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Synthesis, Characterization and Antimicrobial Studies of Some Bivalent Metal Complexes with 1-Phenoloxy-2-(3′-methyl-5′-mercapto-1′,2′,4′-triazole)-2-azaethane

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Metal complexes of the type $[M(PMTE)(H_2O)_2]$ [where M = Mn(II), Co(II) or Ni(II) and PMTE = 1-phenoloxy-2-(3′-methyl-5′-mercapto-1′,2′,4′-triazole)-2-azaethane] and $[Cu(PMTE)]_2$ have been synthesized in neutral medium. The IR spectra of the complexes suggest the coordination of the metal ion and ligand through thiol-sulphur, exocyclic azomethine nitrogen and phenolic oxygen. Octahedral geometry of the complexes except $[Cu(PMTE)]_2$ have been proposed on the basis of elemental analysis, magnetic susceptibility measurement and spectra studies. However, for the Cu(II) complex square-planar geometry has been proposed. Thermal analyses of all the complexes except $[Cu(PMTE)]_2$ show similar pattern of decomposition. Weight loss around *ca.* 210°C in one step with exothermal peak in DTA curve corresponds to loss of two water molecules, characteristic of coordinated water molecule. Decomposition of all the complexes starts at *ca.* 355°C and terminates at *ca.* 780°C with a final residue corresponding to the formation of metal oxide. Fungicidal screening of the complexes show them active against *Aspergillus niger, Fusarium orysporium* and *Helminthosporium oryzae*.

Key Words: 1-Phenoloxy-2-(3′-methyl-5′-mercapto-1′,2′,4′-triazole)-2-azaethane, Complexes, Mn(II), Co(II), Ni(II), (Cu(II), Characterization, Antifungal studies.

INTRODUCTION

Metal complexes with the ligand containing sulphur, nitrogen and oxygen donor atoms have been found useful as potential drugs[1–4]. Considering the importance of such complexes, in the present paper we report the synthesis and characterization of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} complexes with 1-phenoloxy-2-(3′-methyl-5′-mercapto-1′,2′,4′-triazole) 2-azaethane (PMTE) and their fungicidal screening.

EXPERIMENTAL

All the solvents and chemicals were of analytical grade. Reagents and solvents were used without further purification.

The ligand was synthesized in two steps. 4-Amino-5-mercapto-3-methyl-1,2,4-triazole was prepared by reported method[5–7]. Attempt was made to isolate the ligand 1-phenoloxy-2-(3′-methyl-5′-mercapto-1′,2′,4′-triazole)-2-azaethane (PMTE) by the condensation of 4-amino-5-mercapto-3-methyl-1,2,4-triazole and salicylaldehyde but failed. So the complexes were prepared *in situ*.

3-Methyl-4-amino-5-mearcapto-1,2,4-triazole (1 mmol) and salicylaldehyde were taken in ethanolic medium and refluxed for 1/2 h. After getting a clear solution of the ligand, a solution of the appropriate metal salt (1 mmol) in ethanol was added. It was refluxed for 3 h. When precipitate was slowly formed, it was cooled and finally the precipitate was filtered, washed with ethanol and then analyzed by standard methods after being dried *in vacuo*. The colour, melting point and analytical data of the complexes are recorded in Table-1.

TABLE-1
ANALYTICAL DATA OF METAL COMPLEXES OF PMTE

Complex	Colour	m.w., Found (Calcd.)	m.p. (°C)	Found (Calcd.)				
				C	H	N	S	M
$[Cu(PMTE)]_2$	Sand stone	589 (591)	> 250	40.1 (40.6)	2.2 (2.6)	18.5 (18.8)	11.0 (10.8)	21.1 21.4
$[Ni(PMTE)(H_2O)_2]_2$	Greenish white	650 (653.5)	> 250	36.3 (36.8)	3.5 (3.7)	17.1 (17.1)	9.7 (9.8)	18.1 (18.0)
$[Co(PMTE)(H_2O_2)_2]_2$	Light grey	647 (654)	> 250	36.5 (36.7)	3.6 (3.6)	17.0 (17.1)	9.6 (9.7)	18.0 (18.0)
$[Mn(PMTE)(H_2O)_2]_2$	Yellow	640 (646)	> 250	37.0 (37.1)	3.6 (3.7)	17.0 (17.3)	9.8 (9.9)	17.0 (17.0)

TABLE-2
MAGNETIC AND ELECTRONIC SPECTRAL DATA

Complex	μ_{eff} (B.M.)	Bond position cm^{-1} (nm)	Assignments
$[Co(PMTE)(H_2O)_2]_2$	3.83	13,000 (769)	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
		15,200 (657)	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		23,000 (434)	C.T.
$[Ni(PMTE)(H_2O)_2]_2$	2.61	12,500 (800)	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
		17,500 (571)	$^3A_{1g}(F) \rightarrow {}^3T_{2g}(F)$
		25,000 (400)	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
$[Cu(PMTE)]_2$	1.39	16,000 (b) (625)	$^2E_g \rightarrow {}^2T_{2g}$
$[Mn(PMTE)(H_2O)_2]_2$	4.37	18,200 (549)	$^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$
		22,810 (438)	$^6A_{1g}(S) \rightarrow {}^4E_g + {}^4A_{1g}(G)$
		25,000 (400)	$^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$

Infrared spectra in KBr pellets were recorded on a Perkin-Elmer 398 spectrophotometer. Reflectance spectra were recorded on a Cary-2390 spectrophotometer. Room temperature magnetic susceptibilities were measured by Gouy method.

Thermogravimetric analyses were carried out by a Netzch-429. Simultaneous recording of TGA and DTA was done in a thermoanalyzer at a heating rate of 10°C min^{-1} in air.

RESULTS AND DISCUSSION

All the complexes are amorphous, have high melting point and are insoluble in water and common organic solvents. Freshly prepared samples are soluble in DMF and dioxane. Low conductance value observed in DMF for all the complexes indicates that they are non-electrolytes. They are not attacked by acids and undergo decomposition before melting.

Since attempts to isolate the ligand (PMTE) was not successful, the infrared spectra of the ligand could not be recorded. Hence the spectra of the complexes were compared with the spectra of the starting materials and related compounds.

A strong and broad band in the vicinity of 3450–3200 cm^{-1} in the spectra of nickel(II), cobalt(II) and manganese(II) complexes can be assigned to the presence of coordinated water molecules[5]. The broadness of the band is probably due to intramolecular hydrogen bonding. The presence of coordinated water moleculs is further confirmed by the appearance of the additional band at *ca.* 860 cm^{-1} which may be due to wagging modes of vibration[9-11]. However, no such bands in the region were found in the case of copper(II) complex. The spectra of all the complexes show a band of medium intensity at *ca.* 1610 cm^{-1} which may be probably due to the endocyclic ν(C=N) of 3-methyl-5-mercapto-1,2,4-triazole[6]. However, the band at *ca.* 1625 cm^{-1} is broadened suggesting participation of the exocyclic azomethine nitrogen in complexation. Since no band is observed due to carbonyl group in the range 1750–1730 cm^{-1}, it can be suggested that coordination of the amino group with the carbonyl group has taken place. Appearance of bands at *ca.* 780 and 450 cm^{-1} due to ν(C—S) and ν(M—S) in the spectra of complexes indicates the coordination of metal ion through the sulphur atom[12]. A band of medium intensity *ca.* 1570 cm^{-1} suggests the presence of an oxy bridge[13]. This fact has further been supported by the low magnetic moment value of the complexes. Appearance of new bands at *ca.* 480 and 425 cm^{-1} assignable to ν(M—O)[14] and ν(M—N)[15, 16] respectively further supports the coordination through N and O atoms.

The electronic spectrum of cobalt(II) complex shows two bands at 13,000 cm^{-1} and 15,200 cm^{-1} which are assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively. In addition to these transitions an interse charge transfer band has been observed at 23,000 cm^{-1}.

The Ni(II) complex shows three bands at 12,500, 17,500 and 2500 cm^{-1} attributable to $^3A_{1g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)^1$, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions respectively. The magnetic moments of cobalt(II) and nickel(II) complexes at room temperature are 3.83 and 2.61 B.M. respectively which are lower than the expected spin only magnetic moment values. The lower values may be due to partial quenching of paramagnetism, through a process of super exchange.

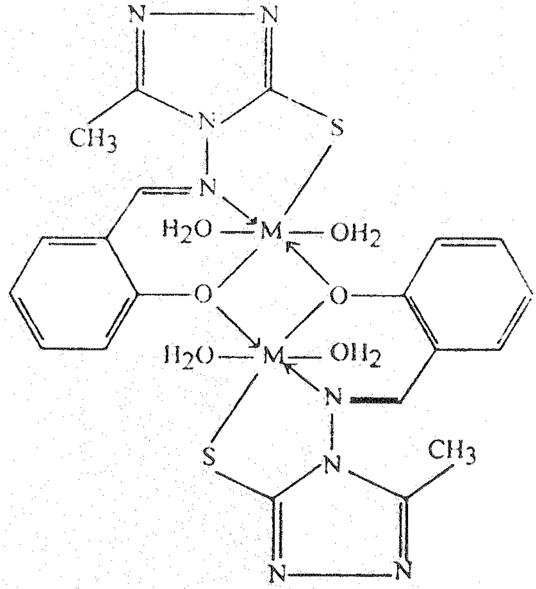
Three shape bands at 18,200, 22,810 and 25,000 cm^{-1} in the electronic spectrum of manganese(II) are assignable to $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, $^6A_{1g}(S) \rightarrow {}^4E_g + {}^4A_{1g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4T_{2g}(P)$ transitions respectively indicating an octahedral field around the metal ion[17–19] respectively. The magnetic moment value of magnanese complex at room temperature is found to be 4.37 B.M., which is lower than the spin only value.

The electronic spectrum of copper(II) complexes shows a broad absorption band at 16,000 cm^{-1} assignable to the transition $^2E_g \rightarrow {}^2T_{2g}$. The broadness of the band suggests a strong Jahn-Teller distortion from octahedral symmetry. The position and nature of this band indicates a planar geometry around the metal ion of the copper(II) complex. The low magnetic moment value of Cu(II) may be assigned to the partial spin pairing between the copper(II) ions through the formation of an oxobridge.

The thermograms of all the complexes show an identical pattern excepting that of copper(II) complex. In case of Cu(II) complex, there was no mass loss up to 350°C indicating the absence of any water molecules. Above 350°C it starts decomposing slowly and finally leaving behind the metal oxide at 760°C.

In all other complexes the first weight loss is encountered at *ca.* 210°C in a single step supported by an exothermic peak at the same temperature in the DTA thermogram. The occurrence of an exothermic peak may be due to bond breaking. Such a behaviour is the characteristic of coordinated water in the same chemical environment[20, 21]. The decomposition proceeds slowly from *ca.* 350°C to *ca.* 780°C in the final residue corresponding to the formation of metal oxide. The thermal stability of the complexes is of the order Ni > Co > Mn > Cu.

Basing on the analytical data, spectral properties and thermal analysis, a binuclear structure may be suggested in which the coordination takes place to the metal centre through azomethine nitrogen, phenolic oxygen and thiol sulphur as shown below:



The antifungal activities of the ligand and its metal complexes were tested against *Helminthosporium oryzae*, *Fusarium exosporium* and *Aspergillus niger* by the method of Horsfall[22]. The evaluation was carried out at 1000 ppm in dioxane. The amount of germination or growth inhibition was determined after inoculation of the fungal spores onto czapexdox agar-agar medium containing the test sample.

The whole system was kept in an incubator for five days at 30 ± 1°C. The percentage inhibition was calculated as follows:

$$\% \text{ of inhibition} = \frac{100(P - Q)}{P}$$

where P = area of colony growth without test sample and Q = area of colony growth with test sample. When metal salts such as copper chloride, cobalt chloride are used as fungicides, they cause damage to the level[23]. However, the coordination compounds do little damage. Among the complexes being reported here, the copper(II) complexes possess the highest fungitoxicity. The fungitoxicity of the complexes has been attributed to the presence of N—C═S moiety[24].

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