

**INTERNATIONAL JOURNAL OF ADVANCES IN PHARMACY,
BIOLOGY AND CHEMISTRY****Research Article****Chelates of 3-methyl-4-benzylideneimino-5-mercapto-
1,2,4-triazole with Cr(III), Fe(III), Co(III), Ru(III), Rh(III)
and Ir(III) characterised by Magnetic and Spectral data****D. Dasharatham***Department of Chemistry, University Arts & Science College, Kakatiya University,
Warangal – 506 009, Andhra Pradesh, India.**ABSTRACT**

Solid chelates of Cr(III), Fe(III), Co(III), Ru(III), Rh(III) and Ir(III) with 3-methyl-4-benzylideneimino-5-mercapto-1,2,4-triazole (HBMT) have been synthesized and characterized by physicochemical techniques. The ligand acts as a monoprotic, bidentate ligand coordinating through nitrogen and sulphur donor sites. The complexes have 1:3 (metal-ligand) stoichiometry. Magnetic data coupled with electronic and ligand field parameters suggest low-spin octahedral geometries for these chelates.

Keywords: Chelates, 3-methyl-4-benzylideneimino-5-mercapto-1,2,4-triazole, Magnetic and Spectral data.

INTRODUCTION

A perusal of the literature¹⁻³ revealed that no work has been done on Cr(III), Fe(III), Co(III), Ru(III), Rh(III) and Ir(III) chelates of 3-methyl-4-benzylideneimino-5-mercapto-1,2,4-triazole (HBMT). Hence, the same was undertaken and its findings are reported in the present note. A variety of polydentates and their metal chelates have been studied in these laboratories^{4,6}.

MATERIALS AND METHODS**Experimental**

Synthesis of HBMT: A mixture of equimolar DMF solutions of 3-methyl-4-amino-5-mercapto-1,2,4-triazole and benzaldehyde was refluxed on a water-bath for 1-2 hr in presence of acetic acid and sodium acetate when a pale-white mass separated. It was separated and crystallized from DMF (m.p. 170°C). The purity of HBMT was checked by elemental analysis, melting point, TLC, Infrared and ¹H NMR spectra.

Synthesis of metal chelates

A mixture consisting of DMF solutions of HBMT (0.03 M) and Cr(III) perchlorate (0.01 M) was refluxed on a water-bath for 2-3 hr, when a

crystalline solid mass was obtained. It was filtered and recrystallised from ethanol. By this procedure, the remaining metal chelates were also synthesized.

The ligand and the metal chelates thus synthesized were characterized by elemental analysis, molecular weight, molar conductance, magnetic, electronic, infrared and ¹H NMR spectra.

RESULTS AND DISCUSSION

Elemental analyses and molecular weight (Table 1) determination revealed 1:3 (metal-ligand) stoichiometry of the metal chelates which have the general composition [M(BMT)₃] where M = Cr(III), Fe(III), Co(III), Ru(III), Rh(III) and Ir(III) and BMT = C₁₀H₉N₄S. The molar conductance data (3.0-7.1 ohm⁻¹ cm² mol⁻¹) of the complexes suggest their non-electrolytic nature. The Co(III), Rh(III) and Ir(III) chelates were diamagnetic, whereas the rest were paramagnetic.

Cr(III) chelate: For Cr(III) chelate μ_{eff} at 308 K was found to be 3.8 BM which is slightly less than the spin-only value for 3 unpaired electrons, as is generally the case with octahedral Cr(III) chelates. Its electronic spectrum in benzene displayed two bands at 17400 and 24600 cm⁻¹, assignable to ⁴A_{2g} →

${}^4T_{2g}(F)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transitions respectively ($\epsilon = 60 - 80 \text{ mol}^{-1} \text{ cm}^{-1}$). These transitions suggest an octahedral geometry^{7,8} for the Cr(III) chelate.

Fe(III) chelate: Its μ_{eff} at 308 K was found to be 2.20 BM which corresponds to a low-spin configuration with one unpaired electron. In benzene the Fe(III) chelate showed three bands at 24900, 29990 and 40000 cm^{-1} assignable to the transition ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ respectively ($\epsilon = 70 - 95 \text{ mol}^{-1} \text{ cm}^{-1}$). Dq and B values of 2162 and 342 cm^{-1} respectively are consistent with octahedral⁹ geometry.

Co(III) chelate: Co(III) chelate was found to be diamagnetic and thus has low-spin octahedral geometry around the central metal-ion with ${}^1A_{1g}$ as the ground term. The electronic spectra of Co(III) chelate in benzene exhibited two bands at 26200 and 32300 cm^{-1} assignable to the transitions ${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$ respectively ($\epsilon = 80 - 100 \text{ mol}^{-1} \text{ cm}^{-1}$) which indicate an octahedral geometry of the molecule.

Ru(III) chelate: The magnetic moment of the Ru(III) chelate at 308 K was found to be 2.0 BM, which did not vary with temperature. It suggests an octahedral geometry of the molecule.

The electronic spectra of Ru(III) chelate displayed three bands at 13600, 17500 and 22750 cm^{-1} which were assigned to ${}^2T_{2g} \rightarrow {}^4T_{1g}$, ${}^2T_{2g} \rightarrow {}^4T_{2g}$ and ${}^2T_{2g} \rightarrow {}^2A_{2g}$ transitions, respectively ($\epsilon = 75 - 110 \text{ mol}^{-1} \text{ cm}^{-1}$). These assignments are characteristic of an octahedral stereochemistry^{10,11} of the Ru(III) chelate.

Rh(III) chelate: The Rh(III) chelate was found to be diamagnetic, as expected for d^6 system with octahedral geometry.

The electronic spectra of Rh(III) chelate showed three bands at 17450, 20000 and 23850 cm^{-1} assignable to ${}^1A_{1g} \rightarrow {}^3T_{1g}$, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively ($\epsilon = 80 - 95 \text{ mol}^{-1} \text{ cm}^{-1}$) indicating octahedral geometry⁹ of the Rh(III) compound.

Ir(III) chelate: Ir(III) chelate was found to be diamagnetic. The electronic spectra of iridium(III) chelate showed two absorption bands at 30900 and 34100 cm^{-1} which were assigned to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively ($\epsilon = 88 - 100 \text{ mol}^{-1} \text{ cm}^{-1}$) revealing its octahedral geometry¹².

Various ligand field parameters such as interelectronic repulsion energies or Racah interelectronic repulsion parameters B and C , Condon shortly parameter F_2 and F_4 , nephelauxetic ratio β , Sinha's parameter δ , Dq and LFSE were evaluated

(Table 2). The values are lower than the free ion value indicating orbital overlap and delocalization of d -orbitals. The β -values obtained are less than unity suggesting considerable amount of covalent character of the metal-ligand bonds.

A comparative study of the IR spectra of HBMT and its metal chelates revealed that the triazole derivative behaved as a bidentate chelating agent, coordinating to the metal-ions through nitrogen and sulphur donor atoms.

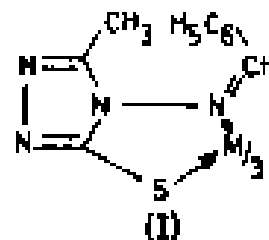
HBMT exhibited bands at 2535 and 1620 cm^{-1} due to $\nu_{\text{S-H}}$ and $\nu_{\text{C=N}}$ modes, respectively. In the spectra of the metal chelates the band at 2535 cm^{-1} disappeared indicating deprotonation of the $-\text{SH}$ group. The shift towards lower side ($\sim 30\text{-}40 \text{ cm}^{-1}$) of the $\nu_{\text{C=N}}$ band in the spectra of the complexes suggested participation of azomethine nitrogen in chelation.

In the spectra of the metal chelates other important bands occurred in the regions 400-440 and 300-285 cm^{-1} which are assigned to $\nu_{\text{M-N}}$ ¹³ and $\nu_{\text{M-S}}$ modes respectively.

To substantiate further the bonding in these metal chelates, ${}^1\text{H}$ NMR spectra of HBMT and its metal chelates were recorded in CDCl_3/TMS . The chemical shift values (δ ppm) of different protons are as under.

The signal due to $-\text{SH}$ proton of the ligand (HBMT) appeared at $\delta 3.81$ ppm, while it disappeared in the spectra of the metal chelates. Singlets due to aliphatic hydrogen at $\delta 8.96$ ppm underwent deshielding in the metal chelates, suggesting coordination of azomethine nitrogen to the metal atom.

Further, singlets and multiplets were observed at $\delta 1.40$ and $\delta 7.65$ ppm in HBMT due to CH_3 and Ar-H protons, which remained unchanged in the metal chelates.



Where M = Cr (III), Fe (III), Co (III),
Ru (III), Rh (III) or Ir (III)

Based on the above evidences, the trivalent metal chelates may be represented by the structure (I).

Table 1: Elemental analyses and molecular weight data of 3-methyl-4-benzylideneimino-5-mercapto-1,2,4-triazole (HBMT) and its Cr(III), Fe(III), Co(III), Ru(III), Rh(III) and Ir(III) chelates

| Ligand / complex | Mol. Weight Found (Calcd.) | Found (Calcd.) (%) | | | | Metal |
|---|----------------------------|--------------------|-------------|---------------|---------------|---------------|
| | | C | H | N | S | |
| [C ₁₀ H ₁₀ N ₄ S] | 215 (218) | 54.96 (55.04) | 4.43 (4.59) | 25.53 (25.69) | 14.52 (14.68) | - |
| [Cr(C ₁₀ H ₉ N ₄ S) ₃] | 701 (703) | 51.02 (51.21) | 3.69 (3.84) | 23.71 (23.89) | 13.24 (13.66) | 6.87 (7.39) |
| [Fe(C ₁₀ H ₉ N ₄ S) ₃] | 705 (707) | 50.62 (50.92) | 3.61 (3.82) | 23.47 (23.76) | 13.19 (13.58) | 7.72 (7.92) |
| [Co(C ₁₀ H ₉ N ₄ S) ₃] | 708 (710) | 50.61 (50.70) | 3.58 (3.80) | 23.35 (23.66) | 13.04 (13.52) | 7.91 (8.31) |
| [Ru(C ₁₀ H ₉ N ₄ S) ₃] | 751 (752) | 47.72 (47.87) | 3.38 (3.59) | 22.07 (22.34) | 12.56 (12.77) | 13.05 (13.43) |
| [Rh(C ₁₀ H ₉ N ₄ S) ₃] | 750 (754) | 47.62 (47.75) | 3.24 (3.58) | 21.82 (22.28) | 12.48 (12.73) | 13.19 (13.66) |
| [Ir(C ₁₀ H ₉ N ₄ S) ₃] | 841 (843) | 42.59 (42.70) | 2.88 (3.20) | 19.62 (19.93) | 10.92 (11.39) | 22.49 (22.78) |

Table 2: Ligand field parameters of Cr(III), Fe(III), Co(III), Ru(III), Rh(III) and Ir(III) chelates of 3-methyl-4-benzylideneimino-5-mercapto-1,2,4-triazole (HBMT)

| Metal chelates | Dq (cm ⁻¹) | B | C | β | δ | F ₂ | F ₄ | LFSE Δ(cm ⁻¹) |
|-------------------------|------------------------|-----|------|--------|--------|----------------|----------------|---------------------------|
| [Cr(BMT) ₃] | 1820 | - | - | - | - | - | - | 21840 |
| [Fe(BMT) ₃] | 2162 | 342 | 1197 | 0.2581 | 2.8743 | 34.2 | 513 | 43240+2P |
| [Co(BMT) ₃] | 2480 | - | - | - | - | - | - | 59520+3P |
| [Ru(BMT) ₃] | 1257 | 175 | 811 | 0.2728 | 2.6660 | 23.18 | 289 | 25140+2P |
| [Rh(BMT) ₃] | 1378 | 111 | 521 | 0.1542 | 5.4865 | 14.87 | 185 | 33072+3P |
| [Ir(BMT) ₃] | 2670 | - | - | - | - | - | - | 64080+3P |

CONCLUSION

In this manuscript, I characterized and explained the novel complexes. Based on the Spectral data and Magnetic Properties.

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