

Structural studies of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II), Hg(II) and Pb(II) metal ions with 2-[(E)-{[3-(methylsulfanyl)-4H-1,2,4-triazol-4-yl]imino}methyl] phenol

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ABSTRACT

Coordination complexes of 2-[(E)-{[3-(methylsulfanyl)-4H-1,2,4-triazol-4-yl]imino}methyl]phenol (MSTIMP) with bivalent metal ions of composition $[M(MSTIMP)_2]$ [$M = \text{Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II), Hg(II)}$ and Pb(II)] have been synthesized in solid state and characterized them with the help elemental analysis, magnetic susceptibility value, electrical conductance measurement, electronic absorption and infrared spectral studies. On the basis of these studies Mn(II), Fe(II), Co(II) and Cu(II) complexes are suggested octahedral structure while those of Zn(II), Cd(II), Hg(II) and Pb(II) with tetrahedral structure. The Ni(II) and Pd(II) complexes are diamagnetic and have square planer structure.

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KEYWORDS

Synthesis;
Characterization;
2-[(E)-{[3-(methylsulfanyl)-4H-1,2,4-triazol-4-yl]imino}methyl]phenol,
bivalent metal complexes.

INTRODUCTION

The studies on complex compound of Schiff base have been subject matter of extensive interest due to their strong complexes forming ability analytical applications and pharmacological activity in various field of biochemical application^[1-7]. The present communication describe the complexes of Schiff base 2-[(E)-{[3-(methylsulfanyl)-4H-1,2,4-triazol-4-yl]imino}methyl]phenol (MSTIMP) with bivalent metal ions Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II), Hg(II) and Pb(II) in solid state.

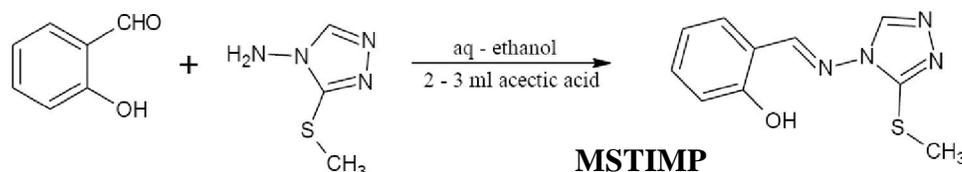
EXPERIMENTAL

All chemicals and solvents used in this study were

of of AR grade of BDH, E. Merck, Nice, and Sd. fine chemicals were procured. Palladium(II) chloride were obtained from Johnson Matthey, London. The ligand MSTIMP was prepared by condensing 3-(methylsulfanyl)-4H-1,2,4-triazol-4-amine with 2-hydroxybenzaldehyde in aqueous ethanol containing few drops of acetic acid at reflux temperature^[8-9]. The ligand was recrystallized from hot ethanol and THF mixture. The yield of product was 96-97%, Melting point of product was 237 °C.

Preparation of Complexes $[M(MSTIMP-H)_2]$ [$M = \text{Mn(II), Fe(II), Co(II), Ni(II), Pd(II), Cu(II), Zn(II), Cd(II), Hg(II)}$ or Pb(II)]

The aqueous ethanolic solution of one millimole metal chloride or metal acetate (in 20ml) was refluxed with hot ethanolic tetrahydrofuran solution of 2 millimole of



ligand (in 20 ml). The resulting solution was treated with 2g sodium acetate and diluted with 40-50 ml of water and separated complexes were digested on steam bath for 30 minutes and cooled. The products were filtered, washed with water and aqueous ethanol and dried in a desiccator over CaCl_2 and finally in an air oven at 60-70°C. The yield of complexes 98-99%. The metal nitrogen and sulphur content of complexes were analyzed by standard procedure^[10]. UV-Vis spectra and IR were get recorded from CDRI Lucknow. Magnetic susceptibility was determined by Gouy method at room temperature. Molar conductivities of freshly prepared solution in DMF were measured on a Systronics Conductivity TDS Meter 308. The analytical results of complexes and ligand are given in TABLE 1.

RESULT AND DISCUSSION

2-[(*E*)-{3-(methylsulfanyl)-4*H*-1,2,4-triazol-4-yl}imino]methyl]phenol (MSTIMP) is a potent sulphur, nitrogen and oxygen donor molecule and is capable of forming strong complexes with metal ions either as monoanionic trivalent coordinating molecule or as monoanionic bidentate donor ligand forming bond with metal atom through deprotonated phenolic oxygen and aldimine nitrogen. The S-(CH_3) ether sulphur is comparatively weak donor atom due to which it does not

coordinate in some metal complexes. The elemental analysis of complexes corresponds to composition $[\text{M}(\text{MSTIMP-H})_2]$ with bivalent metal ions. The complexes are almost insoluble in water and aqueous ethanol but dissolve slightly in acetone, methanol and ethanol. The complexes however dissolve appreciably in DMF and pyridine. The molar conductance values of these complexes are too low in DMF indicating their non-electrolytic nature^[11]. The complexes are stable at room temperature. On heating the complexes in hot air oven up to 180° - 200°C slowly starts losing weight and decomposes above 260°-280°C with change in colour.

The complexes of MSTIMP having composition $[\text{M}(\text{MSTIMP-H})_2]$ when M = Mn(II), Fe(II), Co(II) and Cu(II) are paramagnetic having moment values are 5.93, 4.81, 4.93 and 1.87 BM respectively which occur in the range of six coordinated octahedral geometry of corresponding metal ions^[12-14]. While M = Ni(II), Pd(II), Zn(II), Cd(II), Hg(II) and Pb(II) are diamagnetic. The diamagnetism of Pd(II) and Ni(II) complexes suggested their four coordinated square planar geometry^[15].

The electronic absorption spectrum of ligand shows three electronic band located at 225(ϵ_{max} - 11200), 265(ϵ_{max} - 9100) and a shoulder at 325nm attributed to $\sigma - \pi^*$, $\pi - \pi^*$ and $n - \pi^*$ transition^[17]. The electronic transition of ligand shift to higher wave length in its metal

TABLE 1 : Analytical results and magnetic moment value at 304K in BM

Complexes	Colour	% Analytical result Found (Calculated)			μ_{eff} BM
		metal	nitrogen	sulphur	
[Co(MSTIMP) ₂]	Brown	11.13 (11.22)	21.25 (21.33)	11.92 (12.19)	4.93
[Ni(MSTIMP) ₂]	Orange	11.05 (11.20)	21.28 (21.34)	12.02 (12.19)	Dia
[Cu(MSTIMP) ₂]	Ash colour	11.81 (11.99)	21.05 (21.24)	11.94 (12.03)	1.87
[Mn(MSTIMP) ₂]	Yellow	10.61 (10.55)	21.73 (21.49)	12.13 (12.28)	5.93
[Fe(MSTIMP) ₂]	Yellowish brown	10.62 (10.72)	21.31 (21.45)	12.01 (12.26)	4.81
[Zn(MSTIMP) ₂]	Cream	12.11 (12.23)	21.13 (21.08)	11.93 (12.03)	Dia
[Cd(MSTIMP) ₂]	Cream yellow	19.01 (19.42)	19.28 (19.36)	10.94 (11.06)	Dia
[Hg(MSTIMP) ₂]	Cream yellow	30.11 (30.04)	16.61 (16.77)	9.39 (9.58)	Dia
[Pb(MSTIMP) ₂]	Yellow	30.61 (30.83)	16.42 (16.60)	9.37 (9.52)	Dia
[Pd(MSTIMP) ₂]	Orange	18.43 (18.59)	19.37 (19.50)	11.02 (11.18)	Dia

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complexes (TABLE 2). The Zn(II), Cd(II) and Pb(II) complexes show strong absorption below 400–380 nm assignable to charge transfer transition. The electronic absorption band of [Pd(MSTIMP-H)₂] at 410 nm (24380 cm⁻¹) is assigned to ¹A_{1g} → ¹A_{2g} transition in square planer field^[16]. The electronic absorption spectrum of [Fe(MSTIMP-H)₂] displays strong absorption below 380 nm attributed to charge transfer transition and the medium broad band located at 530 nm can be assigned to ⁵T_{2g} → ⁵E_g transition in octahedral field^[17]. The electronic absorption spectrum of Cu(II) complex [Cu(MSTIMP-H)₂] in ethanol shows ligand absorption at 228 and 275 nm and a strong absorption near 390 nm. The band is attributed to charge transfer transition. The medium to broad band of complex at 630 nm is assigned to ²E_g → ²T_{2g} transition in octahedral field^[13]. The broadness of the transition can be attributed to J.T. distortion and splitting of E_g state to ¹A_{2g} and ¹B_{1g} energy term^[18]. The electronic absorption spectrum of Co(II) complex [Co(MSTIMP-H)₂] shows a weak band as shoulder near 440 nm and a medium band at 520 nm. The electronic transition at 520 nm is attributed to ⁴T_{1g} → ⁴A_{2g} transition and weak shoulder at 440 nm as ⁴T_{1g} → ⁴T_{1g}(P) transition^[18]. Thus the electronic transition of Cu(II), Co(II), Fe(II) and Mn(II) complexes suggested their six coordinated approximately octahedral geom-

TABLE 2 : Electronic absorption bands of ligand and its metal complexes with probable assignment

Compound	Electronic band position (nm)	assignment
MSTIMP	225 (ε _{max} - 11200)	σ → π*
	265 (ε _{max} - 9100)	π → π*
	325 (sh)	n → π*
Zn(MSTIMP) ₂	228 (ε _{max} - 22500)	σ → π*
	265 (ε _{max} - 9500)	π → π*
	370 (br)	C → T
[Pd(MSTIMP) ₂]	275	π → π*
	410	¹ A _{1g} → ¹ A _{2g}
[Ni(MSTIMP) ₂]	272 (st)	π → π*
	370 (st.br)	C → T
[Fe(MSTIMP) ₂]	470	¹ A _{1g} → ¹ B _{1g}
	380 (st.br)	C → T
	530 (br)	⁵ T _{2g} → ⁵ E _g
[Cu(MSTIMP) ₂]	228 (ε _{max} - 24300)	σ → π*
	275 (ε _{max} - 12520)	π → π*
	390 (st.br)	C → T
	630	² E _g → ² T _{2g}
[Co(MSTIMP) ₂]	270 (ε _{max} - 95640)	π → π*
	265 (st.br)	C → T
	440 (sh)	⁴ T _{1g} → ⁴ A _{2g}
	520 (m)	⁴ T _{1g} → ⁴ T _{2g} (F)

sh = shoulder, st = strong, br = broad and m = medium

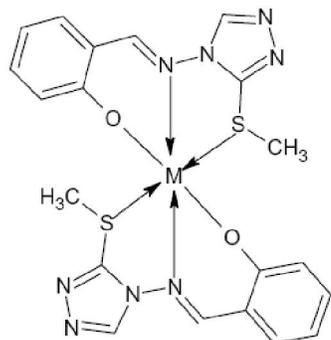
etry^[15-17].

The infrared spectra of ligand and its complexes were recorded as KBr disc on Perkin Elmer 521 spectrophotometer. The infrared spectrum of MSTIMP displays a broad band at 3360 to 3275 cm⁻¹ attributed from ν(OH) of phenolic group. This broad band disappears in almost all metal complexes [M(MSTIMP-H)₂] suggesting coordination of phenolic oxygen on deprotonation of (-OH) group^[18]. The phenyl group, ν(C-H) and S-methyl CH vibrations were located at 2860, 2942 and 3040 cm⁻¹ as weak and sharp band and these are retained in complexes with slight change in their intensity and band positions. The aldimine ν(C=N) of ligand was assigned to a strong band at 1610 cm⁻¹. The triazole ring (C=N) band is assigned to a medium band at 1575 cm⁻¹. The aldimine ν(C=N) vibration is shifted to lower wave number by 5 to 15 cm⁻¹ in complexes. The red shift of ν(C=N) vibration supported the bonding of ligand through (C=N) aldimine nitrogen in almost all complexes. The medium band at 1455 cm⁻¹ in ligand and complexes are attributed to δ(CH₃) band of S-CH₃ group. The phenolic (C-O) stretching vibration of ligand is assigned to medium band at 1205 cm⁻¹ which is shifted to higher wave number in almost all complexes supporting the coordination through deprotonated phenolic oxygen. The ligand displays ν(N-N) at 1285 and ν(C-S-C) vibration at 728 cm⁻¹. The ν(C-S-C) of ligand is not affected appreciably in Pd(II), Cd(II), Zn(II), Hg(II) and Ni(II) complexes whereas it is shifted to lower wave number in Cu(II), Co(II), Fe(II) and Mn(II) complexes by 10–25 cm⁻¹ suggesting the involvement of S-CH₃ sulphur in coordination^[19]. The infrared spectra of MSTIMP displays a number of bands in finger print region located at 1565, 1405, 1362, 1165, 935 and 745 cm⁻¹ and these are not affected appreciably in complexes. The metal complexes display new bands in far infrared region located at 530 ± 10, 435 ± 5, 330 ± 5 cm⁻¹. These I.R bands are assigned to M-O, M-N, M-S stretching vibrations in complexes^[20-21].

CONCLUSION

On the basis of electrical conductance data, magnetic susceptibility value, infrared and electronic absorption spectral studies the probable structure of complexes are shown below. The Mn(II), Fe(II), Co(II) and Cu(II)

complexes are octahedral [figure 1] and bonding of ligand is suggested from deprotonated phenolic oxy-

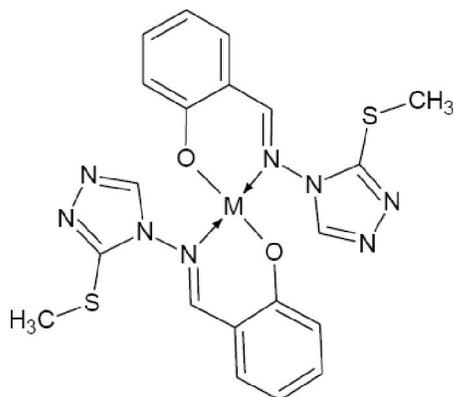


(M = Co(II), Mn(II), Fe(II) or Cu(II))

Figure 1

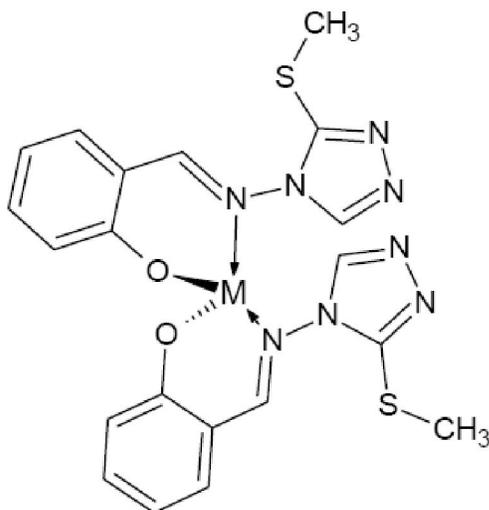
gen, aldimine nitrogen and S-CH₃ sulphur to metal atom.

Ni(II) and Pd(II) complexes are planar [figure 2] while Cd(II), Zn(II), Hg(II) and Pb(II) compounds are



[M = Ni(II) or Pd(II) Planar]

Figure 2



[M = Zn(II), Cd(II), Hg(II) and Pb(II) Tetrahedral]

Figure 3

four coordinated tetrahedral (Figure 3).

ACKNOWLEDGEMENT

The authors thanks the UGC, New Delhi for the financial support in the form JRF.

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