

Transition metal derivatives of 3,4-diphenyl-5-mercapto-1,2,4-triazole

J SINGH* and N K SINGH

Department of Chemistry, U P College, Varanasi 221 005, India

* Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India

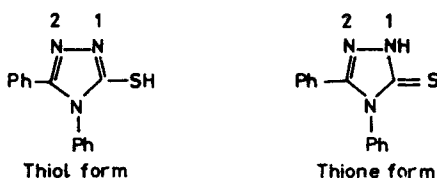
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Abstract. Neutral chelates of 3,4-diphenyl-5-mercapto-1,2,4-triazole (DPMTH) with Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been prepared and characterized by analytical and physicochemical techniques such as magnetic susceptibility measurements, TGA, electronic ESR and IR spectral studies. The IR data suggest that DPMTH behaves as a uninegative bidentate ligand in all the complexes except Fe(II) and Ni(II) where it is tridentate. The complexes have been found to display significant antifungal activity against *A. alternata* and *A. flavus*.

Keywords. Metal complexes; analytical techniques; physicochemical techniques; neutral chelates; mercapto triazole.

1. Introduction

3,4-diphenyl-5-mercapto 1,2,4-triazole (DPMTH) containing a mercapto group can form chelate with transition metal ions in the *thiol* form utilizing the ring nitrogen (N^1) as shown below.



No work has so far been done on the metal complexes of the title ligand. It was therefore thought worthwhile to prepare and characterise its metal complexes and study their fungicidal activity.

2. Experimental

The ligand DPMTH was prepared by the method described earlier (Ram and Pandey 1973) and was crystallized from ethanol (m.p. 295-297°C).

2.1 Preparation and characterization of metal complexes

The complexes were prepared by refluxing metal (II) chloride/sulphate and the ligand in

* To whom all correspondence should be addressed.

Table 1. Analytical data and magnetic moment of the metal complexes

Complex	Colour	Observed (%)			Calculated (%)			μ_{eff}
		M	N	S	M	N	S	
Cu(DPMT) ₂	Dark green	11.24	14.24	11.38	11.18	14.80	11.27	1.80
Ni(DPMT) ₂	Light yellow	10.82	14.64	11.42	10.43	14.92	11.37	2.98
Co(DPMT) ₂	Blue	10.28	14.52	11.38	10.46	14.92	11.36	4.45
Fe(DPMT) ₂	Brown	9.54	14.98	11.28	9.96	15.00	11.43	4.95
Zn(DPMT) ₂	White	11.48	14.62	10.98	11.12	14.75	11.24	Diamag.
Cd(DPMT) ₂	White	17.98	13.58	10.62	18.23	13.62	10.38	Diamag.
Hg(DPMT) ₂	White	28.82	12.06	9.26	28.47	11.92	9.08	Diamag.

a 1:2 molar ratio in ethanol and then adding an aqueous solution of sodium acetate except in the Cu(II) complex. The complexes thus precipitated were digested for ~30 min, filtered, washed with hot ethanol and dried *in vacuo*.

The analyses of the metal and sulphur contents were carried out by standard methods (Vogel 1978; Treadwell and Hall 1958). Nitrogen was analysed by microanalysis. The analytical data are given in table 1.

3. Physical measurements

The magnetic susceptibilities of the complexes were determined by the Faraday method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant and experimental magnetic susceptibilities were corrected (Figgis and Lewis 1960) for diamagnetism. Magnetic moments of the complexes are included in table 1.

The electronic spectra of the complexes were recorded on a Cary-14 spectrophotometer in Nujol. The various absorption bands and their assignments are given in table 2. The ESR spectra were recorded at room temperature as well as at liquid nitrogen temperature in DMF on a Varian X-band spectrometer model E-4 and the spectral parameters calculated using DPPH as the internal standard.

The IR spectra of the ligand and the complexes were recorded with a Perkin Elmer 621 grating infrared spectrophotometer in Nujol mull in the range $4000\text{--}200\text{ cm}^{-1}$. The important IR bands and their assignments are given in table 3.

The antifungal activity was evaluated by agar-plate technique (Horsfall 1945) in Czapek's medium using acetone solutions of the compounds. The percentage inhibition is given in table 4.

4. Results and discussion

The complexes are insoluble in non-polar and polar organic solvents such as chloroform, carbon tetrachloride, ethanol, methanol etc., but soluble in highly coordinating organic solvents such as DMF and DMSO.

4.1 Magnetic moments

The corrected magnetic moments (table 1) suggest spin-free octahedral geometry for Fe(II) and Ni(II) complexes and a tetrahedral geometry for Co(II) complex (Figgis and

Table 2. Electronic spectral bands, their assignments and ligand field parameters.

Compounds	Bands (cm ⁻¹)	Assignments	10 Dq (cm ⁻¹)	B' (cm ⁻¹)	β	β° (%)	LESE (kJ/mole)
Fe(DPMT) ₂	10000, 16600	⁵ T _{2g} → ⁵ Eg(D), t _{2g} → π*	10000	—	—	—	47.71
Co(DPMT) ₂	7020, 8160 15500, 18000	⁴ A ₂ → ⁴ T ₁ (F) ⁴ A ₂ → ⁴ T ₁ (P)	4500	715	0.736	26.4	64.58
Ni(DPMT) ₂	10000, 13700, 16240	³ A _{2g} (F) → ³ T _{2g} (F), ¹ Eg, ³ T _{1g} (F)	10000	877	0.830	17.0	143.10
Cu(DPMT) ₂	16600	² B _{1g} → ² A _{1g} , ² B _{2g} , ² Eg	16600	—	—	—	118.8

Table 3. Infrared spectral bands and their assignments.

Compound	$\nu(\text{NH})$	$\nu(\text{SH})$	Thioamide			$\nu(\text{N-N})$	$\nu(\text{M-S})$	$\nu(\text{M-N})$
			I	II	III			
DPMTH	3110	2750w	1475	1240	1020	995	—	—
Fe(DPMT) ₂	—	—	1450	1260	1035	1060	310	340
Co(DPMT) ₂	—	—	1445	1260	1030	1020	315	325
Ni(DPMT) ₂	—	—	1445	1270	1040	1065	310	330
Cu(DPMT) ₂	—	—	1440	1260	1025	1020	310	345
Zn(DPMT) ₂	—	—	1445	1265	1025	1020	320	340
Cd(DPMT) ₂	—	—	1440	1265	1025	1020	315	340
Hg(DPMT) ₂	—	—	1440	1270	1035	1015	320	345

Table 4. Antifungal activity.

Compound Conc. (ppm)	Average percentage inhibition after three days					
	Organism <i>A. alternata</i>			Organism <i>A. flavus</i>		
	1:100	1:1000	1:10,000	1:100	1:1000	1:10,000
Cu(DPMT) ₂	60	40	20	57	29	07
Ni(DPMT) ₂	65	44	27	46	28	11
Zn(DPMT) ₂	67	36	26	60	33	07
Cd(DPMT) ₂	63	40	33	63	33	17
Hg(DPMT) ₂	73	57	43	66	46	23

Lewis 1964). The μ_{eff} value of copper(II) complex lies in the range reported for square planar Cu(II) complexes (Sacconi and Ciampolini 1964).

4.2 Electronic and ESR spectra

The spectrum of Fe(DPMT)₂ shows a broad *d-d* band at 10000 cm⁻¹ and a more intense charge-transfer band at 16600 cm⁻¹ which may be assigned to ⁵T_{2g} → ⁵E_g(D) and t_{2g} → π* transitions respectively (Lever 1968).

The spectrum of Co(DPMT)₂ shows four bands at 7020, 8160, 15500 and 18000 cm⁻¹. The first two bands may be due to splitting of ν_2 [⁴A₂ → ⁴T₁(F)] while the last two due to the components of ν_3 [⁴A₂ → ⁴T₁(P)]. The energies of ν_2 and ν_3 bands have been selected to be 7550 and 16670 cm⁻¹ respectively by taking the centre of gravity of the total intensity by visual method (Cotton *et al* 1961) and from these values the various ligand-field parameters calculated by the method of Drago (1965) are given in table 2.

Of the three bands occurring in the spectrum of Ni(DPMT)₂ at 10000, 13700 and 16240 cm⁻¹, the first and third may be assigned to ³A_{2g}(F) → ³T_{2g}(F) (ν₁) and ³A_{2g}(F) → ³T_{1g}(F) (ν₂) transitions respectively while the second may be attributed to the spin-forbidden transition ³A_{2g}(F) → ¹E_g in octahedral geometry of the complex. The energy of the spin-forbidden band given by the equation (Lever 1968) 13700 = 8B + 2C - 6B²/10D_q, when solved by assuming C = 4B and substituting

$10Dq = 10000 \text{ cm}^{-1}$ yields values of B_{33} and β_{33} to be 883 cm^{-1} and 0.836 respectively. Further, the ratio $\nu_2/\nu_1 = 1.624$ and the values of β_{35} (0.830) and B_{33} (0.836) being very close to each other suggest an octahedral geometry for $\text{Ni}(\text{MPMT})_2$ (Sacconi 1969; Lever 1968).

The spectrum of $\text{Cu}(\text{DPMT})_2$ shows a broad band at 16600 cm^{-1} assigned to the envelope of ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{2g}$, 2E_g transitions in the square planar environment of $\text{Cu}(\text{II})$ (Proctor *et al* 1968).

Thus the findings from the electronic spectral studies of the complexes regarding their stereochemistry are consistent with the magnetic susceptibility measurements discussed earlier.

In the ESR spectrum of $\text{Cu}(\text{DPMT})_2$ in DMF, the parallel and perpendicular features of ${}^{63}\text{Cu}$ are clearly resolved and are characteristic of axial symmetry. The ESR magnetic parameters for the complex as calculated from the analysis of the spectra at 77°K and room temperature are: $g_{\parallel} = 2.3132$, $g_{\perp} = 2.0530$, $A_{\parallel} = 160\text{G}$, $g_{\text{iso}} = 2.135$, which indicate the trend $g_{\parallel} > g_{\perp}$ free-spin (2.0023) showing that the unpaired electron is in $d_{x^2-y^2}$ orbital of $\text{Cu}(\text{II})$ ion (Goodman and Rayney 1970). The g_{\parallel} and g_{\perp} values depart considerably from the free-spin values indicating a strong axial distortion of the molecule (Lewis *et al* 1966; Van Landschoot *et al* 1976) probably due to the coordination of DMF in the axial positions.

4.3 IR spectra

The IR spectrum of DPMT shows bands at 3110 and 2750 cm^{-1} assigned to $\nu(\text{NH})$ and $\nu(\text{SH})$ groups respectively (Singh *et al* 1980; Gadag and Gajendragad 1980). These bands are absent in the spectra of the complexes indicating removal of the proton from the ligand and subsequent bonding of the metal ion with the thiol sulphur on complexation. The disappearance of thioamide band IV [mainly due to $\nu(\text{C}=\text{S})$] occurring at 960 cm^{-1} in DPMT and appearance of a band in the $720\text{--}730 \text{ cm}^{-1}$ region due to $\nu(\text{C}-\text{S})$ in the spectra of the complexes show bonding through the sulphur (Singh *et al* 1980). The bonding through sulphur is further supported by a negative shift of $25\text{--}35 \text{ cm}^{-1}$ in thioamide I band and positive shift of $20\text{--}30 \text{ cm}^{-1}$ in thioamide II and thioamide III bands in the spectra of the complexes. A positive shift of $\sim 65 \text{ cm}^{-1}$ in $\nu(\text{N}-\text{N})$ in the spectra of $\text{Fe}(\text{II})$ and $\text{Ni}(\text{II})$ complexes and of $\sim 25 \text{ cm}^{-1}$ in others indicate that both the nitrogens of $-\text{C}=\text{N}-\text{N}=\text{C}-$ moiety are involved in bonding in the first case while only one nitrogen is taking part in the other case (Braibanti *et al* 1968). The non-ligand bands occurring in $300\text{--}320$ and $330\text{--}350 \text{ cm}^{-1}$ regions may be tentatively assigned to $\nu(\text{M}-\text{S})$ (Nigam and Pandey 1972; Browall and Interrante 1973) and $\nu(\text{M}-\text{N})$ (Specia *et al* 1974; Paoletti *et al* 1973) modes respectively. The IR spectral studies thus suggest that DPMT act as mononegative tridentate in $\text{Fe}(\text{II})$ and $\text{Ni}(\text{II})$ complexes bonding through sulphur and the two hydrazidic nitrogens and as mononegative bidentate in all other complexes bonding through sulphur and one hydrazidic nitrogen.

4.4 Fungicidal test

The antifungal activity given in table 4 show that the complexes are fairly toxic to both the species of fungi. However, the fungi toxicity against *A. altarnata* is more than that for *A. flavus*. At a very dilute concentration all the five compounds have been a more superior fungicide against *A. altarnata*.

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