Cr(III) , Mo(VI) and W(Vl) with some nitrogen and sulphur containing ligands (Thiourea, Thisemicarbazide, 1-phenyltetrazoline)

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Abstract: The coordination chemistry of sulphur containing ligands has recently assumed greater importance in view of the fact that several of these compounds have been found to be biologically active and have found uses in medicine as well as in industry. Some sulphur compounds have been found to be useful as protective agents against hazardous radiations. While spin-magnetic moment is insensitive to environment of metal ions. The spin value for the magnetic moment of chromium (III) complexes is 3.87 BM. The experimentally observed magnetic moments for chromium (III) complex with 5-subtituted tetrazoles have been found to be in the range of 3.87 to 5.33. Magnetic moment for octahedral spin free chromium (III) complexes, but there is slight decrease from their spin only value of 3.87 BM. Effect or in other words it may be because of positive spin- orbit coupling effect which results in electron delocalization. This may also be due to weak Cr-Cr super exchange interaction or it may be due to small magnetic anisotropy resulting from the distortion of octahedral symmetry irrespective of the nature of the bond involved. As the complexes are appreciably soluble in DMF, it may be concluded that the complexes are monomeric and lowering of magnetic moment may be because of spin-orbit magnetic anisotropy. This paper deals with the various experimental data obtained on the investigations of the complexes prepared in this work on the basis of their physico – chemical data.

Keywords: **Chromium (III) complex, Spin Value, nitrogen, sulphur, ligands, thiourea, thisemicarbazide, phenyltetrazoline, magnetic moment, anisotropy**

I. INTRODUCTION

Knowledge of the nature of metal complexes of organic sulphur compounds is an important requirement for understanding the interaction of metal ions. Some sulphur containing organic compounds have been found to be useful as protective agents against hazardous radiations. Sometimes due to transfer of charge from ligand to metal or metal to ligand, bands appear in the ultra - violet region of the spectrum. A broad and strong bond present at 3420 cm^{-1} in the spectrum of the ligand may be assigned to υNH mode of vibration. The broadness of this band may be due to different degree of hydrogen bonding. There is a broad and weak band at 3050 cm-^{1} in the spectrum of the ligand which may have contribution from υNH + υCH could vibrations. Rao and Venkataraghvan [1] on examing the spectrum of tetrazole (pK_a = 4.84) in very dilute solutions found the υNH –bond around 3145 cm^{-1} which considerably lower in the position than its position in other organic secondary amines or 1-substituted tetrazoline-5-thiones which is more electronegative than tetrazoles (pK_a = 3.75) the absorption band near 3050 cm^{-1} is assigned to superimposed bands of υNH and υCH. The bands in the region of 3000 – 2700 cm^{-1} in the spectrum say be due to υNH and υCH mode of vibrations of NH and CH groups present in different environments in the crystal lattice of solid 1-pheynyltetrazoline-5-thione ligand. This paper is supported by work of Tosien and Leabas on para-substituted benzene, Wiberly and co-workers on ortho, meta and para- substituted benzene and Shindo on nitrogen hetrocycles .

A weak band present t 2540 cm^{-1} in the spectrum of the ligand which may be due to υSH mode of vibrations. Spectra of these ligands in the 1600 – 2000 cm^{-1} region indicate that the weak bands in this regions are because of the substitution in the phenyl ring. Whiffen and Thomson originally proposed the range of 760 -740 cm^{-1} for the position of the out of plane [2,3]. C-H bonding absorption of the mono-substituted aromatics and this has been widened slightly by Colthup to 760 – 730 cm^{-1}[4]. Whiffen has pointed out that mono-substituted materials also absorb strongly near 690 cm^{-1} where ortho substituted materials do not absorb. This latter correlation has been confirmed by Colthup, by Randall et al. and by Cannon and Sutherlan [5,6,7]. Thus the bands at 750 (s) and 683 (s) cm^{-1} in the spectrum of 1-phenyltetrazoline-5-thione may be assigned to out of plane C-H bending mode of mono-substituted phenyl group. The 1597 (s)cm^{-1} band may be due to υC=C mode of vibration.

Organic compound having a thioamide group (H-N-C=S) give rise to four thioamide bands in their infrared spectra. These four bands generally appear in the region of 1500, 1250- 135, 1000 and 750 – 850 cm^{-1}. Thus the strong bands at 1512 and 1490 cm^{-1} in the spectrum of 1-phenyltetrazoline-5-thione may be the thioamide band has contributions from δN-H and υC=N, the thioamide band II appears at 1280 cm^{-1} as a strong band, the thioamide band III appears at 1045 cm^{-1} and the thioamide band IV appears at 785 cm^{-1} .

II. EXPERIMENTAL METHOD

Interpretation of IR spectral bands of Thioures:

Infrared spectra of thiourea have been studied by several workers. A number of Investigators have been made into the characteristic vibration and possible forms of the normal coordination of molecule containing the thioamide group and several alternatives suggestions have been proposed. The spectrum observed for free thiourea agrees very well with that reported by Stewart, by Yamaguchi et al. and by Aitken et al [8, 9, and 10].
However, Aitken et al. performed normal coordinate analysis of thiourea. Some bands are also found in the spectrum of thiourea which were not indicated or assigned by Aitken et al. or Yamaguchi et al. However, some such indications were found in Stewart paper. When Stewart recorded the spectrum of thiourea in potassium bromide complex was formed and some of the bonds get split. Similar observation has also bend found in this work.

1418	1420
	1390
736	743
	733
635	643
	633

Stewarts analysis given the NH_2 rocking mode as coincident at 1090 cm^{-1}. The calculation of Yamaguchi et al. showed that they should be distinct and in fact a second band, although much weaker broader was observed at about 1200 cm^{-1}. The band t 1090 $cm^{-1}$was also observed by Aitken et al. but they assigned that band as a contribution of CN_2 symmetric stretch and NH_2 rocking mode. Aitken et al. did not observe any band about 1200 cm^{-1}.
The CS stretching coordinate is distributed principally among three vibrations, the major proportion at 733cm^{-1}, and approximately equal proportions in 1420 and 487 cm^{-1}.
Rao and Venkataraghavan's NCS bands I, II, III and IV for thiourea corresponds to 1470 (predominantly NCN asymmetric stretch with some NH_2 deformation), 1430 (predominantly NCN symmetric stretch with some NH_2 rock, CS stretch and NCN deformation), 1100cm^{-1} (predominantly NH_2 rocking with some NCN symmetric stretch) and 720cm^{-1} (predominantly CS stretch with some CN_2 symmetric stretch, CN_2 deformation and NH_2 rock) which was assigned by Suzuki also as $\upsilon C{=}S + \pi NH_2$.
Jensen and Nielsen's corresponds a band at 630 cm^{-1} which they ascribe at least in part to CS stretch, has confidently assigned to an out of plane vibration by most of other workers, an assignment supported by Raman and polarization studies. Thus thioamine of thioura fall of following places.

Thioamide Band	Frequency in cm^{-1}
I	1470
II	1430
III	1100
IV	720

It has been reported that for monodentate sulphur ligands (such as thiocynate ion), band IV (C---S) has been used as diagnostic or metal –ligand bonding. Metal sulphur bonding results in red shift or about 50 cm^{-1} in the thioamide band IV and metal nitrogen bonding generally results in either no shift of the order of 30-40 cm^{-1} in this band. A red shift of the order of about 100 cm^{-1} in the thioamide band IV is an indication of a bridging system.

Thiourea is chemically interesting ligands in that it has several different possible modes of bonding to a metal ion. It may coordinate through the non-bonding to metal ion. It may coordinate through the non-bonding electron pairs of the nitrogen atom. This mode, however, has not been conclusively established by single crystal studies, but only infrared from the infrared spectroscopy. Alternatively thiourea may bind to metal ion via sulphur atom.

For this mode, there are two means by which the sulphur atom donates electrons.

(a) Electrons from the non-bonding sp^2 lobes or
(b) Electrons from a delocalised π-molecular orbital.

Observed and calculated vibrational frequencies of Thiosemicarbazide and their assignments :

The assignments of infrared spectral bands of thiosemicarbazide are based on earliar studies. The bands of the regions 3000 – 3300 cm^{-1} the spectra of the ligand are assigned to υNH and υC=N vibration respectively. It is found ligand thiosemicarbazide displays three four distinct bands in 3/μ region. These bands are located at 3360 (m), 3245 (s) and 3170 (s) cm^{-1} attributed to υNH_2 , υNH and υNH_2 vibrations of thiosemicarbazone part has been found that ligand displays a strong band at 1645 cm^{-1} attributable to δNH_2. The $(NH_2)_2$ stretch of the ligand located at 3170 cm^{-1} is not affected but the NH stretch of the ligand which is assigned to a band near 3360 cm^{-1} almost disappears in neutral inner chelate.
The ligand contain potential thioamide group and it is well known that compounds containing thioamide group (HNC=S) displays four characterstics thioamide bands located in the region 1530-1480, 1400-1310, 1280-1000 and 1000-720 cm^{-1} originating from different nodes of vibration of (C=N), (C=S) and NH group. The band located at 1540-1480 cm^{-1} has major contribution of δ(NH) vibration. The second thioamide band is mainly due to minor contribution of (C=N) stretches. The last two bands are due to (C-N) stretch and (C=S) stretch. The third band has major contribution of υ(C-N) and minor contribution from υ(C=S) while the last one is due to major contribution of υ(C=S) vibration and 620-670 cm^{-1} medium band is due to major contribution of υ(C-S) vibrations.

Interpretation of Infrared spectrum of $[Cr(TU)_2(NH_3)Cl_3].3H_2O$

A comparision of the spectra of the thioura and the complex brings the following facts to light:

1]. There are strong broad bands at 3365 and 3160cm^{-1} which have been assigned $\upsilon_a NH_2$ and $\upsilon_s NH_2$ modes of thiourea and it has 3rd medium band at 3260 cm^{-1} which have been assigned to υNH mode of vibration of thiourea. However, there is big hump of absorption in the range of 3700-2400 cm^{-1} region in the absorption in the range of 3700-2400 cm^{-1} region in the spectrum of the complex. This indicates the presence of intense hydrogen bonding between H atoms of the lattice water molecules, thiourea and NH_3 with the N atoms of thiourea, NH_3 coordinated Cl atoms and O atom of the lattice water molecule.

2]. There is a weak broad band at 2020 cm^{-1} in the spectrum of thiourea but this type of band is present at 2080 cm^{-1} in the spectrum of the complex.

3]. There is a weak broad band at 2660-2680 cm^{-1} region of the spectrum of the ligand which may be assigned to υSH mode of vibration of the thiol form of thiourea which indicates coordination of thiourea molecules to Cr (III) on through sulphur atom.

4]. There is a strong broad band at 1600 cm^{-1} in the spectrums of the ligand assigned to δNH_2 mode of vibration. This band blue shifts to 1630 cm^{-1} as broad and strong band.

5]. The 1470 cm^{-1} and 1430cm^{-1} strong bands of the liquid have major contribution from υC=S which shifts to 1400cm^{-1} on complexation conforming coordination of the thiourea molecules to Cr(III) ion in this complex through S atom.
6]. There is a weak band at 1390cm^{-1} in the spectrum of the thiourea ligand which is assigned to δNH_2 mode of vibration. This shift to 1400 cm^{-1} on complexation indication coordination to the thiourea molecules to Cr (III) ion in this complex.

7]. There is a medium band at 1100cm^{-1} in the spectrum of the thiourea ligand which have contribution from δNH_2 +υC=S. The intensity of this band considerably decreases on coordination and a new broad weak band is observed at 1010cm^{-1}.
8]. There is a medium band at 720cm^{-1} in the spectrum of the thiourea ligand assigned to $\upsilon C{=}S + \delta NH_2$. This band shifts and one band shifts to 750 cm^{-1} and the other shifts to 700cm^{-1}.

9]. There is a doublet of bands at 620 and 630 cm^{-1} in the spectrum of thiourea molecule which have also contribution from υNH_2 + υC=S. The shifting of this band to 610 cm^{-1} also supports coordination of thiourea molecule to Cr (III) ion through its S atom.

10]. A very broad and strong band centred at 470cm^{-1} is due to out of plane modes of vibration of NH_2 group. This band blue shift to 525 cm^{-1} which excludes the possibility of thiourea molecules coordinating through its thiocarbonyl S atom.

11]. A strong and medium multiplet type of band at 305 cm^{-1} and a shoulder at 320cm^{-1} are present in the infrared spectrum of this complex but there is no such band in the infrared spectrum of thiourea. Hence these bands may be assigned υCr-Cl (trans) + υCr-Cl (Cis) mode of vibrations in the complex. This conclusively proves the presence of coordinated cis and trans Cl atoms in the complex.

12]. There is a new weak band at 220cm^{-1} in the spectrum of the complex which is not present in the spectrum of thiourea. Hence, it may be assigned to υCr=S mode of vibration, which also supports coordination of thiourea molecules to Cr (III) ion through its thiocarbonyl sulphur atom.
13]. A new weak band at 460 cm^{-1} in the spectrum of the complex may assigned to υCr-NH_3 mode of vibration. This indicates the presence of coordinated NH_3 molecule in this complex.

Hence the following octahedral structures may be suggested for this complex (Figure 1).

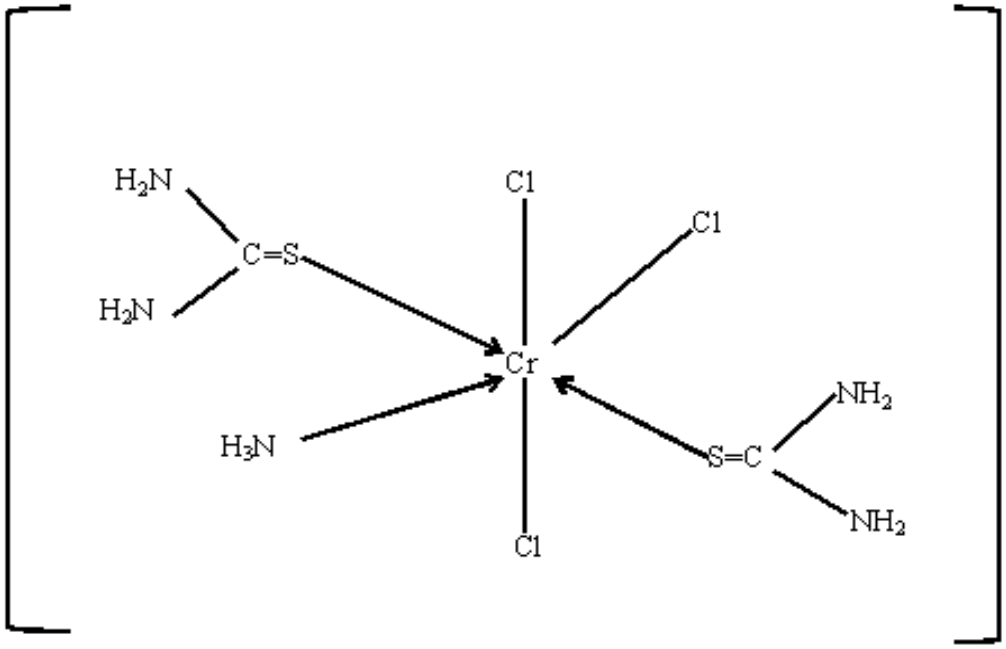

Fig. 1 : Structure of **[Cr (TU) $_2$ (NH_3) Cl $_3$].3H_2O**

Interpretation of ^{1}H NMR Spectra of Thiourea (TU) and [Cr (TU) $_2$ (NH_3) Cl $_3$].3H_2O

It has only one very strong signal centred at δ = 7.4 ppm corresponding to its four equivalent protons (H_2NCONH_2) the two amide groups. However the NMR spectrum of the complex [Cr (TU) $_2$ (NH_3) Cl_3].3H_2O in D_6 – Dimethyl sulphoxide solvent has only one broad signal at δ = 0-85 ppm which indicates equivalence of all the protons. Such as large shifting of the proton signal to a very high field indicates that there is intense hydrogen bonding in the crystal lattice so that all the H atoms have become equivalent in the complex lattice of [Cr (TU) $_2$ (NH_3) Cl_3].3H_2O. This agrees to the conclusion drawn from the infrared spectrum of the complex.

Interpretation of Infrared spectrum of [Cr (TSC) $_2$ Cl $_2$(OH)(H_2O)]

1]. There is a very broad and strong multiplet unresolved band in the range of 3640 to 2300 cm^{-1} centred at 3120 cm^{-1}. This may be due to (υNH_2 + υNH_2+ υOH))-mode of vibrations. The large broadness of this band indicates intense hydrogen bonding in this complex molecule.

2]. There is a medium new band at 2060cm^{-1} in the spectrum of the complex is not present in the spectrum of the ligand. This indicates the presence of ›C=N skeleton in the complex which is possible only when thiol form of the ligand has part in coordination.

3]. There are a very strong bands at 1645 cm^{-1} and 1620 cm^{-1} in the spectrum of the ligand. These band have been assigned to δNH_2 modes of bending vibration. These bands shift to 1625cm^{-1} in the complex. Red shifting of the 1645 cm^{-1} band indicates absence of coordination of the thiosemicarbazide ligand to the Cr (III) ion through nitrogen atom of the NH_2 – group.

4].This is a strong band at 1530 cm^{-1} in the spectrum of the ligand which is assigned to βNH_2 + υNH_2. This band shifts to 1540 cm^{-1} on complexation. This also indicates absence of coordination of the ligand to the Cr(III) ion through nitrogen atom of the N-H group.

5]. The 1400 cm^{-1} weak band and 1310 cm^{-1} medium band of the ligand one thioamide band I and thioamide band II which are mixed band having contributions from υC=S and υCN modes. 1400 cm^{-1} band has blue shifted to 1430 cm^{-1} and 1310 cm^{-1} band blue shifted to 1400 cm^{-1} . This may be due to coordination of the ligand to the metal ion through suphur atom.

6]. There is a strong band at 1280cm^{-1} in the spectrum of the ligand which has been assigned to υC=S. This band red shift to 1220 which further supports coordination of the ligand to the Cr(III) ion through S atom.

7]. The 1160 cm^{-1} (m) and 1000 cm^{-1} bands of the ligand also shift 1120 cm^{-1} and 1020cm^{-1} with considerable reduction in their intensities which also supports coordination through S atom.

8]. A medium band at 720 cm^{-1} in the spectrum of the ligand has main contribution from υC-S mode of vibration. Its red shifted to 690 cm^{-1} confirms coordination of the ligand to the metal ion through S atom.

9] .The presence of coordination through S atom is also supported by the presence of the multiplet υCr-S band at 230 cm^{-1}.

10]. A broad unresolved multiplet medium band at 320cm^{-1} confirms the presence of coordinated cis- chlorine atoms in this complex.

11]. The presence of very broad and very weak band at 500 cm^{-1} in the spectrum of the complex proves the presence of lattice water.

The presence of a new weak band at 410 cm^{-1} indicates the presence of υOH + υH_2O coordinated group.
Thus the following distorted octahedral structure say be assigned tentatively to this complex

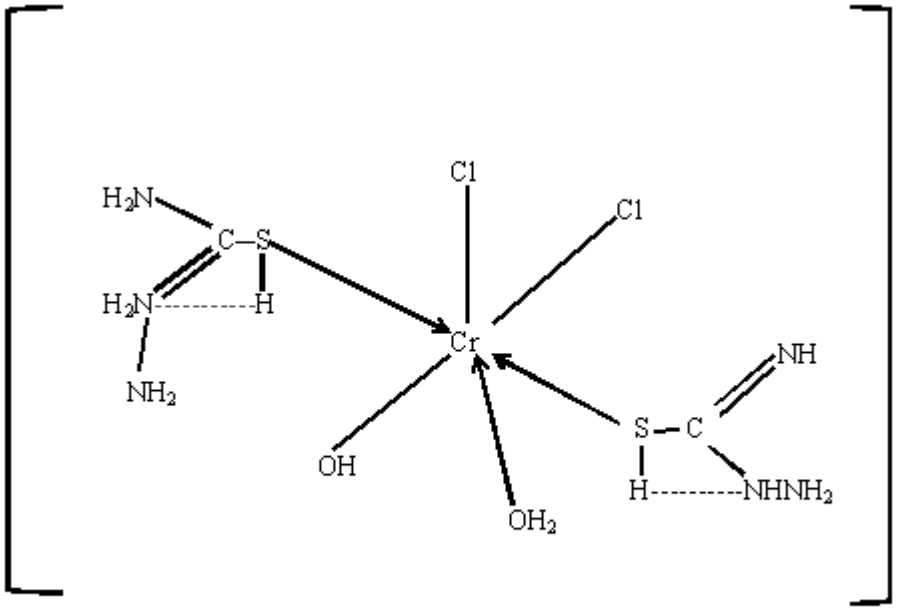

Fig. : Structure of **[Cr (TSC)$_2$ Cl$_2$(OH)(H$_2$O)]**

Interpretation of Electronic spectra of [Cr (TSC)$_2$ Cl$_2$(OH)(H$_2$O)]

The electronic spectrum of thiosemicarbazide contains three absorption bands centred at 205 nm, 240 nm, and 320 nm which may assigned to $\pi \rightarrow \pi^*$ transition, $n \rightarrow \pi^*$ (I) and $n \rightarrow \pi^*$ (II). On complexation, the π-π^* transition remains at 205 nm, which indicates absence of coordination through the double bond of the ligand. The absence of , $n \rightarrow \pi^*$ (I) and $n \rightarrow \pi^*$ (II) transition indicate the coordination of the ligand through S atom of the thiocarbonyl group of the semicarbazide ligand.

Results and Discussion

This paper deals with the results and discussion of the various experimental data obtained on the investigations of the complexes prepared in this work on the basis of their physio – chemical data, their molecular formula and structures have been assigned and by means of the far IR spectra of the complexes, the nature of the metal- ligand bonding have been established.

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