL ethanol containing a drop of glacial acetic acid, was mixed with hot solution of MSTB (4 mM) in 50 ml of absolute alcohol with stirring. The solution was digested on a water bath for about an hour. The resulting yellow coloured complex was filtered and then washed with hot water, absolute alcohol and finally with ether. The residue was dried. Elemental analysis (%), calculated (found) for $Zn(C_{11}H_9N_4SO)_2$: C, 47.50 (47.53); H, 3.20 (3.24); N, 20.14 (20.16); O, 5.70 (5.76); S, 11.54 (11.52); Zn, 11.73 (11.77); melting point: 219-221 °C, solubility: DMF and DMSO.

Preparation of 4-{(E)-[(3-methyl-5-sulphanyl-4H-1,2,4-triazol-4-yl)imino]methyl}benzaldehydemercury(II)

Hot solution of mercury(II) chloride (2 mM) in 50 mL of absolute alcohol was mixed with hot solution of MSTB (4 mM) in 50 mL of absolute alcohol with stirring. The resulting grey coloured solid isolated on adding not many drops of sodium acetate solution was filtered and then washed with hot water, absolute alcohol and ether. The residue was dried. The resulting compound was dried at 110-120 °C. Elemental analysis (%), calculated (found) for $Hg(C_{11}H_9N_4SO)_2$: C, 38.20 (38.23); H, 2.60 (2.61); N, 16.19 (16.22); O, 4.67 (4.63); S, 9.28 (9.26); Hg, 29.00 (29.05); melting point: 218-220 °C, solubility: DMF and DMSO.

Results and Discussion

The molar conductances of all the complex solutions in DMSO are in the range of 11.09-59 $\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$. The low conductance value of the solutions of synthesised complexes clearly reveals that complexes are neutral and act as non-electrolytes in solution^{16,17}.

The results of C, H, N, S and O analysis showed that Ag(I) forms ML type complexes while Zn(II) and Hg(II) form ML_2 type complexes. The Co(II) and Ni(II) complexes of MSTB are of ML_2 type with two molecules of water. Thermal analysis of MSTB complexes reveal the presence of water molecules in the Co(II) and Ni(II) complexes. The thermograms of Co(II) and Ni(II) complexes suggest a two stage disintegration process. The first stage, that is in the range 120-223 °C corresponds to the weight reduction because of loss of coordinated water molecules. The second stage decomposition in the range 250-600 °C, is sharp and which relates to the disintegration of organic matter and metal oxide formation. TGA plot of Co(II) complex is shown in Fig. 1. Other metal complexes are stable upto 200 °C and decompose after that owing to the disintegration of organic matter and metal oxide formation.

The magnetic susceptibility studies of complexes reveal that among all metal complexes, only Co(II) and Ni(II) complexes are exhibiting paramagnetic behaviour. The number of unpaired electrons in Co(II) complex may be either three or one. But the magnetic moment data of Co(II)-MSTB was found to be 4.87 BM, which corresponds to the magnetic moment value of high spin octahedral complex. The three fold degeneracy of $^4T_{1g}$ of the ground state of octahedral complex is responsible for the high degree of orbital contribution. The magnetic moment value of Ni(II)-MSTB complex was found to be 3.22 BM, which indicates that the value is in the order of magnetic moments of octahedral Ni(II) complexes^{18,19}. If the Ni(II)-MSTB complex is having

tetrahedral geometry, then the orbital contribution is found to be more than the orbital contribution observed in the octahedral complex^{17,18}. Therefore the magnetic moment value should have been greater than the observed value in the case of complex with tetrahedral geometry. Hence it is clear Ni(II)-MSTB complex is having distorted octahedral geometry. Spectral data further gives much support to the prediction.

The types of proton and carbon environments of the ligand MSTB can be known from the 1H and ^{13}C NMR spectra as shown in Fig. 2. The ligand contains six different types of protons. Therefore six different peaks are observed in the (Fig. 2a) 1H NMR spectrum of MSTB as follows.

1H NMR (400 MHz; DMSO- d_6) δ (ppm): 8.06-8.08 (s, 2H, ArH), 8.12-8.14 (s, 2H, ArH),

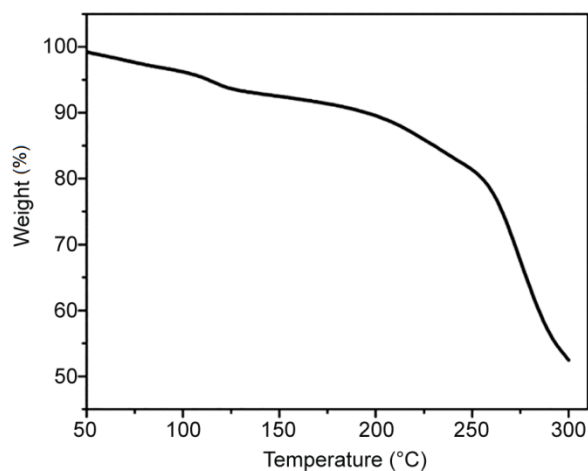


Fig. 1 — TGA of Co(II) Schiff base complex

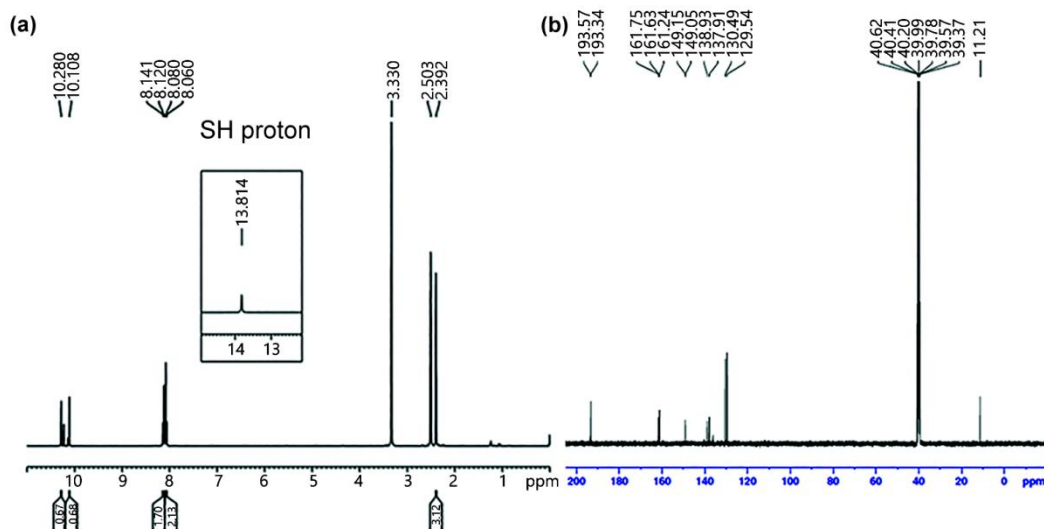


Fig. 2 — (a) 1H and (b) ^{13}C NMR spectra of MSTB

13.8 (s, 1H,SH), 2.3 (s, 3H, CH₃), 10.1 (s, 1H, CHO), 10.2 (s, 1H, N=C-H)

¹³CNMR spectrum (Fig. 2b) gives nine peaks corresponding to nine different carbon environments as follows.

¹³CNMR (DMSO), δ (ppm): 11.21, 129.54, 130.49, 137.91, 138.93, 149.15, 161.24, 161.75, 193.57.

Electronic spectral band positions and the type of transitions for the complexes of MSTB are given in Table 1. The spectra of Co(II) and Ni(II) complexes are shown in Fig. 3. In general, spectrum of cobalt complex with octahedral geometry shows three bands corresponding to the following transitions,

$$\vartheta_1 = {}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F); \vartheta_2 = {}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) \text{ and } \vartheta_3 = {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$$

The normal ratio of the frequencies of the second transition ν_2 (18 Dq) to the first transition ν_1 (8 Dq) for octahedral Co(II) complexes, is 2.2^{20,21}. The absorption band due to first transition was not recorded in the spectrum of the Co(II) complex (Fig. 3a). The value of \bar{B} for Co(II) in the complex is lesser than the Co(II) free ion value of 1117 cm⁻¹. It explains the high degree of covalency between the metal and the ligand in the complex²².

For Ni(II) in octahedral environment, in the electronic spectrum one can also expect three bands corresponding to the following transitions,

$$\vartheta_1 = {}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F); \vartheta_2 = {}^3A_{2g}(F) \rightarrow {}^4T_{1g}(F) \text{ and } \vartheta_3 = {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$$

For octahedral Ni(II) complexes, the expected ratio of the frequencies of the second transition ν_2 (18 Dq) to the first transition ν_1 (10 Dq) is around 1.8^{18, 23,24,25}. The absorption band corresponding to first transition was not recorded in the spectra of the Ni(II) complex (Fig. 3b). The value of \bar{B} for Ni(II) in the complex is lesser than the Ni(II) free ion value²² of 1082 cm⁻¹. It verifies the high degree of covalency between the metal and the ligand in the complex.

The IR spectra of the ligand and complexes will give an insight to the bonding sites. The ligand contains four possible ligating atoms viz. two ring nitrogens at position 1 and 2, the sulphur atom of the thiol(thione) group and nitrogen of the azomethine group. The ligand contains thioamide moiety which exist in tautomeric forms to be specific thiol and thione forms (Fig. 4). The IR spectrum of the ligand is likely to show four characteristic thioamide bands and are expected to undergo shift in the metal complexes

Table 1 — Electronic spectral band positions and their possible assignments

Complex	Band position	Assignment	10 Dq	\bar{B}	β
Co(C ₁₁ H ₁₀ N ₄ SO).2H ₂ O	7408	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	9259	937	0.84
	16667	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$			
	19609	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$			
Ni(C ₁₁ H ₁₀ N ₄ SO).2H ₂ O	8546	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	8546	677	0.63
	15384	${}^3A_{2g}(F) \rightarrow {}^4T_{1g}(F)$			
	20408	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$			

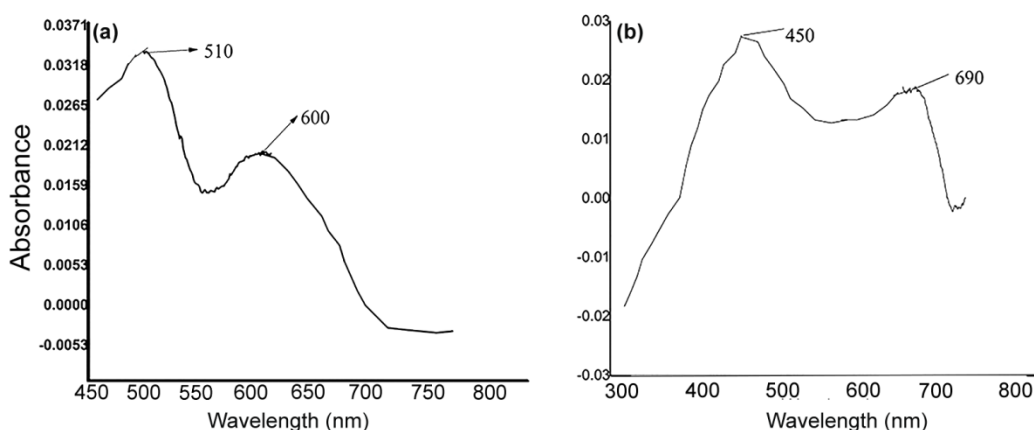


Fig. 3 — Electronic spectra of (a) Co(II)- and (b) Ni(II)- Schiff base complex

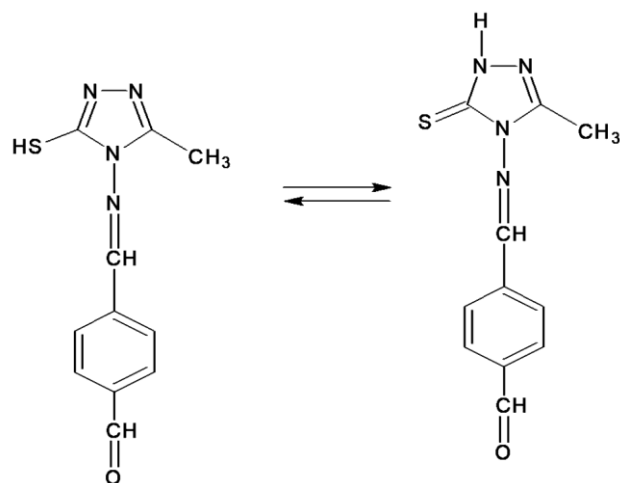


Fig. 4 — Thiol-thione forms of MSTB

and give a knowledge to the bonding scheme. Formation of complex at a convenient donor site as an impact of deprotonation is in conformity with balanced charge.

The inquiry currently is to determine the linkage of metal ions with either contributor site (N or S) of the thioamide. It is relevant to expect that for 'b' class Ag(I), Hg(II) or borderline metals Co(II), Ni(II), Zn(II), the readily polarisable sulphur atom of the ligand would be the ideal donor site rather than the less readily polarisable nitrogen atom. If the bonding takes place through sulphur as suggested above $\nu(\text{C-S})$ and then it would distract the delocalization of charge so as to constrain it between C and N of the thioamide group. As an outcome, the IR band of the C=N group should move towards greater wavenumber side while the band of C=S should shift towards the lower wavenumber side. During the formation of the complex, thioamide band II of the ligand, having significant contribution from, $\nu(\text{C=N})$ and thioamide band IV due to, $\nu(\text{C=S})$, should move to greater and lower wavenumber sides, respectively. During the formation of the complex, the shifts in the thioamide band II and IV confirm the inclusion of sulphur in bonding.

Simultaneous coordination to the metal ion through nitrogen of the azomethine group and sulphur atom of the thiol(thione) results in the development of a five membered chelate structure which perhaps may be most preferred arrangement. Also, the ring nitrogen atoms may furnish extra coordination sites, leading to polymeric structure. To decide between the two, recourse is made to the following observations.

The IR spectrum of ligand has the bands in the region 3400 cm^{-1} due to $\nu(\text{N-H})$, in the region 2900 cm^{-1} due to $\nu(\text{-C-H})$ and in the region 1980 cm^{-1} due to $\nu(\text{=C-H})$. Thioamide band I which has a major contribution from $\delta(\text{N-H})$ and minor contributions from $\nu(\text{C=N})$ and $\nu(\text{C-H})$, is observed around 1559 cm^{-1} in the spectrum of ligand. If the charge localisation occurs between C and N as discussed above, this band should move towards higher wavenumber side. However the contribution from $\nu(\text{C=N})$ being minor, such a shift would not be considerable. During complex formation deprotonation of the ligand takes place and $\delta(\text{N-H})$ disappears in the spectra of complexes. As an overall effect thioamide band I shift slightly towards lower wavenumber side. Thioamide band II suffers a substantial shift towards larger wavenumber side. The thioamide band II at 1240 cm^{-1} in the spectrum of ligand shifts to around 1269 cm^{-1} in the spectra of complexes.

Thioamide band III having a major input from $\nu(\text{C=N})$ and a minor input from $\nu(\text{C=S})$, in the region around 960 cm^{-1} in the spectrum of the ligand is found to be shifted slightly towards larger wavenumber side in spectra of complexes. Thioamide band IV suffers a substantial shift towards the lower wavenumber side. At 850 cm^{-1} thioamide band IV is observed in the spectrum of ligand. It moves to around 760 cm^{-1} in spectra of complexes. The band at 1000 cm^{-1} in the spectrum of ligand is due to $\nu(\text{N-N})$ of triazole. It moves towards the lower wavenumber side in the spectra of complexes of metal. It reveals that the nitrogen of azomethine forms the bond with the metal in the complex. Bands in the region around 1700 cm^{-1} due to aldehyde group and in the region around 3100 cm^{-1} due to aromatic ring are found in spectra of both ligand as well as complexes. New bands corresponding to $\nu(\text{-M-N})$ and $\nu(\text{-M-S})$ appears around 518 cm^{-1} and 454 cm^{-1} , respectively in spectra of the complexes. The spectra of Co(II) and Ni(II) complexes show the bands at around 912 cm^{-1} characteristic of coordinated water. All the IR bands and shifts are represented in Table 2.

Based upon various studies conducted and by the knowledge of the preferred geometries, it is concluded that Ag(I) complex has linear polymeric structure (Fig. 5a), Zn(II) and Hg(II) complexes have tetrahedral structures (Fig. 5b) and Co(II) and Ni(II) complexes have octahedral structures (Fig. 5c).

Table 2 — IR band positions (cm^{-1}) and their probable assignments of MSTB and its complexes

Ligand	Complexes		Assignments
	Ag(I), Zn(II), Hg(II)	Co(II), Ni(II)	
3400	-----	-----	$\nu(\text{N-H})$
3100	3100 \pm 10	3100 \pm 10	Aromatic ring
2900	2862 \pm 10	2877 \pm 10	$\nu(-\text{C-H})$
1980	1959 \pm 10	1937 \pm 10	$\nu(\text{C}=\text{H})$
1700	1700 \pm 10	1700 \pm 10	Aldehyde
1698	1693 \pm 5	1698 \pm 5	$\nu(\text{C}=\text{N})$
1559	1548 \pm 10	1539 \pm 5	Thioamide band I
1240	1269 \pm 10	1269 \pm 10	Thioamide band II
1100	1100 \pm 10	1050 \pm 10	$\nu(\text{N-N})$ triazole
960	1000 \pm 10	1000 \pm 10	Thioamide band III
850	760 \pm 5	760 \pm 5	Thioamide band IV
-----	-----	912	Coordinated water
-----	518 \pm 10	518 \pm 10	$\nu(\text{M-N})$
-----	454 \pm 10	454 \pm 10	$\nu(\text{M-S})$

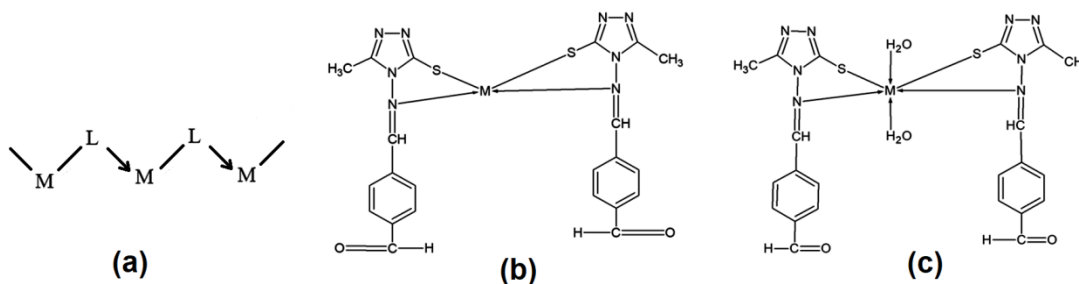


Fig. 5 — Geometries of (a) Ag(I), (b) Hg(II), Zn(II), (c) Co(II), Ni(II) complexes

Conclusions

A novel Schiff base 4-{(E)-[3-methyl-5-sulphonyl-4H-1,2,4-triazol-4-yl]imino)methyl} benzaldehyde (MSTB) and its complexes with Ag(I), Hg(II), Cu(II), Ni(II) and Co(II) have been prepared and characterized. Basing on the analytical studies it can be concluded that the ligand molecules ligate with metal ions, through nitrogen of the azomethine group and thiol sulphur after deprotonation.

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