



Reactions of 2-thioxoper hydro-1, 3-thiazin-4 ones with Oxovanadium (IV), Chromium (III), Manganese (II), Iron (II) and Iron (III)

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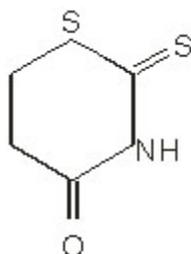
ABSTRACT

In this paper, the reaction of 2-thioxoperhydro – 1, 3 – thiazin – 4 ones; with VO(IV), Cr(III), Mn(II), Fe(II) and Fe(III) ions lead to the formation of $M(TP)_x (H_2O)_y$ [$M=Mn(II), Cr(III), Fe(III)$; $x=1$ or 2; $y=2$ or 3], $VO(TP)_2$ and $[Fe(TPH)Cl_2(PPh_3)_2]$. These complexes have been characterized by analytical, magnetic, thermogravimetric and spectral (IR, UV and Visible) studies and their tentative structures are proposed.

Key words: Spectroscopic methods, Metal complexes, Fungicides, Pesticides.

INTRODUCTION

Many metal complexes of ligands having N, O and S as donor atoms have been used as fungicides and Pesticides.¹ In view of this, the synthesis and characterization of a few transition metal complexes with some pyrrole derivatives were reported earlier.^{2,5} As a continuation, this paper reports the synthesis and characterization of several Complexes of 2-Thioxoperhydro – 1, 3 – Thiazin – 4 ones various metal ions



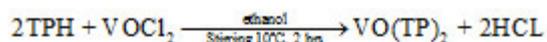
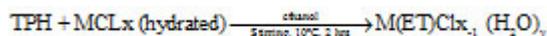
EXPERIMENTAL

All the chemicals used were either of AR or chemically pure grade 2-thioxoper hydro – 1, 3 – thiazin – 4 ones, here after referred as TPH, dichlorobis (Triphenyl Phosphine) iron (II) were Prepared according to methods described in literature.^{6,7}

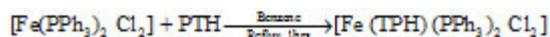
Preparation of metal Complexes

The ligand (1mmol) in ethanol (25ml) was added dropwise with constant stirring to a appropriate metal chloride (1mmol) in ethanol (25ml). The stirring was continued for 2hrs. at 10°C. The resultant solution was filtered and the filtrate was kept in refrigerator for overnight where by a crystalline complex of the complex was formed. It was washed several times with ethanol, ether and dried in vacuo.

The representative equations for the formation of the complexes are given as



The dichloro (TPH) bis (triphenyl phosphine) Iron (II) Complex, $[\text{Fe}(\text{ETH})\text{Cl}_2(\text{PPh}_3)_2]$, was isolated when dichlorobis (triphenyl phosphine) Iron (II), (1.25g ~ 1mmol) was dissolved in benzene (20ml) by warming and to this a benzene solution of TPH (0.15g ~ 1mmol in 10 ml) was added. The reaction mixture was refluxed for 1 hrs and the resulting brownish solution concentrated to half of its original volume. On addition of petroleum ether (15ml, 40-60°), a green precipitate of the complex was formed.



Analyses of complexes

Metal, Sulphur, Chloride and Phosphorus were analyzed by the literature procedure.^{8,9} Carbon, hydrogen and nitrogen analyses were performed by the microanalytical section of chemistry department B.H.U. Varanasi. The analytical results are given in Table-1.

Physical Measurements

Infrared Spectra of the ligand and Complexes in KBr were obtained on a Perkin-Elmer Spectrophotometer model 580. Melting points of the complexes are observed on Fisher-Johns melting points apparatus and reported without further corrections. The electronic Spectra of the ligand and complexes were recorded on a carry-17D in chloroform. The magnetic susceptibilities of the complexes were determined at room temperature

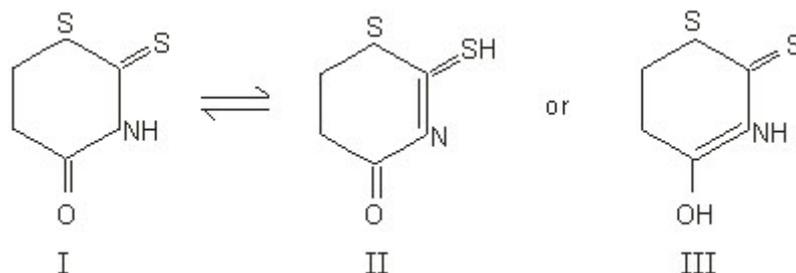
on a Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant and experimental magnetic susceptibilities were corrected for diamagnetism.¹⁰

RESULTS AND DISCUSSION

All the complexes are found to be non-ionic and soluble in CH_2Cl_2 , CHCl_3 , DMF and DMSO. Assuming that the metal ions adopt normally preferred geometries in their complexes, the analytical data (Table-1) suggests the bidentate nature of TPH in all the Complexes irrespective of whether the ligand is bidentate or monodentate, it can coordinate with metal ions through any two or one of the three viz., nitrogen, oxygen and sulphur. The spectral studies of the ligand and its complexes were carried out to explore possible modes of linkages in the complexes. The IR Spectra of the complexes were quite complicated because of the extensive mixing of various modes of vibrations in the ligand. The systematic shift of the bands, which can be assigned with some certainty, has been used to deduce the bonding of TPH involved in complex formation. These bands are grouped under the following headings for the sake of convenience of discussion.

Infrared Spectral Studies

In IR Spectra of $[\text{M}(\text{TP})(\text{Cl})_x(\text{H}_2\text{O})_y]$ $[\text{M}=\text{Mn}(\text{II}), \text{Cr}(\text{III}), \text{Fe}(\text{III}); x=1 \text{ or } 2; y=2 \text{ or } 3]$ and VO(TP)_2 Complexes. The shift in the band positions in the IR spectra of these complexes have been found to be similar. The characteristic IR bands of the ring skeleton (3100, 3000, 1470, 1360, 720) were present in the spectrum of the ligand¹¹ and did not shift in the spectra of complexes (maximum shift ± 5 (cm). This indicates that S of the ring (-S-) is not participating in the bond formation. Further, the absence of any band in the region 2500-2600 cm^{-1} indicates that in solid state TPH exist in thione form (I) and not in thiol form (II) or (III)



Thus the formation of M-S or M-O covalent bonds from the replacement of hydrogen ions by metal ions is improbable in any chemical reactions. Assuming the bonding in complexes with –C(S)NH C(CO) – moiety of the ligand, major shifts in the positions of thioamide and amide bands are expected. The following are the general observations in their spectra.

- (i) The $\nu(\text{NH})$ of the ligand at 3160 cm^{-1} disappeared in the spectra of all the complexes suggesting deprotonation of the ligand.
- (ii) The amide band I $\nu(\text{CO})$ at 1710 cm^{-1} in shifted to lower wave number ($\Delta\nu = +20\text{ cm}^{-1}$) indicating the involvement of carbonyl oxygen in bond formation.
- (iii) The positions of thioamide bands and II having contributions from $\nu(\text{CN})$ or $\delta(\text{NH})$ and those of amide bands II and III in the region $1500\text{--}1000\text{ cm}^{-1}$ either did not shift or shifts were too small to draw any definite conclusion from their direction.
- (iv) The thioamide band IV at 750 cm^{-1} due to $\nu(\text{C}\cdots\text{S})$ of the ligand shifted slightly towards higher wave numbers, suggesting non involvement of thiocarbonyl sulphur in bond formation.
- (v) A weak band at 645 cm^{-1} due to $\nu(\text{NH})$ of the NCO group^{15,18} disappeared in the spectra of the complexes.
- (vi) Three new bands observed in the regions $290\text{--}325$, $290\text{--}310$ and $270\text{--}320\text{ cm}^{-1}$ in the spectra of complexes, which were absent in the spectrum of the ligand are tentatively assigned to $\nu(\text{M-N})$, $\nu(\text{M-O})$ ^{19,20} and $\nu(\text{M-Cl})$ ²¹ modes, respectively.
- (vii) A strong band at 970 cm^{-1} in the spectrum of VO(IV) complexes is tentatively assigned to the $\nu(\text{V=O})$ mode.^{22,23}
- (viii) A medium intensity band in the region $1050\text{--}1125\text{ cm}^{-1}$ in the spectra of Cr(III) Fe (III) and Mn(II) complexes has been assigned to the rocking²⁴ modes of coordinated water.

[Fe(TPH)₂Cl₂(PPh₃)₂]

- (i) The ligand band at 3160 cm^{-1} due to $\nu(\text{NH})$ shifted towards the lower wave numbers and appeared around 3110 cm^{-1} , suggesting increased electronegativity of the nitrogen atom of the –C(S)NH C(O)- moiety and

Table 1 : Analytical data, Colour Melting Points and Magnetic Moments of Complexes

Compound	Colour	Melting points (°C)	Magnetic (B.M.)	Found (%) Calcd						
				C	H	N	S	Cl	P	Metal
[VO(TP) ₂]	Light green	145 ^d	1.71	13.22 (13.39)	2.44 (2.25)	3.58 (3.90)	17.56 (19.86)	-	-	14.32 (14.19)
[Cr(TP)(H ₂ O) ₂ Cl ₂]	Green	165 ^d	3.56	16.64 (16.74)	2.24 (2.10)	4.68 (4.88)	22.20 (22.35)	24.64 (24.71)	-	18.28 (18.12)
[Mn(TP)(H ₂ O) ₃ Cl]	Dirty green	180 ^d	5.71	16.44 (16.54)	3.56 (3.47)	4.60 (4.82)	21.86 (22.08)	12.08 (12.21)	-	18.72 (18.92)
[Fe(TPH)Cl ₂ (PPh ₃) ₂]	Green	160	5.20	60.88 (61.20)	5.28 (5.14)	1.68 (1.74)	8.08 (7.07)	8.68 (8.81)	7.82 (7.70)	7.12 (6.94)
[Fe(TP)(H ₂ O) ₂ Cl ₂]	Light green	205	5.50	15.46 (15.55)	2.78 (2.67)	4.42 (4.53)	20.82 (20.76)	22.84 (22.96)	-	18.16 (18.08)

- absence of deprotonation in the complex.
- (ii) The thioamide band I and II (arising due to coupled vibrations of $\delta(\text{NH})$ and $\nu(\text{CN})$ at 1540 and 1345 cm^{-1} shifted towards higher wave number, 1560 and 1355 cm^{-1} , respectively.
- (iii) The broad bands at 1000 and 750 cm^{-1} of the free ligand shifted towards lower wave numbers (10 cm^{-1}). The bands have been assigned to thioamide band III having major contributions from $\nu(\text{C-C})$, $\nu(\text{C-N})$ and $\nu(\text{C=S})$ in the normal coordinate. The shift in
- the positions of these bands towards lower wave numbers in the complex further confirmed the bonding of the metal ion through thiocarbonyl sulphur.
- (iv) In the spectra of complexes, the positions of the ligand band at 490 cm^{-1} assigned to $\delta(\text{C=S})$, shifted towards lower number ($\sim 20\text{cm}^{-1}$).
- (v) The characteristic bands of triphenyl phosphine were found in the spectra of complexes.²⁵
- (vi) The non ligand bands occurring in the region

Table 2 : Spectral bands of ligands and complexes

Complexes	$\nu(\text{NH})$	$\nu(\text{CO})$	Thioamide bands			
			I	II	III	IV
$\text{C}_4\text{H}_5\text{NoS}_2$	3160br	1710s	1540s	1345s	100s	750s
$\text{VO}(\text{TP})_2$	-	1690s	1542s	1350m	980m	770m
$[\text{Cr}(\text{TP})(\text{H}_2\text{O})_2 \text{Cl}_2]$	-	1690s	1540s	1345s	1005m	775m
$[\text{Mn}(\text{TP})(\text{H}_2\text{O})_3 \text{Cl}]$	-	1690s	1545s	1350m	1005m	775m
$[\text{Fe}(\text{TPH}) \text{Cl}_2 (\text{PPh}_3)_2]$	3110br	-	1560s	1355s	990	740m
$[\text{Fe}(\text{TP})(\text{H}_2\text{O})_2 \text{Cl}_2]$	-	1695s	1545s	1345s	990m	750m

Table 3 : Electronic spectra of the ligands and complexes

Compound	$\lambda_{\text{max}}(\text{nm})$	Assignments
$\text{C}_4\text{H}_5\text{NOS}_2$	260s	$\pi \rightarrow \pi^*$
	450m	$\eta \rightarrow \pi^*$
$[\text{VO}(\text{TP})_2]$	368	IL
	415	CT
	625	$d_{xy} \rightarrow d_{xz}, d_{yz}$
	715	
$[\text{Cr}(\text{TP})(\text{H}_2\text{O})_2 \text{Cl}_2]$	275	IL
	415	CT
	515	${}^4\text{A}_2\text{g}(\text{F}) \rightarrow {}^4\text{T}_1\text{g}(\text{F})$
	660	${}^4\text{A}_2\text{g}(\text{F}) \rightarrow {}^4\text{T}_2\text{g}(\text{F})$
$[\text{Mn}(\text{TP})(\text{H}_2\text{O})_3 \text{Cl}]$	275	IL
	415	CT
	625	${}^6\text{A}_1\text{g}(\text{S}) \rightarrow {}^4\text{T}_2\text{g}(\text{G})$
$[\text{Fe}(\text{TP})(\text{H}_2\text{O})_2 \text{Cl}_2]$	275410	ILCT
	620	${}^6\text{A}_1\text{g}(\text{S}) \rightarrow {}^4\text{T}_2\text{g}(\text{G})$
$[\text{Fe}(\text{TPH}) \text{Cl}_2 (\text{PPh}_3)_2]$	260	$\pi \rightarrow \pi^*$
	270	IL
	415	CT
	980	${}^5\text{T}_2\text{g} \rightarrow {}^5\text{E}_g$

325 and 300 cm^{-1} in the spectra of the complexes are tentatively assigned to $\nu(\text{M-N})$ and $\nu(\text{M-S})$ modes, respectively.^{26,28}

Thermogravimetric analysis of the Complexes of Cr(III), Fe(III) and Mn(II)

The thermogravimetric analyses of these complexes reveal interesting features and corroborate some assumptions made on the basis of infrared spectral studies. In Cr(III) and Fe(III) complexes, the mass loss starts at 130°C and there's a sharp inflexion between 160-170°C with a mass loss of 10.4 to 10.5% indicating the presence of two coordinated water molecules (theoretical mass loss for two water molecules is 10.0-10.1%). The thermogram of Mn(II) complex show two inflexions and of three water molecules in two steps. Removal of the first molecule of the water is slow and that of second and third is rapid. The mass loss starts at 125°C and a sharp inflexion is observed at 145°C with a mass loss of 6.5% corresponding elimination of one water molecule (theoretical mass loss for one water molecule is 6.2%) The second inflexion is observed at 170°C with mass loss of 12.8% (The theoretical mass loss is 13.2%) further, the bands appearing in the region of 1050-1125 cm^{-1} in the IR spectra of these complexes due to rocking modes of coordinated water disappear from the spectra of the complexes when heated up to 180°C. This provides strong evidence for the coordinated water molecule.

Magnetic Susceptibility Measurements

The complex of Cr(III) and Fe(III) were found to be paramagnetic and exhibited magnetic moments of 3.56 and 5.48 B.M., respectively, which are typical of high spin species. The Presence of a ligand (bident ate), two water molecules and two chloride ions in the inner coordination sphere makes these complexes hexa-coordinated. It is therefore, assumed that these metal ions form hexa-coordinated, octahedral, high spin complexes.

The complexes of Fe(II) and Mn(II) exhibited magnetic moments 5.18 and 5.7 B.M., respectively. The magnetic moment of the Fe(II) complex is slightly lower than the observed value (generally high spin Fe(II) complexes exhibited a magnetic moment value larger than 5.2 B.M.). It is possibly due to either distortion from octahedral

geometry or solid state effects. Further, the value of magnetic moment of Mn(II) complexes is the same in both octahedral and tetrahedral environments of the ligand, Since ${}^6\text{S}$ ground state persists in both the symmetries.²⁹ The number of ligands around these metal ions in five (one bidentule) and six coordinated octahedral geometry is assumed for these metal ions.

The magnetic moment of VO(IV) complex is 1.71 B.M., corresponding to one unpaired electron. The electronic spectrum of the complex in characteristic of square pyramidal geometry.²⁵

Electronic spectral studies

The uv spectrum of ligand in CHCl_3 exhibited bands at 260s and 450w nm. These bands have been assigned to $\pi \rightarrow \pi^*$ and $\nu \rightarrow \pi^*$ transitions respectively.³⁰ The weak band at 450 nm, the lower in energy than other band of the ligand at 260 nm, is assigned to $\eta \rightarrow \pi^*$ transition as a result of the following reasons :

- (i) In general, $\eta \rightarrow \pi^*$ transitions involving N or sulphur atom occur at a lower energy region and are less intense on account of laportz forbidden transitions than $\pi \rightarrow \pi^*$ transition (laportz allowed).
- (ii) The nature and position of the band at 450 nm is solvent dependent (chloroform, 450, alcohol 460 nm).
- (iii) The band is absent from the spectra of silver complex owing to the stabilization of the energy of lone pairs of the electron on complex formation).³¹

The uv and visible spectrum of Cr(III) complexes exhibited bands at 275, 415, 515, and 660 nm. The very high intensity of the bands at 415 and 270 nm indicates that these are $\text{M} \rightarrow \text{L}$ Charge transfer and intraligand bands respectively. However, the weak bands 660 and 515 nm are assigned to ${}^4\text{A}_2\text{g}(\text{F}) \rightarrow {}^4\text{T}_2\text{g}(\text{F})$ and ${}^4\text{A}_2\text{g}(\text{F}) \rightarrow {}^4\text{T}_1\text{g}(\text{F})$, respectively. The third characteristic weak band due to ${}^4\text{A}_2\text{g}(\text{F}) \rightarrow {}^4\text{T}_1\text{g}(\text{P})$, expected around 270 nm is not observed owing to the presence of a strong charge transfer band at 275 nm. Theses bands are the characteristic of Cr(III) complexes.³²

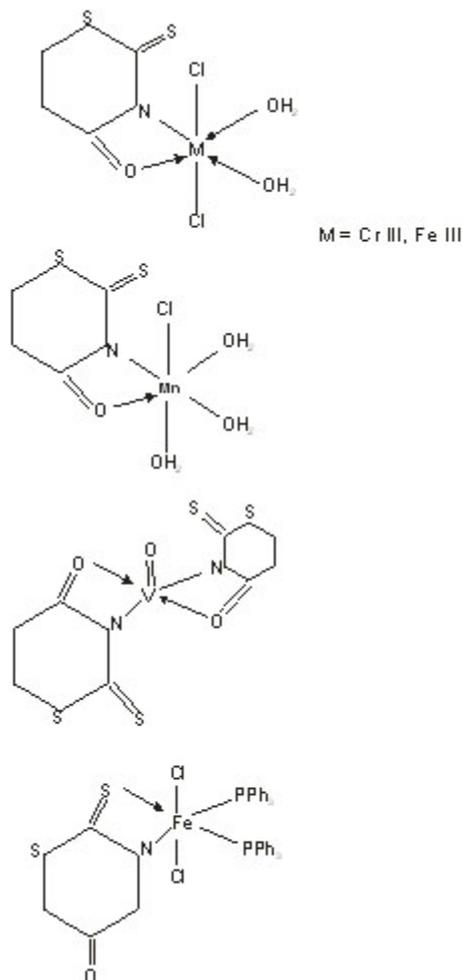
Fe (III) complex shows absorption bands at 620 and 410 nm while Mn(II) complex shows the

absorption bands at 625 and 415 nm. Both the complexes show a very strong band at 275 nm characteristic of intraligand transitions. The bands at 620 in Fe(III) complex and at 625 nm in Mn (II) complex are assigned to ${}^6A_1g \rightarrow {}^4T_2g(G)$ and the bands at 410, 415 nm in Fe (III) and Mn (II) complexes respectively are assigned to $M \rightarrow L$ charge transfer transitions. These observations are inconsistent with the octahedral geometries of the complexes.^{33,34}

The spectrum of $[Fe(TPH)Cl_2(PPh_3)_2]$ shows absorption bands 260, 270, 415 and 980 nm. The band at 980 nm is assigned to ${}^5T_2g \rightarrow {}^5Eg$ while the bands at 415 and 270 nm are assigned to $M \rightarrow L$ charge transfer and intraligand bands respectively.³⁵ The band at 260 nm is the characteristic bands due to $\pi \rightarrow \pi^*$ transitions of the phenyl group of triphenyl phosphine.

The spectrum of VO (IV) complex showed four bands at 368, 415, 625 and 715 nm. The bands at 625 and 715 nm are assigned to $d_{xy} \rightarrow d_{yz}$, d_{xz} , typical of square pyramidal geometry of VO(IV) complex.^{36,38} The bands at 415 and 368 nm are assigned to $M \rightarrow L$ and intraligand and CT bands respectively.

Thus, on the basis of analytical spectral IR, uv and magnetic measurement data, the following tentative structures have been assigned to the complexes.



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