Journal Homepage: - www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI: 10.21474/IJAR01/13750
DOI URL: http://dx.doi.org/10.21474/IJAR01/13750

ISSN NO. 2320-5407

RESEARCH ARTICLE

SYNTHESIS, SPECTROSCOPIC, THERMAL AND BIOLOGICAL STUDIES ON MANGANESE(III), IRON(III) AND COBALT(III) COMPLEXES WITH BIS(MERCAPTO AZOLES)

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Manuscript Info

Manuscript History
Received: 19 September 2021
Final Accepted: 24 October 2021
Published: November 2021

Key words:-
Manganese(III), Iron(III), Cobalt(III), Bis(Mercapto Azoles), U.V./Visible, IR, H NMR, Antifungal, Antiviral, Antibacterial

Abstract

Complexes of bis(mercapto azoles) i.e. bis(mercapto triazoles), bis(mercapto thiadiazoles) and bis(mercapto oxadiazoles) (LH_2) with manganese(III), iron(III) and cobalt(III) have been prepared in methanol in the presence of sodium hydroxide and binuclear products of the type $Na[M(L)_2(H_2O)_2]$ have been isolated. Tentative structural conclusions are drawn for these complexes based upon elemental analyses, electrical conductance, magnetic moment and spectral (electronic, infrared and ^{1}H NMR) data. The thermal stability and mode of decomposition for the complexes have been studied by TG, DTA and DSC techniques. The antifungal, antiviral and antibacterial activities of the ligands and their corresponding complexes were also investigated.

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Introduction:-

The chemistry of transition metal complexes containing heterocyclic thione donors continues to be of interest on account of their interesting structural features and also because of their biological importance [1-4]. The combination of the exocyclic thione/thiol group and the heterocyclic molecule, which may contain nitrogen, oxygen or sulphur or a combination thereof, generates a group of molecules with considerable coordination potential [1]. The coordination behaviour of such molecule depends upon reaction conditions, nature of metal ion and pH of the medium. The stimulus for much of the research into the coordination chemistry of heterocyclic thione/thiol donors status from their wide ranging applications [5-7] viz., in analytical chemistry; in metal finishing and electroplating industries; use as polyolefin stabilizers and as vulcanization accelerators. Fungicidal, insecticidal and acaricidal activities have also been reported. Other biological applications include thyrotoxic activity, centred nervous system depressant and a platinum pyridine thione complex has been patented for clinical use in cancer treatment [1]. However, so far no report is available on the coordination behaviour of bis(mercaptoazoles). So, it was considered worthwhile to investigate the synthetic and structural aspects of the complexes of manganese(III), iron(III) and cobalt(III) with three novel series of heterocyclic liagnds bearing mercapto group.

The structures of various mercapto azoles, used as ligands for the present work, are shown below:

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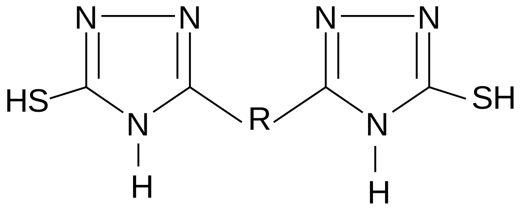
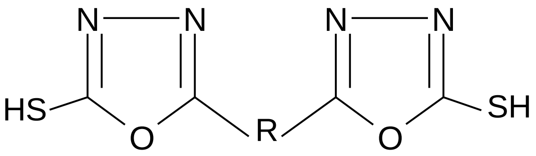
Bis(mercapto triazoles)



R= C_6H_4 ($MTPH_2$), $(CH_2)_2$ ($MTEH_2$), $(CH_2)_4$ ($MTBH_2$)

(I)

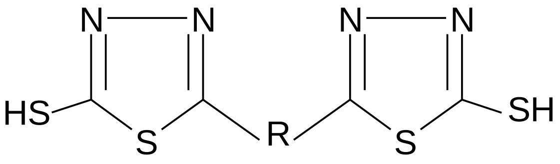
(A) Bis(mercapto oxadiazoles)



R= C_6H_4- ($MOPH_2$), -$(CH_2)_2$- ($MOEH_2$), -$(CH_2)_4$- ($MOBH_2$)

(II)

(C) Bis(mercapto thiadiazoles)



R= C_6H_4- ($MThPH_2$), -$(CH_2)_2$- ($MThEH_2$), -$(CH_2)_4$- ($MThBH_2$)

(III)

Experimental

The solvents were purchased from Merck and metal salts were purchased from Aldrich. Buchi 530 apparatus was used to determine the melting points. Elemental analysis was performed with a Vario EL III Carlo Erba 1105 CHN analyser and elemental (C, H, N) analysis indicated that calculated and observed values were within acceptable limits. IR spectra were recorded in KBr using Shimadzu 8201 PC model spectrophotometer while NMR spectra were recorded in DMSO-d_6 solvent by a Bruker DRX-300 spectrometer using tetramethylsilane as an internal reference. Thermogravimetric analysis (TGA) data of the complexes were studied using a Perkin Elmer-STA 6000 thermal analyser instrument.

The ligands were prepared as reported earlier [8].

(i) Preparation of manganese(III) and iron(III) complexes with 4,4'-bis(5-mercapto-1,3,4-triazole-2-yl)phenyl ($MTPH_2$)

To a solution of manganese(III) acetate or iron(III) chloride (0.02 mol) in methanol (40 cm^3) was added 4,4'-bis(5-mercapto-1,3,4-triazole-2-yl)phenyl ($MTPH_2$) (0.02 mol). To the resulting solution, saturated ethanolic solution of NaOH was added and the mixture was refluxed for 8-12 h. The coloured precipitate, thus obtained, was thoroughly washed with methanol and dried in vacuo. Yield 60-68%.

(ii) Preparation of cobalt(III) complexes with 4,4'-bis(5-mercapto-1,3,4-triazole-2-yl)phenyl ($MTPH_2$)

Mercaptotriazole ($MTPH_2$) (0.02 mol) was added to a solution of cobalt(II) acetate (0.02 mol) in methanol(40 cm^3). To the resulting solution, saturated ethanolic solution of KOH and H_2O_2 (30%, 6 cm^3) and the mixture was refluxed for 15 h. The coloured precipitate, thus obtained, was thoroughly washed with methanol and dried in vacuo. Yield 60-65%.

The same procedure was adopted for the synthesis of chromium(III), manganese(III), iron(III) and cobalt(III) derivatives with other bis(mercaptotriazoles) such as 1,2-bis(5-mercapto-1,3,4-triazole-2-yl)ethane ($MTEH_2$) and

1,4-bis(5-mercapto-1,3,4-triazole-2-yl) butane (MTBH$_2$). For the sake of brevity, the details are summarized in **Table 1**. The analytical data of the products are given in **Table 2**.

(iii) Preparation of manganese(III) and iron(III) complexes with 4,4'-bis(5-mercapto-1,3,4-oxadiazole-2-yl)phenyl (MOPH$_2$)

To a solution of manganese(III) acetate or iron(III) chloride (0.02 mol) in methanol (40 cm^3) was added 4,4'-bis(5-mercapto-1,3,4-oxadiazole-2-yl)biphenyl (MOPH$_2$) (0.02 mol). To the resulting solution, saturated ethanolic solution of NaOH was added and the mixture was refluxed for 8-13 h. The coloured precipitate, thus obtained, was thoroughly washed with methanol and dried in vacuo. Yield 60-70%.

(iv) Preparation of cobalt(III) complexes with 4,4'-bis(5-mercapto-1,3,4-oxadiazole-2-yl)phenyl (MTPH$_2$)

Bis(mercapto oxadiazole) (MOPH$_2$) (0.02 mol) was added to a solution of cobalt(II) acetate (0.02 mol) in methanol(40 cm^3). To the resulting solution, saturated ethanolic solution of KOH and H_2O_2 (30%, 6 cm^3) and the mixture was refluxed for 15-16 h. The coloured precipitate, thus obtained, was thoroughly washed with methanol and dried in vacuo. Yield 65-70%.

The same procedure was adopted for the synthesis of chromium(III), manganese(III), iron(III) and cobalt(III) derivatives with other bis(mercaptooxadiazoles) such as 1,2-bis(5-mercapto-1,3,4-oxadiazole-2-yl)ethane (MOEH$_2$) and 1,4-bis(5-mercapto-1,3,4-oxadiazole-2-yl) butane (MOBH$_2$). For the sake of brevity, the details are summarized in **Table 3**. The analytical data of the products are given in **Table 4** .

(v) Preparation of manganese(III) and iron(III) complexes with 4,4'-bis(5-mercapto-1,3,4-thiadiazole-2-yl)phenyl (MThPH$_2$)

To a solution of manganese(III) acetate or iron(III) chloride (0.02 mol) in methanol (40 cm^3) was added 4,4'-bis(5-mercapto-1,3,4-thiadiazole-2-yl)biphenyl (MThPH$_2$) (0.02 mol). To the resulting solution, saturated ethanolic solution of NaOH was added and the mixture was refluxed for 8-16 h. The coloured precipitate, thus obtained, was thoroughly washed with methanol and dried in vacuo. Yield 65-70%.

(vi) Preparation of cobalt(III) complexes with 4,4'-bis(5-mercapto-1,3,4-thiadiazole-2-yl)phenyl (MThPH$_2$)

Mercapto thiadiazole (MThPH$_2$) (0.02 mol) was added to a solution of cobalt(II) acetate (0.02 mol) in methanol(40 cm^3). To the resulting solution, saturated ethanolic solution of KOH and H_2O_2 (30%, 6 cm^3) and the mixture was refluxed for 12-15 h. The coloured precipitate, thus obtained, was thoroughly washed with methanol and dried in vacuo. Yield 66-68%.

The same procedure was adopted for the synthesis of chromium(III), manganese(III), iron(III) and cobalt(III) derivatives with other bis(mercaptothiadiazoles) such as 1,2-bis(5-mercapto-1,3,4-thiadiazole-2-yl)ethane (MOEH$_2$) and 1,4-bis(5-mercapto-1,3,4-thiadiazole-2-yl) butane (MOBH$_2$). For the sake of brevity, the details are summarized in **Table 5**. The analytical data of the products are given in **Table 6**.

Results And Discussion:-

Manganese(III) acetate, iron(III) chloride and cobalt(III) acetate react with bis(mercaptoazoles) (LH$_2$) viz., bis(mercaptotriazoles), bis(mercapto- oxadiazoles) or bis(mercaptothiadiazoles) in 1:2 molar ratio, respectively, in methanol the presence of sodium hydroxide to binuclear products of type $Na[M(L)_2(H_2O)_2]$, according to following equation:

$$[MX_3] + LH_2 \xrightarrow{NaOH} Na[M(L)_2(H_2O)_2]$$

(M= Mn(III), Fe(III) or Co(III); LH$_2$= 4,4'-Bis(5-mercapto-1,3,4-triazole-2-yl) biphenyl (MTPH$_2$), 1,2-bis(5-mercapto-1,3,4-triazole-2-yl)ethane (MTEH$_2$), 1,4-bis(5-mercapto-1,3,4-triazole-2-yl) butane (MTBH$_2$); 4,4'-bis(5-mercapto-1,3,4-oxadiazole-2-yl) biphenyl (MOPH$_2$), 1,2-bis(5-mercapto-1,3,4-oxadiazole-2-yl)ethane (MOEH$_2$), 1,4-bis(5-mercapto-1,3,4-oxadiazole-2-yl) butane (MOBH$_2$); 4,4'-bis(5-mercapto-1,3,4-thiadiazole-2-yl) biphenyl, 1,2-bis(5-mercapto-1,3,4-thiadiazole-2-yl) ethane (MThEH$_2$), 1,4-bis(5-mercapto-1,3,4-thiadiazole-2-yl) butane (MThBH$_2$))

The physical properties and the analytical data of the complexes are given in Tables 1-6. The complexes are coloured solids and are soluble in dimethylformamide and dimethylsulphoxide. The electrical conductance measurements in dimethylformamide are consistent with their non-electrolytic nature. The presence of coordinated water molecules in these complexes has been inferred from thermogravimetric study, which show weight loss at ca. 160^{o}C corresponding to two water molecules.

Magnetic Moment

At room temperature magnetic moment of the powdered polycrystalline manganese(III) complexes is observed between 4.80 – 4.90 B.M. which is in excellent agreement with the spin only moment (4.90 μ_B) for a high spin d^4 (S = 2) configuration normally observed for mononuclear manganese(III) complexes [9].

The magnetic moments of iron(III) complexes lie around 5.0-5.2 B.M. at room temperature which are lower than the usual value (5.90 B.M.)

Cobalt(III) complexes are diamagnetic.

Electronic Spectra

The electronic spectral bands of manganese(III), iron(III) and cobalt(III) complexes are given in **Table 7**.

The visible spectra of manganese(III) complexes have almost identical features containing multiple absorption bands mostly in the form of shoulders. In DMF solution two prominent bands associated with d-d transitions are observed in the 15,220–16,200 and 18,250–19,100 cm^{-1} range along with a high intensity band at ca 21500–22360 cm^{-1}. Consequently three spin–allowed d-d transitions $^4B_{1g}\rightarrow{}^5A_{1g}$, $^5B_{1g}\rightarrow{}^5B_{2g}$ and $^4B_{1g}\rightarrow{}^5E_g$ are possible in this type of system [9].

The electronic spectrum of iron(III) complexes shows several bands at 12,200-12880, 19,200–19,940 and 24100–24,990 cm^{-1} which may be assignment to transitions $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4A_{1g}, E_g$. The positions of these bands indicate [9] that these complexes are octahedral in nature. In addition to these bands, a charge-transfer band at ca. 32500 cm^{-1} is also observed which may be assigned to Fe ($e_g \rightarrow \pi^*$ (ligand) transition. The magnetic moment and the ligand field parameters indicate that it is of the spin–free octahedral type.

a) The electronic spectra of cobalt(III) complexes show bands in the regions 16,000-16,450, 19,590-22,610 and 24,215-25,400 cm^{-1}. The positions of these bands resemble those reported [9] for other six-coordinated cobalt(III) complexes and may be assigned to $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively. The appearance of three bands in cobalt(III) complexes indicates a low symmetry ligand field.

b)

Infrared Spectra

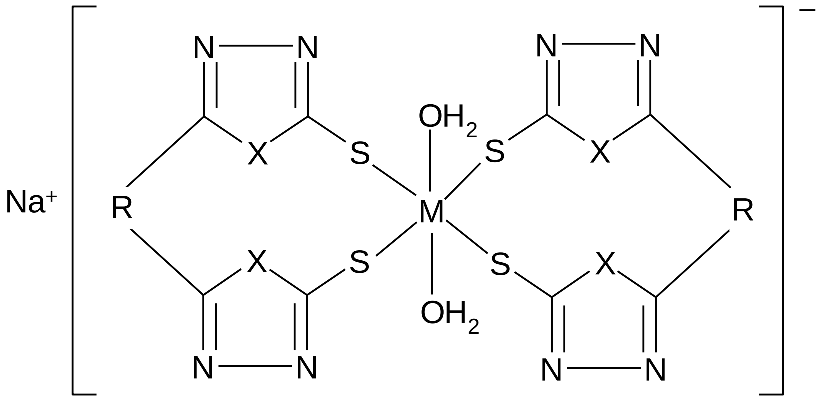
The assignments of infrared spectral bands of the ligands and the complexes are based on earlier studies on similar ligands [10-16]. The infrared spectra of bis(mercaptotriazoles), bis(mercaptooxadiazoles) and bis(mercaptothiadiazoles) show one weak band at 2480-2550 cm^{-1} due to the -SH group vibration. However, in the spectra of complexes the band disappears indicating the coordination through sulphur after deprotonation. This is further supported[4] by the appearance of band at ca. 340-380 cm^{-1}, assignable to ν(M-S). A strong band in the region of 1585-1560 cm^{-1} in the ligands is characteristics [14, 15] of ν(C=N) (ring) group. However, in the complexes the position of this band remains at the same position, indicating the non-coordination of the ring nitrogen to metal ion. The infrared spectra of bis(mercaptotriazoles) show one band at 3150 cm^{-1} assignable [17] to ν(N-H). The bands due to ν(C-O-C) in bis(mercaptooxadiazoles) appear at ca. 1290 cm^{-1} (symmetric) and 1350 cm^{-1} (asymmetric); while bis(mercaptothiadiazoles) show band at ca. 660-650 cm^{-1} due to ν(C-S) [16]. The position of infrared bands due to phenyl and heterocyclic (triazole, oxadiazole or thiadiazole) ring do not change in the complexes indicating the non-coordination of nitrogen (triazole ring), oxygen (oxadiazole ring) or sulphur (thiadiazole ring) atoms. The complexes show one strong band at ca. 3400 cm^{-1} which may be due to coordinated water molecule. This is further confirmed by the appearance of medium band at ca. 500 cm^{-1}, assignable to ν(M-O).

Thus, the infrared spectra reflected that all bis(mercaptoazoles) i.e. bis(mercaptotriazoles), bis(mercaptooxadiazoles) and bis(mercaptothiadiazoles) act as dibasic bidentate chelating agents coordinating through two thiol sulphur atoms.

Proton Magnetic Resonance Spectra

The proton magnetic resonance spectra of ligands and their corresponding cobalt(III) complexes were recorded in DMSO-d_6. The intensities of all the resonance lines were determined by planimetric integration. The signal due to –SH proton appears at ca. δ 8.8-9.0 in the ligands which disappears in the corresponding cobalt(III) complexes.

Thus, on the basis of elemental analyses, electrical conductance and spectral data, the following structure (IV) is tentatively proposed for chromium(III), manganese(III), iron(III) and cobalt(III) complexes.



(IV))

X = NH, O or S; R = -C_6H_4-C_6H_4-, -$(CH_2)_2$ or --$(CH_2)_4$;
M = Mn(III), Fe(III) or Co(III)

Antifungal Activity

Sugarcane, a major source of sugar and important cash crop, is extensively grown worldwide. Diseases are one of the major constraints in the profitable cultivation of sugarcane [18,19]. About one hundred diseases of sugarcane caused by virus, fungi, bacteria, phytoplasma and nematodes have been reported from different parts of the world [20] and 84 diseases have been reported from India. Fungal diseases are causing alarming losses in sugarcane production of India.

Among fungal diseases red-rot by Colletotrichum falcatum [21], wilt caused by Fusarium moniliforme and Fusarium oxysporum [22] , pineapple caused by Ceraticystis paradox and leaf spots caused by Curvularia lunata, Curvularia pallescence, Epicocum nigrim and Periconia atropurpuria are the main diseases which are responsible for loss in sugarcane production in India. Among these, fungi Colletotrichum falcatum (Red rot) and Fusarium oxysporum (fusarium sett or stem rot, pokkah boeng, knife cut, and wilt) are the most important pathogens that may be transmitted primarily by planting infected setts. Curvularia pallescence is the important foliar pathogens of sugarcane, sometimes causing enormous losses to sugar industry.

Different chemical compounds have been used as chemotherapeutants to control sugarcane diseases. A large number of inorganic compounds of mercury, lead, copper and sulphur have been used as fungicides to prevent fungal diseases of sugarcane. However several of these inorganic compounds are dangerous to human beings and host plants [23]. The increasing consciousness of the hazards involved in the use of such fungicides has reinforced the need for more efficient and harmless compounds. A number of synthetic organic compounds are now known to be useful in the control of various fungal diseases in plants [24, 25].

Antifungal effect of all prepared complexes were studied against three pathogenic fungal strains by agar plate technique; the antifungal activity outcome were recorded as percentage of inhibtion and compared with standard drug Fluconazole. For each compound 1% standard solution was prepared in DMSO and 1mL of the solution was mixed with 9mL of the solvent. Three concentration viz. 10, 100, 1000 ppm stock solutions were prepared for each compound and 1 mL of each concentration solution was mixed with 9 mL of agar medium in sterilized petriplates. After the medium was prepared, fungus strain was inoculated in the center of each plate and assay plates were incubated at $29^0 \pm 2^0$C for seven days.

Metal complexes containing bis(mercapto azoles) also showed **(Tables 8-10)** promising results in inhibiting the mycelial growth of all the test fungi. Complexes with bis(mercapto thiadiazoles) are found to be more active than complexes with bis(mercapto triazoles) which in turn show better activity than bis(mercapto oxadiazoles). Manganese(III) complex with 1,2-bis(5-mercapto-1,3,4-thiadiazol-2-yl)butane (MThBH$_2$) is found to be 100% inhibitory to mycelial growth for all the species of fungi at 1000 ppm concentration. Other derivatives also show promising antifungal results against all test fungi from 35% to 92% at 1000 ppm concentration.

The minimum inhibitory concentration (MIC) of the two most active manganese(III) complexes were determined. Three concentrations 1000, 2000 and 3000 ppm of each test compound with respect to the culture medium were prepared. The fungistatic/ fungicidal nature of the active chemicals was determined in three replicates using the test fungi following the procedure of Garbour and Houston [26]. This was done by observing if revival of growth of the inhibition mycelial disks occurred following transfer to a chemical-free medium.

Manganese(III) complexes with 2-(2-chlorophenyl)1,3,4-oxadiazole-5-yl)dithiocarbazinate (OCPOD) and 1,2-bis(5-mercapto-1,3,4-thiadiazol-2-yl)butane ($MThBH_2$) show superiority over the commercial fungicides Bavistin, Blitox-50, Topsin-M and Dithiane M-45 during the present study. These comounds are about 3-4 times more active than the tested commercial fungicides (Table 11) which are being used in sugarcane fungal disease management.

Screening Data Conclusions

1. There is significant alteration in the antifungal activity with the change in the nature of organic group attached to metal ion.
2. Metal complexes are found to be more active than their corresponding ligands. In other words, chelation increases the fungicidal activity.
3. For any particular species of fungus, manganese(III) derivatives show better activity than iron(III) derivatives which in turn show better activity than cobalt(III) derivatives. Chromium(III) complexes show least activity as compared to manganese(III), iron(III) and cobalt(III) derivatives.
4. The activity decreases on dilution.

Table 1:- Reactions of cobalt(III) acetate, iron(III) chloride, manganese(III) acetate with bis(mercaptotriazoles).

Reactants	**Molar ratio**	**Refluxing time (h)**	**Solvent**	**Product**	*B.* Colour	**% yield**	**Decomp. Temp. ^{0}C**
$Mn(OAc)_3$ + $MTPH_2$	1:1	12	MeOH	$Na^+[Mn(MTP)_2(H_2O)_2]^-$	Brown	62	200
$Mn(OAc)_3$ + $MTEH_2$	1:1	12	MeOH	$Na^+[Mn(MTE)_2(H_2O)_2]^-$	Light Brown	60	160
$Mn(OAc)_3$ + $MTBH_2$	1:1	12	MeOH	$Na^+[Mn(MTB)_2(H_2O)_2]^-$	Brown	68	180
$FeCl_3$ + $MTPH_2$	1:1	8	MeOH	$Na^+[Fe(MTP)_2(H_2O)_2]^-$	Brown	65	170
$FeCl_3$ + $MTEH_2$	1:1	8	MeOH	$Na^+[Fe(MTE)_2(H_2O)_2]^-$	Brown	68	180
$FeCl_3$ + $MTBH_2$	1:1	8	MeOH	$Na^+[Fe(MTB)_2(H_2O)_2]^-$	Brown	62	180
$Co(OAc)_3$ + $MTPH_2$	1:1	15	MeOH	$Na^+[Co(MTP)_2(H_2O)_2]^-$	Dark Brown	60	185
$Co(OAc)_3$ + $MTEH_2$	1:1	15	MeOH	$Na^+[Co(MTE)_2(H_2O)_2]^-$	Dark Brown	63	215
$Co(OAc)_3$ + $MTBH_2$	1:1	15	MeOH	$Na^+[Co(MTB)_2(H_2O)_2]^-$	Light Brown	65	150

$MTPH_2$ = 1, 2’ Bis(5-mercapto 1, 3, 4-triazole-2yl)phenyl
$MTEH_2$ = 1, 2’ Bis(5-mercapto 1, 3, 4-triazole-2yl)ethane
$MTBH_2$ = 1,4’ Bis(5-mercapto 1, 3, 4-triazole-2yl)butane

Table 2:- Analytical data of manganese(III), Iron(III), cobalt(III) complexes with bis(mercaptotriazoles)

Complex	II. MOLECULAR FORMULA	**Analyses(%)**									
		Found					**Calculated**				
		C	**H**	**N**	**S**	**M**	**C**	**H**	**N**	**S**	**M**
$Na^+[Mn(MTP)_2(H_2O)_2]^-$	$C_{20}H_{16}N_{12}S_4O_2MnNa^+$	36.1	2.3	25.1	19.1	8.2	36.2	2.4	25.3	19.3	8.3
$Na^+[Mn(MTE)_2(H_2O)_2]^-$	$C_{12}H_{16}N_{12}S_4O_2MnNa^+$	25.2	2.8	29.4	22.4	9.6	25.4	2.8	29.6	22.6	9.7
$Na^+[Mn(MTB)_2(H_2O)]^-$	$C_{16}H_{24}N_{12}S_4O_2MnNa^+$	30.4	3.8	27.0	20.3	8.6	30.8	3.8	27.0	20.5	8.8
$Na^+[Fe(MTP)_2(H_2O)_2]^-$	$C_{20}H_{16}N_{12}S_4O_2FeNa^+$	36.0	2.3	25.1	19.2	8.3	36.1	2.4	25.3	19.3	8.4
$Na^+[Fe(MTE)_2(H_2O)_2]^-$	$C_{12}H_{16}N_{12}S_4O_2FeNa^+$	25.1	2.7	29.4	22.2	9.6	25.3	2.8	29.6	22.5	9.8
$Na^+[Fe(MTB)_2(H_2O)]^-$	$C_{16}H_{24}N_{12}S_4O_2FeNa^+$	30.4	3.8	26.8	20.2	8.8	30.8	3.8	26.9	20.5	9.0
$Na^+[Co(MTP)_2(H_2O)_2]^-$	$C_{20}H_{16}N_{12}S_4O_2CoNa^+$	35.8	2.3	25.1	19.1	8.7	36.0	2.4	25.3	19.3	8.8

$Na^+[Co(MTE)_2(H_2O)_2]^-$	$C_{12}H_{16}N_{12}S_4O_2CoNa^+$	24.0	2.6	27.8	21.1	9.7	24.0	2.7	28.0	21.3	9.8
$Na^+[Co(MTB)_2(H_2O)]^-$	$C_{16}H_{24}N_{12}S_4O_2CoNa^+$	30.4	3.7	26.4	20.3	9.2	30.6	3.8	26.8	20.4	9.4

$MTPH_2$ = 1, 2' Bis(5-mercapto1, 3, 4-triazole-2yl)phenyl
$MTEH_2$ = 1, 2' Bis(5-mercapto1, 3, 4-triazole-2yl)ethane

Table 3:- Reactions of manganese(III) acetate, iron(III) chloride, cobalt(III) acetate with bis(mercaptoxadiazoles).

Reactants	**Molar ratio**	**Refluxing time (h)**	**Solvent**	**Product**	A. Colour	**% yield**	**Decomp. Temp. ^{0}C**
$Mn(OAc)_3$ + $MOPH_2$	1:1	13	MeOH	$Na^+[Mn(MOP)_2(H_2O)_2]$	Brown	62	180
$Mn(OAc)_3$ + $MOEH_2$	1:1	13	MeOH	$Na^+[Mn(MOE)_2(H_2O)_2]$	Light brown	68	190
$Mn(OAc)_3$ + $MOBH_2$	1:1	12	MeOH	$Na^+[Mn(MOB)_2(H_2O)_2]$	Brown	70	180
$Fe(OAc)_3$ + $MOPH_2$	1:1	10	MeOH	$Na^+[Fe(MOP)_2(H_2O)_2]$	Brown	64	170
$Fe(OAc)_3$ + $MOEH_2$	1:1	8	MeOH	$Na^+[Fe(MOE)_2(H_2O)_2]$	Brown	62	180
$Fe(OAc)_3$ + $MOBH_2$	1:1	8	MeOH	$Na^+[Fe(MOB)_2(H_2O)_2]$	Dark brown	65	185
$Co(OAc)_3$ + $MOPH_2$	1:1	16	MeOH	$Na^+[Co(MOP)_2(H_2O)_2]$	Dark brown	65	190
$Co(OAc)_3$ + $MOEH_2$	1:1	15	MeOH	$Na^+[Co(MOE)_2(H_2O)_2]$	Dark brown	66	170
$Co(OAc)_3$ + $MOBH_2$	1:1	15	MeOH	$Na^+[Co(MOB)_2(H_2O)_2]$	Brown	70	200

$MOPH_2$= 1, 2' Bis(5-mercapto 1, 3, 4-oxadiazole-2yl)phenyl
$MOEH_2$ = 1, 2' Bis(5-mercapto 1, 3, 4-oxadiazole-2yl)ethane
$MOBH_2$ = 1,4' Bis(5-mercapto 1, 3, 4-oxadiazole-2yl)butane

Table 4:- Analytical data of manganese (III) , iron(III), cobalt(III) complexes with bis (mercaptooxadiazoles).

Complex	**Molecular Formula**	B. Analyses(%)									
		Found					C. Calculated				
		C	**H**	**N**	**S**	**M**	**C**	**H**	**N**	**S**	**M**
$Na^+[Mn(MOP)_2(H_2O)_2]^-$	$[C_{20}H_{12}N_8S_4O_6Mn]Na^+$	37.1	1.8	17.2	19.7	8.3	37.3	1.9	17.4	19.9	8.5
$Na^+[Mn(MOE)_2(H_2O)_2]^-$	$[C_{12}H_{12}N_8S_4O_6Mn]Na^+$	26.1	2.0	20.1	23.2	10.0	26.3	2.1	20.4	23.4	10.0
$Na^+[Mn(MOB)_2(H_2O)_2]^-$	$[C_{16}H_{20}N_8S_4O_6Mn]Na^+$	31.5	3.2	18.2	15.8	9.1	31.8	3.3	18.5	15.9	9.1
$Na^+[Fe(MOP)_2(H_2O)_2]^-$	$[C_{20}H_{12}N_8S_4O_6Fe]Na^+$	37.1	1.9	17.1	19.6	8.6	37.3	1.9	17.3	19.8	8.7
$Na^+[Fe(MOE)_2(H_2O)_2]^-$	$[C_{12}H_{12}N_8S_4O_6Fe]Na^+$	26.1	2.0	20.3	23.1	10.1	26.2	2.1	20.4	23.3	10.2
$Na^+[Fe(MOB)_2(H_2O)_2]^-$	$[C_{16}H_{20}N_8S_4O_6Fe]Na^+$	32.8	3.2	18.2	21.0	9.2	32.0	3.3	18.4	21.1	9.2
$Na^+[Co(MOP)_2(H_2O)_2]^-$	$[C_{20}H_{12}N_8S_4O_6Co]Na^+$	37.0	1.7	17.1	19.6	9.0	37.1	1.8	17.3	19.8	9.1
$Na^+[Co(MOE)_2(H_2O)_2]^-$	$[C_{12}H_{12}N_8S_4O_6Co]Na^+$	24.0	1.9	18.4	21.2	9.7	24.0	2.0	18.6	21.3	9.8
$Na^+[Co(MOB)_2(H_2O)_2]^-$	$[C_{16}H_{20}N_8S_4O_6Co]Na^+$	31.4	3.2	18.3	21.0	9.6	31.6	3.3	18.5	21.1	9.7

$MOPH_2$= 1, 2' Bis(5-mercapto 1, 3, 4-oxadiazole-2yl)phenyl

$MOEH_2$ = 1, 2’ Bis(5-mercapto 1, 3, 4-oxadiazole-2yl)ethane
$MOBH_2$ = 1,4’ Bis(5-mercapto 1, 3, 4-oxadiazole-2yl)butane

Table 5:- Reactions of manganese(III) acetate, iron(III) chloride, cobalt(III) acetate with bis (mercaptothiadiazoles).

Reactants	**Molar ratio**	**Refluxing time(h)**	D. Solvent	**Product**	E. Colour	**% yield**	**Decomp. Temp. ^{0}C**
$Mn(OAc)_3$ + $MThPH_2$	1:1	16	MeOH	$Na^+[Mn(MThP)_2(H_2O)_2]^-$	Light brown	65	200
$Mn(OAc)_3$ + $MThEH_2$	1:1	16	MeOH	$Na^+[Mn(MThE)_2(H_2O)_2]^-$	Light brown	70	185
$Mn(OAc)_3$ + $MThBH_2$	1:1	16	MeOH	$Na^+[Mn(MThB)_2(H_2O)_2]^-$	Light brown	70	180
$FeCl_3$ + $MThPH_2$	1:1	10	MeOH	$Na^+[Fe(MThP)_2(H_2O)_2]^-$	Dark brown	66	170
$FeCl_3$ + $MThEH_2$	1:1	8	MeOH	$Na^+[Fe(MThE)_2(H_2O)_2]^-$	Brown	65	180
$FeCl_3$ + $MThBH_2$	1:1	10	MeOH	$Na^+[Fe(MThB)_2(H_2O)_2]^-$	Brown	66	190
$Co(OAc)_3$ + $MThPH_2$	1:1	15	MeOH	$Na^+[Co(MThP)_2(H_2O)_2]^-$	Dark brown	67	180
$Co(OAc)_3$ + $MThEH_2$	1:1	12	MeOH	$Na^+[Co(MThE)_2(H_2O)_2]^-$	Dark brown	66	190
$Co(OAc)_3$ + $MThBH_2$	1:1	12	MeOH	$Na^+[Co(MThB)_2(H_2O)_2]^-$	Brown	68	170

$MThPH_2$ = 1, 2’-Bis(5-mercapto 1, 3, 4-thiadiazole-2yl)phenyl
$MThEH_2$ = 1, 2’-Bis(5-mercapto 1, 3, 4-thiadiazole-2yl)ethane
$MThBH_2$ = 1,4’-Bis(5-mercapto 1, 3, 4-thiadiazole-2yl)butane

Table 6:- Analytical data of manganese(III), iron(III) and cobalt(III) complexes with bis(mercaptothiadiazoles).

III. COMPLEX	**Molecular Formula**	**Analyses(%)**									
		Found					**Calculated**				
		C	**H**	**N**	**S**	**M**	**C**	**H**	**N**	**S**	**M**
$Na^+[Mn(MThP)_2(H_2O)_2]^-$	$[C_{20}H_{12}N_8S_8O_2Mn]Na^+$	39.6	1.9	18.4	21.1	9.0	39.8	2.0	18.6	21.2	9.1
$Na^+[Mn(MThE)_2(H_2O)_2]^-$	$[C_{12}H_{12}N_8S_8O_2Mn]Na^+$	28.3	2.2	22.0	25.1	10.6	28.4	2.3	22.1	25.2	10.8
$Na^+[Mn(MThB)_2(H_2O)_2]^-$	$[C_{16}H_{20}N_8S_8O_2Mn]Na^+$	34.0	3.5	20.0	22.6	9.6	34.2	3.6	20.0	22.8	9.8
$Na^+[Fe(MThP)_2(H_2O)_2]^-$	$[C_{20}H_{12}N_8S_8O_2Fe]Na^+$	39.6	1.9	18.4	21.0	9.0	39.8	2.0	18.5	21.1	9.1
$Na^+[Fe(MThE)_2(H_2O)_2]^-$	$[C_{12}H_{12}N_8S_8O_2Fe]Na^+$	28.2	2.3	22.0	25.0	11.0	28.4	2.4	22.0	25.2	11.0
$Na^+[Fe(MThB)_2(H_2O)_2]^-$	$[C_{16}H_{20}N_8S_8O_2Fe]Na^+$	34.0	3.4	19.7	22.6	9.8	34.2	3.6	19.9	22.7	10.0
$Na^+[Co(MThP)_2(H_2O)_2]^-$	$[C_{20}H_{12}N_8S_8O_2Co]Na^+$	39.4	3.2	18.3	21.0	9.6	39.6	3.3	18.5	21.1	9.7
$Na^+[Co(MThE)_2(H_2O)_2]^-$	$[C_{12}H_{12}N_8S_8O_2Co]Na^+$	28.0	2.2	22.0	25.0	11.6	28.2	2.3	22.1	25.0	11.6
$Na^+[Co(MThB)_2(H_2O)_2]^-$	$[C_{16}H_{20}N_8S_8O_2Co]Na^+$	34.0	3.4	19.6	22.5	10.3	34.0	3.5	19.8	22.7	10.4

$MThPH_2$ = 1, 2’-Bis(5-mercapto 1, 3, 4-thiadiazole-2yl)phenyl
$MThEH_2$ = 1, 2’-Bis(5-mercapto 1, 3, 4-thiadiazole-2yl)ethane
$MThBH_2$ = 1,4’ -Bis(5-mercapto 1, 3, 4-thiadiazole-2yl)butane

Table 7:- Magnetic Moment (B.M.) and Electronic Spectral Data (cm^{-1}) for Manganese(III) Iron(III) and Cobalt(III) complexes with Bis(mercapto azoles).

Complex	**μ_B**	Bands Observed (cm^{-1})	**Assignments**	**ν_2/ν_1**	**Dq**	**B**	**C**	**β**
Na[Mn(MTP)$_2$(H$_2$O)$_2$]	4.80	15560 18400 21600	${}^5B_{1g} \rightarrow {}^5A_{1g}$ ${}^5B_{1g} \rightarrow {}^5E_g$ ${}^5B_{1g} \rightarrow {}^5B_2g$	1.20	1556	635	2921	0.66
Na[Mn(MTE)$_2$(H$_2$O)$_2$]	4.85	15220 18900 21850	-do-	1.24	1522	620	2852	0.66
Na[Mn(MTB)$_2$(H$_2$O)$_2$]	4.87	15900 18850 22360	-do-	1.20	1590	648	2985	0.67
Na[Fe(MTP)$_2$(H$_2$O)$_2$]	5.0	12575 19500 24730	${}^6A_{1g} \rightarrow {}^4T_{1g}$ ${}^6A_{1g} \rightarrow {}^4T_{2g}$ ${}^6A_{1g} \rightarrow {}^4A_{1g}$	1.55	749	681	3200	0.66
Na[Fe(MTE)$_2$(H$_2$O)$_2$]	5.0	12350 19360 24200	-do-	1.53	733	667	3063	0.65
Na[Fe(MTB)$_2$(H$_2$O)$_2$]	5.1	12490 19600 24600	-do-	1.56	745	677	3181	0.66
Na[Co(MTP)$_2$(H$_2$O)$_2$]	Dia.	16300 20800 24610	${}^1A_{1g} \rightarrow {}^3T_{2g}$ ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ${}^1A_{1g} \rightarrow {}^1T_{2g}$	1.27	2400	600	2880	0.57
Na[Co(MTE)$_2$(H$_2$O)$_2$]	Dia.	16110 20400 24300	-do-	1.26	2370	592	2841	0.57
Na[Co(MTB)$_2$(H$_2$O)$_2$]	Dia.	16200 22610 25215	-do-	1.39	2458	615	2950	0.59
Na[Mn(MOP)$_2$(H$_2$O)$_2$]	4.80	15500 18300 21590	${}^5B_{1g} \rightarrow {}^5A_{1g}$ ${}^5B_{1g} \rightarrow {}^5E_g$ ${}^5B_{1g} \rightarrow {}^5B_2g$	1.17	1550	632	2972	0.65
Na[Mn(MOE)$_2$(H$_2$O)$_2$]	4.85	15200 18250 21500	-do-	1.20	1520	620	2852	0.64
Na[Mn(MOB)$_2$(H$_2$O)$_2$]	4.90	15860 18955 22150	-do-	1.20	1586	647	2976	0.66
Na[Fe(MOP)$_2$(H$_2$O)$_2$]	5.1	12200 19200 24660	${}^6A_{1g} \rightarrow {}^4T_{1g}$ ${}^6A_{1g} \rightarrow {}^4T_{2g}$ ${}^6A_{1g} \rightarrow {}^4A_{1g}$	1.57	745	677	3185	0.66
Na[Fe(MOE)$_2$(H$_2$O)$_2$]	5.0	12400 19330 24100	-do-	1.45	730	660	3036	0.64
Na[Fe(MOB)$_2$(H$_2$O)$_2$]	5.1	12490	-do-	1.57	744	674	3082	0.66

		19590 24580						
Na[Co(MOP)$_2$(H$_2$O)$_2$]	Dia.	16190 20330 24510	$^1A_{1g} \rightarrow {}^3T_{2g}$ $^1A_{1g} \rightarrow {}^1T_{1g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$	1.27	2390	597	2865	0.57
Na[Co(MOE)$_2$(H$_2$O)$_2$]	Dia.	16100 20200 24290	-do-	1.26	2369	592	2841	0.57
Na[Co(MOB)$_2$(H$_2$O)$_2$]	Dia.	16118 22590 25200	-do-	1.38	2456	614	2947	0.59
Na[Mn(MThP)$_2$(H$_2$O)$_2$]	4.90	15900 18520 21800	$^5B_{1g} \rightarrow {}^5A_{1g}$ $^5B_{1g} \rightarrow {}^5E_g$ $^5B_{1g} \rightarrow {}^5B_2g$	1.19	1590	648	2980	0.66
Na[Mn(MThE)$_2$(H$_2$O)$_2$]	4.80	15610 18900 21990	-do-	1.21	1561	637	2930	0.65
Na[Mn(MThB)$_2$(H$_2$O)$_2$]	4.87	16200 19100 22400	-do-	1.17	1620	661	3040	0.68
Na[Fe(MThP)$_2$(H$_2$O)$_2$]	5.2	12700 19800 24810	$^6A_{1g} \rightarrow {}^4T_{1g}$ $^6A_{1g} \rightarrow {}^4T_{2g}$ $^6A_{1g} \rightarrow {}^4A_{1g}$	1.55	751	683	3140	0.66
Na[Fe(MThE)$_2$(H$_2$O)$_2$]	5.1	12530 19400 24450	-do-	1.55	740	670	3082	0.65
Na[Fe(MThB)$_2$(H$_2$O)$_2$]	5.2	12880 19940 24990	-do-	1.53	754	685	3151	0.67
Na[Co(MThP)$_2$(H$_2$O)$_2$]	Dia.	16300 20580 24750	$^1A_{1g} \rightarrow {}^3T_{2g}$ $^1A_{1g} \rightarrow {}^1T_{1g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$	1.26	2414	603	2897	0.58
Na[Co(MThE)$_2$(H$_2$O)$_2$]	Dia.	16200 20300 24490	-do-	1.25	2389	597	2867	0.57
Na[Co(MThB)$_2$(H$_2$O)$_2$]	Dia.	16450 20770 25400	-do-	1.26	2478	619	2973	0.59

Table 8:- Fungitoxic screening data of manganese(III), iron(III) and cobalt(III) complexes with bis(mercapto triazoles).

Compound	**Percent Mycelial Inhibition**			**Compound dose (ppm)**					
	a) **Collectotrichum falcatum**			**Fusarium oxysporum**			*b)* **Curvularia pallescence**		
	10	**100**	**1000**	**10**	**100**	**1000**	**10**	**100**	**1000**
Na[Mn(MTP)$_2$(H$_2$O)$_2$]	62.1	70.1	82.4	60.0	67.1	82.5	61.0	68.1	82.1
Na[Mn(MTE)$_2$(H$_2$O)$_2$]	60.1	65.1	81.7	59.2	54.1	80.6	58.1	65.2	80.5
Na[Mn(MTB)$_2$(H$_2$O)$_2$]	64.2	73.2	90.5	62.1	70.7	86.1	62.7	69.1	85.0
Na[Fe(MTP)$_2$(H$_2$O)$_2$]	50.0	52.1	60.1	50.2	55.7	60.1	50.5	67.2	69.6
Na[Fe(MTE)$_2$(H$_2$O)$_2$]	42.4	48.1	55.2	45.6	50.0	55.8	48.2	56.0	63.2
Na[Fe(MTB)$_2$(H$_2$O)$_2$]	55.2	60.6	68.2	52.4	61.8	68.4	55.8	60.6	71.0
Na[Co(MTP)$_2$(H$_2$O)$_2$]	40.2	44.1	57.1	42.5	51.6	59.8	46.0	52.7	64.8
Na[Co(MTE)$_2$(H$_2$O)$_2$]	39.2	40.0	55.3	40.4	47.6	54.6	39.6	42.8	56.2
Na[Co(MTB)$_2$(H$_2$O)$_2$]	42.1	51.6	65.2	40.8	51.0	64.4	49.5	55.0	65.3

Table 9:- Fungitoxic screening data of manganese(III), iron(III) and cobalt(III) complexes containing bis(mercapto oxadiazoles).

Compound	**Percent Mycelial Inhibition Compound dose (ppm)**								
	c) **Collectotrichum falcatum**			Fusarium oxysporum			*d)* **Curvularia pallescence**		
	10	**100**	**1000**	**10**	**100**	**1000**	**10**	**100**	**1000**
Na[Mn(MOP)$_2$(H$_2$O)$_2$]	56.1	65.1	78.2	55.5	62.0	78.1	56.0	63.0	79.1
Na[Mn(MOE)$_2$(H$_2$O)$_2$]	55.2	60.0	77.2	54.3	51.0	75.6	53.0	62.1	75.2
Na[Mn(MOB)$_2$(H$_2$O)$_2$]	58.2	69.2	85.1	55.1	65.2	81.3	57.5	64.0	81.2
Na[Fe(MOP)$_2$(H$_2$O)$_2$]	45.2	50.1	56.2	45.2	50.2	55.6	45.8	62.1	66.9
Na[Fe(MOE)$_2$(H$_2$O)$_2$]	37.2	44.3	52.1	40.6	46.0	50.3	43.1	51.7	59.4
Na[Fe(MOB)$_2$(H$_2$O)$_2$]	51.2	56.6	63.7	46.2	55.4	64.1	50.6	55.2	65.8
Na[Co(MOP)$_2$(H$_2$O)$_2$]	35.4	40.9	55.2	38.2	45.3	55.6	41.5	48.2	59.8
Na[Co(MOE)$_2$(H$_2$O)$_2$]	35.1	39.0	50.3	35.2	42.6	50.2	34.7	39.8	55.2
Na[Co(MOB)$_2$(H$_2$O)$_2$]	37.8	48.4	60.1	36.6	45.2	60.2	45.2	51.3	60.1

Table 10:- Fungitoxic screening data of manganese(III), iron(III) and cobalt(III) complexes containing bis(mercapto thiadiazoles).

Compound	**Percent Mycelial Inhibition Compound dose (ppm)**								
	e) **Collectotrichum falcatum**			Fusarium oxysporum			*f)* **Curvularia pallescence**		
	10	**100**	**1000**	**10**	**100**	**1000**	**10**	**100**	**1000**
Na[Mn(MThP)$_2$(H$_2$O)$_2$]	72.6	78.1	93.6	70.0	77.2	92.6	70.0	76.1	92.8
Na[Mn(MThE)$_2$(H$_2$O)$_2$]	70.2	76.7	92.8	69.4	75.2	91.6	69.2	75.0	90.0
Na[Mn(MThB)$_2$(H$_2$O)$_2$]	75.2	82.0	**100.0**	72.8	81.7	**100.0**	74.5	78.9	**100.0**
Na[Fe(MThP)$_2$(H$_2$O)$_2$]	60.1	64.1	70.2	60.0	66.8	70.2	62.6	68.8	78.6
Na[Fe(MThE)$_2$(H$_2$O)$_2$]	50.4	55.2	64.2	55.6	58.9	65.8	58.5	66.6	72.6
Na[Fe(MThB)$_2$(H$_2$O)$_2$]	65.5	70.0	79.2	64.4	70.2	78.6	66.8	71.6	80.0
Na[Co(MThP)$_2$(H$_2$O)$_2$]	50.5	54.2	67.2	52.8	60.8	68.8	56.2	61.0	72.8
Na[Co(MThE)$_2$(H$_2$O)$_2$]	47.2	50.8	65.6	50.2	57.1	64.8	49.6	52.7	66.8
Na[Co(MThB)$_2$(H$_2$O)$_2$]	52.3	61.8	76.2	51.8	60.0	74.2	59.8	65.2	75.6

Table 11:- Efficacy of manganese(III) complexes compared with synthetic fungicides against sugarcane pathogens.

Common names of fungicides / chemical	**Trade name**	**MIC (ppm) against**		
		C. falcatum	F. oxysporum	C. pallescence
Carbendazim	Bavistin	4000	3000	4000
Copper oxychloride	Blitox 50	4000	3000	2000
Mancozeb	DithaneM-45	4000	3000	4000
Thiophanate methyl	Topsin M	4000	4000	4000
[Mn(OCPOD)$_3$]	–	1000	1000	1000
Na[Mn(MThB)$_2$(H$_2$O)$_2$]	–	1000	1000	1000

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