

Published by Society for Advancement of Sciences®

J. Biol. Chem. Research. Vol. 34, No. 2: 983-992, 2017 (An International Peer Reviewed / Refereed Journal of Life Sciences and Chemistry) Ms 34/02/0809/2017 All rights reserved ISSN 2319-3077 (Online/Electronic) ISSN 0970-4973 (Print)



**RESEARCH PAPER** 

Dr. Aradhna Verma http://<u>www.sasjournals.com</u> http://<u>www.jbcr.co.in</u> jbiolchemres@gmail.com

Received: 10/12/2017 Revised: 29/12/2017 Accepted: 30/12/2017

# Chelating Properties of Thiocarboxy-Hydrazide Based NNNN–Tetradentate Ligands: Cr(III), Mn(III), Fe(III) and Co(III) Complexes with Benzoyl Acetone Thiocarboxyhydrazide

# Aradhana Verma

ASPG College, Sikandrabad, Distt-Bulandshahar, UP, India

# ABSTRACT

The ligands which are capable of undergoing thiol-thione tautomerism can act as mono as well as polydentate ligands. A number of thiosemicarbazones containing nitrogen heterocycles<sup>(1,2)</sup> are known for their carcinostatic activity which by loss of protons from their tautomeric thiol forms can act as potential tridentate ligands sequestering metal ions involved in carcinogenesis. Trivalent heavy metal ion complexes with such ligands exhibit much interesting electronic spectra. The steric and electronic consequences of unsaturation in the ring system are very important in the design of macrocyclic chelating agents. In this paper we prepared metal chelates of trivalent chromium, manganese, iron and cobalt with macrocyclic derived from thiocarboxyhydrazide and benzoylacetone. The chelates have been characterized on the basis of chemical analysis, magnetic, electronic, infrared and conductance measurement studies. Keywords: Macrocyclic, IR, Magnetic and Electronic Spectra.

## INTRODUCTION

A number of thiosemicarbazones containing nitrogen heterocycles (Webb et al., 1986, Lee et al., 1986) are known for their carcinostatic activity which by loss of protons from their tautomeric thiol forms can act as potential tridentate ligands sequestering metal ions involved in carcinogenesis. Earlier studies on the metal complexes of 2–furaldehyde thiosemicarbazone were largely solution studies and were concerned only with the possible cases of these complexes in spectrophotometric and gravimetric estimations (Webb et al., 198). Complexes of transitional metal ions with 2–furaldehyde thiosemicarbazone (FTSC) have been prepared. All the complexes studied are found to be non–electrolytes in methanol. The complexes of Co(II) and Cu(II) exhibit paramagnetism, whereas those of other metal ions are diamagnetic. The infrared spectra reveal that the ligand acts as monovalent bidentate, making use of sulphur in thiol form and one nitrogen atom for coordination to the central metal ion. Electronic spectra of Co(II), Ni(II) and Cu(II) complexes suggest a regular square planar geometry. Electron paramagnetic resonance spectrum confirms the square planar configuration for Cu(II) complex.

J. Biol. Chem. Research

The thermal decomposition behaviour of the complexes has been studied by TG and DTA techniques. Transition metal dithio phosphinato complexes were studied (Mandal et al., 1998). A difference was observed in the 10Dq values of dithiophosphinato and the corresponding dithiophosphato complexes in which the phosphorous atom of the ligand was bonded to carbon and oxygen respectively. A comparative study of the adduct forming behavior (Politi and Chaimaich, 1986) of Nis<sub>4</sub>–Chromophores of bis (dimethyldithiophosphato) nickel(II), Ni(dtp)<sub>2</sub> and bis (3,4–dimethyl dithiophosphinato) nickel(II), Ni(3,4–Me<sub>2</sub>dtpi)<sub>2</sub> with various nitrogen donors are known. Steric factors and the basicities of the donor molecules appear to control the formation of the adducts; depending upon the structure of the donor molecules the NiS<sub>4</sub> chromophore forms both 1:1 pentacoordinate and 1:2 hexacoordinate high–spin addition compounds with monodentate donors whereas with aliphatic bidentate donors 1:3 complexes with NiN<sub>6</sub> chromophores are obtained.

The steric and electronic consequences of unsaturation in the ring system are very important in the design of macrocyclic chelating agents. Most of the macrocycles prepared are highly conjugated and yield complexes that exhibit extensive electron delocalisation. This delocalisation often contributes in a major way to the unusual properties associated with these compounds. In addition, the extensive conjugation usually dictates an essentially planar ligand system. If the macrocycle is aromatic, the resulting complexes may also show additional stability. These ligands which are capable of undergoing thiol–thione(-N=C-SH) $\Rightarrow$ (NH-C=S) tautomerism can act as mono as well as polydentate ligands (Preti and Tosi, 1974, 1976 a,b,c). Trivalent manganese complexes are generally high spin and are expected to be susceptible to Jahn–Teller distortions causing them to deviate from idealized  $O_h$  symmetry either by a trigonal distortion or by a tetragonal elongation or compression and they also exhibit interesting electronic spectra (Ran and Teotia, 1980).

The spectroscopic and magnetic properties of several Iron(III) model systems have been investigated and compared with those of certain iron containing proteins. Iron(III) has been found to form both octahedral (Fatta and Lintvedt, 1972) and tetrahedral complexes depending upon the nature of the ligand fields. Cobalt(III) invariably forms octahedral complexes and recently quite a large number of such complexes have been reported (Rana, 1975, Teotia, 1980).

The +3 oxidation state of manganese has been well characterized by the preparation of a number of anionic, cationic and neutral complexes and a good number of mixed chelate and mixed ligand complexes (Isobe K & Kawaguchi, 1975, Stults et al., 1979, Stults et al., 1975). The complexes were generally obtained starting from the manganese(III) compounds.

In the present chapter metal chelates of trivalent: chromium manganese, iron and cobalt with macrocyclic derived from thiocarboxyhydrazide and benzoylaceton are described. The chelates have been characterized on the basis of chemical analysis, magnetic, electronic, infrared and conductance measurement studies.

## MATERIALS AND METHODS

All the chemicals used were either chemically pure or of AR–grade. The solvents were dried by standard procedures and deaerated just prior to use. Thiocarbohydrazide and benzoyl acetone were procured from B.D.H. England (U.K.). Electrical conductivity determinations were made using Siemen's conductivity bridge with Pt–black electrodes having cell constant of 0.66.

# Synthesis and Isolation of Complexes

# Chromium(III) Complexes

2.16 g (0.02 mole) thiocarbohydrazide dissolved in 60 ml dry methanol was mixed with methanolic solution of 20 ml (0.02 mole – 3.24 gm) of benzoylacetone and stirred for one hour. 0.01 mole of metal salt dissolved in 50 ml. methanol was added followed by the addition of a few drops of methanolic Potassium hydroxide.

The mixture was refluxed for 6–8 hours on steam bath. It was concentrated to half its volume and kept for three to four days. The coloured solid crystalline mass was separated, filtered, dried and collected in vacuum desiccator. The nitrato complexes were prepared using metal nitrates. Bromo and thiocyanate complexes were prepared by metathesis process by adding potassium bromide and ammonium thiocyanate into metal chloride solution and filtering off, potassium and ammonium chloride precipitates.

# Manganese(III) Complexes

Manganese(III) acetate was prepared by dissolving thiocarbohydrazide (0.02 mole) (2.20 g) in methanol (50 ml) was added to 0.02 mol (3.24 gm) methanolic solution (50 ml) of Benzoyl acetone and refluxed for two hour. 1.0 gm of manganese(III) acetate dissolved in 20 ml of ethanol was added followed by 2–3 drops of glacial acetic acid and refluxed whole contents for 6–8 hours on water bath. After completion of reaction, excess solvent was removed through distillation and concentrated to half of its volume, when dark coloured crystalline mass appeared. It was filtered, washed, dried and collected under vacuum over anhydrous silica gel.

# Iron(III) Complexes

The schiff base was synthesized by the condensation of Benzoyl acetone and Thiocarboxyhydrazide in (2:2) stoichiometric ratios (Srinivas et al., 1991). To this 0.02 mol ferric chloride hexahydrate in ethanol (20 ml) was added. The resultant dark blackish green mixture was refluxed on a water bath for 6–8 hours. The micro crystalline product formed was separated by filtration, washed twice with ethanol and finally with ether and dried. Yield 70–80 %. The complexes were also prepared independently by mixing ferric chloride, benzoylacetone and thiocarboxyhydrazide in (1:2:2) molar ratio in ethanol and refluxing for 6–8 hours and proceed as above.

# Cobalt(III) Complexes

Ethanolic solution of cobalt(II) chloride, benzoylacetone; thiocarboxyhydrazide in 1:2:2 molar ratio were reacted. Ethanolic sodium hydroxide was added to it till faintly alkaline and then air was bubbled through the resulting solution for four to six hours when the colourless solution darkened. Now whole content was refluxed for four to five hours on steam bath. After concentration and cooling compounds were separated out. These were filtered, washed with ethanol, ether and dried in vacuum.

# **RESULTS AND DISCUSSION**

Elemental analysis carried out by standard methods was consistent with the formulations of the compounds. The molar conductances for  $10^{-3}$  M solutions of complexes in nitrobenzene medium were measured reveal their uni–univalent nature. The molecular weight measurements (Rast method using camphor) indicate that compounds are monomeric. Chemical analysis indicate that the metal chelates derived from thiocarboxyhydrazide and benzoylacetone may be represented as  $[M(C_{22}H_{24}N_8S_2)X_2]X$  where M=Cr(III), Mn(III), Fe(III) and Co(III) and X= Cl, Br, NO<sub>3</sub>, NCS for Cr(III) and Fe(III) while OAc for Mn(III) and (OH) for Co(III). Presence of anion outside the coordination sphere was confirmed by adding silver nitrate solution and heating the complex with copper wire (NO<sub>3</sub><sup>-</sup> anion) (Table 1).

# **Infrared Spectral Studies**

In the IR–spectra of complexes a broad band occuring in the range  $3600-3100 \text{ cm}^{-1}$  with a peak at about  $3250 \text{ cm}^{-1}$  may be assigned to bands due to  $\upsilon(NH)$ , which appears in the range (Dongli et al., 1994, Srivastava et al., 1996)  $3400-3200 \text{ cm}^{-1}$  for the free ligand. The lowering of the  $\upsilon(NH)$  band by ~40 cm<sup>-1</sup> indicates coordination through nitrogen (Gupta et al., 1995, Yong–Xiang et al., 1994) which is further supported by the shift of  $\delta(NH)$  from 1650 cm<sup>-1</sup> to 1610–1630 cm<sup>-1</sup>. The absence of (C=O) stretching vibrations and those of  $-NH_2$  group indicate that  $-NH_2$  groups of thiocarboxyhydrazide have condensed with carbonyl groups of benzoylacetone. However–NH group of thiocarboxyhydrazide coordinate to the metal atom (Sharma et al., 1989).

The infrared spectra of the ligand show a strong band at 1630 cm<sup>-1</sup> which is assigned to the u(C=N) vibration. The frequency of this band is lowered by ~15–20 cm<sup>-1</sup> in the complexes. The lowering in the frequency of this band is an indication of the coordination of unsaturated nitrogen of the azomethine linkage (Gang and Yuan,<sup>1</sup>1994). The absence of any (SH) band around 2600–2530 cm<sup>-1</sup> in the IR– spectra of free ligand excludes the possibility of the existence of its thiol form at least in the solid state. The role of the thiocarbamyl group (–NH–C=S) in complex formation is generally inferred from the consideration of the cannonical forms. These forms are more accessible due to higher polarisibility of the sulphur atom.

This indicates if metal attachment takes place through sulphur atom that would leads to a decrease in the thiocarbonyl stretching force and an increase of (C–N) frequency (Preti and Tosi, 1976, Gajendragad and Agarwal, 1975). In the present case, IR–bands around 1450 cm<sup>-1</sup> in the metal complexes correspond to 1470 cm<sup>-1</sup> band of the free ligand molecule which is assigned to  $v_{as}(N-C-N)$  of the thiocarboxyhydrazide derivative. The observed decrease in frequency in the complexes may be due to the drainage of electron from azomethine nitrogen atom on complex formation and not through thiol form. In addition the bands at 1120 and 895 cm<sup>-1</sup> which are due to v(C = S) and/or v(C = N) do not suffer change. All these bands either do not become weak, shifted towards lower frequency side disappeared or appreciably decreases in the bond order of (C=S) group, showing non involvement of thiocarbonyl group in complex formation (Aravindakshan and Nair, 1981).

The infrared spectra of trivalent metal chelates indicate that  $-NH_2$  groups of thiocarboxyhydrazide have condensed with carbonyl groups of benzoyl acetone moiety forming 16–membered macrocycle which attaches to the metal atom through two azomethine nitrogen atoms and two imine nitrogen atoms forming four, six membered chelate rings.

#### Magnetic and Electronic Spectral Studies

#### Chromium(III) Complexes

The magnetic moments of chromium(III) complexes were found to be in the range of 3.74–3.85 B.M. corresponding to high spin octahedral chromium (III) complexes (Burger, 1973).

In cubic fields only one ligand field parameter Dq is required to describe the spectra whereas in the quadrate field two more ligand field parameters, Ds and Dt are needed because of the added axial fields. The axial ligand field Dt is very similar to Dq in that both are matrix elements of the fourth order harmonic potential (Permareddi, 1969). In the limit of crystal field formalism it can be shown that Dt = 4/7 (Dq<sup>E</sup>–Dq<sup>A</sup>) for an octahedral complex [MX<sub>4</sub>Y<sub>2</sub>].

The electronic spectra of chromium (III) complexes in dimethylformamide solution display number of bands in the region ~16000–17000, ( $\upsilon_1$ ), 20800–21500 ( $\upsilon_2$ ), 25500–26000 ( $\upsilon_3$ ) and 29000–29500 cm<sup>-1</sup> ( $\upsilon_4$ ), respectively and are consistent with tetragonal geometry of these complexes because instead of three, four transitions are observed arising from the lifting of degeneracy of the orbital triplets in tetragonal complexes. The bands may be assigned to

$${}^{4}B_{1g} \rightarrow {}^{4}E_{g} \text{ (a), } {}^{4}B_{1g} \rightarrow {}^{4}B_{2g} \text{, } {}^{4}B_{1g} \rightarrow {}^{4}E_{g} \text{ (b) and } {}^{4}B_{1g} \rightarrow {}^{4}A_{2g} \text{,}$$

respectively in order of increasing energy, assuming the effective symmetry to be  $D_{4h}$ . Thus, first two bands are the splits of first band designated as  ${}^{4}T_{2g}$  and the other two are splits of the band  ${}^{4}T_{1g}$  in quadrate fields and can be represented as (Preti and Tosi, 1976):



J. Biol. Chem. Research

Vol. 34 (2): 983-992 (2017)

The scheme is applicable to systems where an octahedral complex is trans disubstituted by another ligand. The Dt values have been calculated, the splitting of the first quartet not only depends upon the magnitude of Dt but also upon its sign. For a positive Dt the splitting of first quartet and becomes smaller as the Dt value is increased as a consequence of non–crossing of <sup>4</sup>E levels and for a negative value of Dt, <sup>4</sup>A<sub>2</sub> and <sup>4</sup>B<sub>2</sub> levels are so close to each other that only three transitions may be observed instead of four component structure. This applies to the present complexes which are trans-disubstituted derivatives of parent O<sub>h</sub> complexes belonging to D<sub>4h</sub> symmetry.

Thus, using various energy level equations, radial parameters Ds, DQ and DT are calculated. These classical parameters are related to Normalised Spherical Harmonic Hamiltonian parameters. Using transition equations, the values of absolute NSH parameters DQ, DS, Dt are calculated and given in Table 2. The amount of distortion calculated in terms of DT/DQ, indicates that these complexes are moderately distorted.

## **Manganese Complexes**

The magnetic moment value determined using Gouy method of 4.90 B.M. indicate the presence of four unpaired electrons corresponding to high–spin manganese(III) state with  ${}^{5}E_{g}$ –ground term.

The electronic spectra of the complex show three bands at ~13500, ~22900 and ~25000 cm<sup>1</sup>. Only one spin–allowed transition  ${}^{5}E_{g} \rightarrow {}^{5}T_{2g}$  is expected for weak field octahedral manganese(III) complexes. The presence of three bands in these complexes indicates lowering of the O<sub>h</sub> symmetry due to Jahn–Teller distortion. The complexes are expected to be tetragonally distorted with D<sub>4h</sub> symmetry and the bands can be assigned to the transitions,  ${}^{5}B_{1g} \rightarrow {}^{5}A_{1g}$  (~13500 cm<sup>-1</sup>),  ${}^{5}B_{1g} \rightarrow {}^{5}B_{2g}$ (~22900 cm<sup>-1</sup>) and  ${}^{5}B_{1g} \rightarrow {}^{5}E_{g}$  (~25000 cm<sup>-1</sup>) as suggested by Davis et al. (1968) and Lever (1968). The lowest band of all the complexes was found to be broad which confirms the Jahn–Teller distortion experienced by these complexes. The higher energy band ~35600 cm<sup>-1</sup> in all the complexes may be assigned to  $\pi \rightarrow \pi^*$  charge transfer due to azomethine linkage (Boucher, 1974). The spectral analysis may be made by using various energy levels equations and the values of DS, Dt and Dq are calculated. These values are used to calculate the absolute NSH–ligand field parameters, which gives distortion (DT/DQ).

## **Iron Complexes**

The magnetic moments for iron complexes lie in 5.80–5.86 BM range at room temperature. These values suggest that these complexes are high spin six–coordinate. In high spin octahedrally coordinated iron(III) systems of electronic composition  $3d^5$ , the ground state is  ${}^6A_1$  and for this ground term no reduction in the magnetic moment is observed below spin–only value by spin–orbit coupling.

The electronic spectra of iron (III) complexes display number of bands in region ~17000–18000, ~19600 and 24500–24850 cm<sup>-1</sup>, and another broad band in the higher region ~33500 cm<sup>-1</sup>, respectively. These bands may be assigned to

$$^{6}\mathsf{A}_{1g} \rightarrow {}^{4}\mathsf{T}_{1g} \, ({}^{4}\mathsf{E}), \, {}^{6}\mathsf{A}_{1g} \rightarrow {}^{4}\mathsf{T}_{1g} \, ({}^{4}\mathsf{A}_{2}), \, {}^{6}\mathsf{A}_{1g} \rightarrow {}^{4}\mathsf{T}_{2g}$$

and charge transfer, respectively in order of increasing energy. The bands observed at ~17530 and ~24570 cm<sup>-1</sup> may probably be due to the splitting of  ${}^{4}T_{1g}$  state and thus it appears that these complexes are distorted octahedral conforming to D<sub>4h</sub> symmetry.

The splitting of other bands could not be observed, perhaps because of the commencement of charge-transfer region immediately after it. The assignments given for these spectral bands are comparable with those reported earlier. The values of 10Dq could not be obtained directly since correct energy level equations are not known.

## Cobalt(III) Complexes

The cobalt(III) complex of the macrocycles derived from thiocarbohydrazide and Benzoyl acetone is diamagnetic in nature.

The electronic spectra of the complex exhibit three bands in 15000–30000 cm<sup>-1</sup> region and are typical of pseudo–octahedral complexes of trivalent cobalt. The present complex show various bands at ~16250, 21750, 25500 and 35500 cm<sup>-1</sup>, respectively and may be assigned to  ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ , respectively in order of increasing energy. The first two bands are the split of one spin–allowed band, because octahedral trivalent cobalt complexes display only two bands in visible and near infrared region and theoretical studies have shown that the assignments of these bands are  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ , in order of the increasing energy. Since the complex under study exhibit three bands in the spectra the lower two bands are the split of one band into two components thus show a deviation from  $O_h$  symmetry perhaps due to inequality of ligands and the assignments have been made assuming the effective symmetry to be  $D_{4h}$ .

The values of ligand field parmeters Dq, Ds and Dt have been calculated and from these values of NSH ligand field parameters DQ, DS and DT and the amount of distortion is calculated in forms of DT/DQ. The values of DT/DQ indicate moderate distortion in the complex. (Table-2)

# Far Infrared Spectra

The far infrared spectra of the complexes of trivalent chromium, manganese, iron and cobalt in the region  $650-200 \text{ cm}^{-1}$  are given in figures. The assignments of bands are made by comparing the spectra of these complexes with those reported for nitrogen containing ligands (Laxma Reddy et al., 1986). The bands observed ~480–500, 340–370, ~400–425 and 530–560 cm<sup>-1</sup> may be assigned to  $\nu(Cr-N)$ ,  $\nu(Mn-N)$ ,  $\nu(Fe-N)$  and  $\nu(Co-N)$  vibrations of azomethine ring, respectively and are consistent with six–coordinate octahedral geometry around the metal atom (Anita Rai et al., 2000). The appearance of bands ~525 cm<sup>-1</sup> in the spectra of cobalt complexes, assignable to  $\nu(Co-O)$  indicate that OH group is coordinated to the metal atom in these complexes (Bullock, 1967).

# **u(M–X);** X = Cl/Br

The spectra of halocomplexes of Cr(III) and Fe(III) show various bands ~330,  $\upsilon$ (Cr–Cl), 240  $\upsilon$ (Cr–Br), 325  $\upsilon$ (Fe–Cl) and 210 cm<sup>-1</sup>  $\upsilon$ (Fe–Br), respectively and substantiate the coordination of anions in these complexes. The vibrations are well within the range reported for six–coordinate octahedral complexes.

## $NO_3^{-}$ Group

The appearance of a strong band around 1310 cm<sup>-1</sup> and the absence of the bands characteristic of ionic nitrate (1390, 830 cm<sup>-1</sup>) indicate the presence of coordinated nitrate only. The combination bands ( $v_2 + v_3$ ) and ( $v_2 + v_5$ ) appear in the ranges 1790–1760 cm<sup>-1</sup> and 1720–1710 cm<sup>-1</sup> whereas the combination bands ( $v_2 + v_1$ ) and ( $v_2 + v_4$ ) are observed in the ranges 2530–2500 cm<sup>-1</sup> and 2300–2290 cm<sup>-1</sup> respectively. The positions and the magnitudes of the separation of these combination bands are in fair agreement with the values observed for other metal ions in which chelating monodentate nature of the nitrate group is shown on the basis of X–ray diffraction studies.

## υ**(OH)**

Broad bands in the cobalt (III) complex around 3400 and 1020 cm<sup>-1</sup> assignable to  $\nu$ (OH) and  $\nu$ (C–OH) respectively are clearly shifted to lower values and thereby indicate the presence of coordinate alcohol. Broadness of the bands can be due to hydrogen bonding.

## (NCS<sup>-</sup>) Group

IR spectrum displays a broad band (Hussain Reddy and Sambasiva Reddy, 2001) at 2360 cm<sup>-1</sup> attributable to uC=N of the S–bonded thiocyanate group (Hussain Reddy et al., 2000, Hussain Reddy et al., 1999). The C–S stretching frequency of the thiocyanate group occurs at 702 cm<sup>-1</sup> supporting the presence of an S–bonded thiocyanate group.

## υ(CH₃COO<sup>−</sup>) Group

In acetato complex a weak band is obtained at about 1580 cm<sup>-1</sup>. This may be due to asymmetric (COO) stretching of the acetate group. The symmetric (COO) stretching band of the acetate group has been obscured due to macrocyclic ligand vibrations (Habtemariam et al., 2001, Anderson et al., Vogler and Kunkely, 2002).

Thus taking into account, the analytical data and physical properties of the complexes six coordinated distorted octahedral structure in which  $N_4$  moiety forms the basal plane and the anion group coordinated at axial position may be suggested for all these complexes.





Table 1. Analytical data of Trivalent Metal ion Complexes of Cr(III), Fe(III), Mn(III) and Co(III) with Benzoyl Acetone Thiocarboxyhydrazone.

		% Chemical Analysis									
Complex	Colour	Found (Calculated)									
		С	Н	Ν	S	Х	Μ				
	Green	42.13	3.70	17.16	9.88	16.94	8.03				
		(42.40)	(3.85)	(17.99)	(10.28)	(17.10)	(8.35)				
	Light	34.80	3.08	13.85	8.01	30.84	6.23				
	Green	(34.92)	(3.17)	(14.81)	(8.46)	(31.74)	(6.87)				
	Dark	37.12	3.30	20.95	8.89		7.10				
$[CI(C_{22}\Pi_{24}IN_8S_2)(INO_3)_2]INO_3$	Green	(37.60)	(3.41)	(21.93)	(9.11)		(7.40)				
	Green	42.88	3.33	21.74	22.84		6.96				
$[Cr(C_{22}H_{24}N_8S_2)(NCS)_2](NCS)$		(43.47)	(3.47)	(22.31)	(23.18)		(7.53)				
	Reddish	42.01	3.36	16.84	9.87	16.86	8.73				
$[Fe(C_{22}H_{24}N_8S_2)CI_2]CI_1$		(42.14)	(3.83)	(17.88)	(10.21)	(17.00)	(8.91)				
	Brownish	33.70	3.03	13.95	7.96	30.84	7.20				
	Green	(34.74)	(3.15)	(14.73)	(8.42)	(31.58)	(7.35)				
[Fe(C <sub>22</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]NO <sub>3</sub>	Reddish	36.33	3.25	20.78	9.0		7.60				
	Brown	(37.40)	(3.40)	(21.81)	(9.06)		(7.91)				
[Fe(C <sub>22</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )(NCS) <sub>2</sub> ](NCS)	Green	42.97	3.36	21.88	22.43		7.94				
		(43.23)	(3.45)	(22.19)	(23.05)		(8.04)				
[Mn(C <sub>22</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )(CH <sub>3</sub> COO) <sub>2</sub> ](CH <sub>3</sub> COO)	Dark	47.98	4.66	15.94	8.99		7.35				
	Green	(48.28)	(4.74)	(16.09)	(9.19)		(7.89)				
	Dark Red	45.60	4.54	18.80	10.88		9.56				
	Dark Ked	(45.99)	(4.70)	(19.51)	(11.15)		(10.26)				

X = Cl, Br etc.

Table 2. Magnetic and Spectral Data of Trivalent Metal Ion Complexes of Benzoyl Acetone
Thiocarboxyhydrazone.

Complex	Spectral Bands Cm <sup>-1</sup>				Dq	Dt	DS	DT	DQ	DT DQ	μ <sub>eff</sub> (B.M.)
$[Cr(C_{22}H_{24}N_8S_2)Cl_2]Cl$	16510	20920	25830	29340	2092	482	4878	6580	49713	0.132	3.76
$[Cr(C_{22}H_{24}N_8S_2)Br_2]Br$	16960	21520	25930	29165	2152	517	4560	7133	50872	0.1402	3.68
$[Cr(C_{22}H_{24}N_8S_2)(NO_3)_2]NO_3$	16815	21340	25520	29550	2134	510	5415	6976	50415	0.1383	3.82

[Cr(C <sub>22</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )(NCS) <sub>2</sub> ](NCS)	16520	20870	26660	29420	2087	485	5083	9865	49635	0.198	3.80
$[Fe(C_{22}H_{24}N_8S_2)Cl_2]Cl$	17530	17715	19434	24570							5.80
$[Fe(C_{22}H_{24}N_8S_2)Br_2]Br$	17160	17760	19040	24810							5.86
[Fe(C <sub>22</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]NO <sub>3</sub>	17620	17825	19560	24660							5.84
[Fe(C <sub>22</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )(NCS) <sub>2</sub> ](NCS)	17320	17980	19220	24554							5.82
[Mn(C <sub>22</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )(CH <sub>3</sub> COO) <sub>2</sub> ] (CH <sub>3</sub> COO)	13630	17615	20434	35000	1761	450	4041	6283	41164	0.15	4.92
[Co(C <sub>22</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )(OH) <sub>2</sub> ](OH)	16260	21740	25500	35610	2174	463	4935	7553	43554	0.17	4.83



Fig. 1: I.R. Spectra of Cr(III) complexes.



Fig. 2. I.R.Spectra of Fe(III) complexes.



Fig. 3: I.R. Spectra of Mn(111) & Co(111) complexes.

#### ACKNOWLEDGEMENTS

I would like to thank to Prof. S.K. Agrawal for his valuabale and consistent support throughout to carry out this work. I am also grateful to my colleagues and seniors for their encouragement and support to complete my research work.

#### REFERENCES

- Webb, S.P., Philips, L.A., Yeh, S.W., Tolbert, L.M. and Clark, J.H. (1986). Picosecond Kinetics of the Excited-State, Proton-Transfer Reaction of 1-Naphthol in Water; *J Phys Chem*, 90, 5154-5164.
- Lee, J.G., Robinson, G.W., Webb, S.P., Philips, L.A. and Clark, J.H. (1986). Hydration dynamics of protons from photon initiated acids, *J Am Chem Soc*, 108, 6538-6542.
- Webb, S.P., Yeh, S.W., Philips, L.A., Tolbert, M.A. and Clark, J.H. (1998). How does excited-state antiaromaticity affect the acidity strengths of photoacids? *J Am Chem Soc*, 106, 7286.

- Mandal, D., Pal, S.K. and Bhatacharyya, K. (1998). Excited-State Proton Transfer of 1-Naphthol in Micelles, J Phys Chem A, 102, 9710-9714.
- Politi, M.J. and Chaimaich, H. (1986). Water activity in reversed sodium bis(2-ethylhexyl) sulfosuccinate micelles, J Phys Chem, 90, 282-287.
- **Preti, C. and Tosi, G. (1976).** Coordination compounds of manganese(II) with Tetrahydro-1,4-thiazin-3-one and Thiazolidine-2-thione, *Aust. J. Chem*, 29, 543.
- Preti, C. and Tosi, G. (1976). Tautomeric equilibrium study of thiazolidine-2-thione. Transition metal complexes of the deprotonated ligand, *Can. J. Chem*, 54, 1558-1562.
- Preti, C. and Tosi, G. (1974). Study of the Reactions of Chromium(II1) Halides and Heterocyclic Ligands Containing Group VA and VIA Donor Atoms *Can. J. Chem*, 52, 2845-2850.
- Preti, C. and Tosi, G. (1976). Preparation, magnetic and spectral studies of some transition metal complexes of benzoxazole-2-thione, *J. Inorg. Nucl. Chem*, 38, 1125.
- Ran, V.B. and Teotia, M.P. (1980). Synthesis & Characterisation of Co(II), Ni(II) & Cu(II) Complexes of a Tridentate Macrocyclic Ligand, *Ind. J. Chem*, 19A, 267-268.
- **Fatta, A.M. and Lintvedt, R.L. (1972).** Ligand field spectra of some tris(1,3-diketonato)iron(III) chelates. Electronic repulsion parameters and the nephelauxetic effect, Inorg. Chem. 11, 88-92.
- Rana, V.B., Jain, P.C., Swami, M.P. and Srivastava, A.K. (1975). Thiosemicarbazones as ligands—I. Spectrochemical studies on trivalent metal complexes of 1-phenyl-orthohydroxy-4benzamido thiosemicarbazone," *Journal of Inorganic and Nuclear ChemistryJ. Inorg. Nucl. Chem.*, 37, 1826-1828.
- Teotia, M.P., Gurtu, J.N. and Rana, V.B. (1980). Dimeric 5-and 6-coordinate complexes of tri and tetradentate ligands, *J Inorg. Nucl. Chem.*, 42, 821-31.
- **Isobe, K. and Kawaguchi, S. (1975).** Some Mixed-Ligand Manganese(III) Complexes Produced by the Reactions of Tris(acetylacetonato)manganese(III) with Hydrogen Halides in Organic Solvents, *Bull. Chem. Soc.* Japan, 48 (1), 250-257.
- Stults, B.R., Day, R.O., Marianelli, R.S. and Day, V.W. (1979). Distortions of the coordination polyhedron in high-spin manganese(III) complexes. 2. Crystal structure of thiocyanatobis (acetylacetonato)manganese(III) *Inorg. Chem*, 18, 1847-1852.
- Stults, B.R., Day, R.O., Marianelli, R.S. and Day, V.W. (1975). Distortions of the coordination polyhedron in high-spin manganese(III) complexes. I. Synthesis and characterization of a series of five- and six-coordinate bis(acetylacetonato)manganese(III) complexes. Crystal structure of azidobis(acetylacetonato)manganese(III), *Inorg. Chem*, 14, 722-730.
- Srinivas, B., Arulswamy, N. and Zacharias, P.S. (1991). Catalytic and magnetic properties of a new series of binuclear copper(II) complexesPolyhedron, 10, 731-736.
- **Dongli, C., Handang, J., Hongyun, Zh, Deji, C., Jina, Y. and Jian, L.B. (1994).** Studies on acetylferrocenyl nicotinoyl and isonicotinoyl hydrazones and their coordination compounds with transition metals—IIPolyhedron, 13, 57-62.
- Srivastava, S., Pandey, O.P. and Sengupta, S.K. (1996). Binuclear oxovanadium(IV) complexes of phthalazine hydrazone ligands, *Trans Met Chem.* 21, 262-265.
- Gupta, N., Srivastava, B.K., Rai, R., Pandey, O.P. and Sengupta, S.K. (1995). Bis (Cyclopentadienyl) Titanium/Zirconium(IV) Derivatives with Schiff Bases Derived from 1,4-Dihydrazinophthalazine Synth react inorg met–org, *Chem.*, 25, 1177-1189.
- Yong–Xiang, M., Zhong–Lin, L., Qing–Bao, S. and Xiao–Li, W. (1994). CHELATE COMPLEXES OF FORMYLFERROCENE AND ACETYLFERROCENE SALICYLHYDRAZONE WITH TRANSITION METALS, J Coord Chem, 32, 353-359.
- Sharma, V.K., Pandey, O.P. and Sengupta, S.K. (1989). Synthesis, spectroscopic and thermal studies on ruthenium(III), rhodium(III) and iridium(III) complexes with hydrazones derived from 2,6-diacetylpyridine and different aromatic hydrazides, *Trans Met Chem*, 14, 263-266.

- **Gang, Z. and Yuan, C. (1994).** Synthesis and physicochemical studies on S-methyl-β-N-(ferrocenyl) methylenedithiocarbazate and its rare earth complexes Trans Met Chem, 19, 218-220.
- Preti, C. and Tosi, G. (1976). Preparation, magnetic and spectral studies of some transition metal complexes of benzoxazole-2-thioneNucl, *J Inorg. Chem*; 38, 1125-1129.
- Gajendragad, M.R. and Agarwal, U. (1975). Complexing behaviour of 1,3,4-thiadiazole-2-thiol-5amino—I: Complexes of Fe(II), Co(II), Ru(III), Ru(II), Rh(III), Pd(IV), Ir(III) and Pt(IV) J Inorg. Nucl. Chem. 37, 2429-2434.
- Aravindakshan, K.K. and C.G.R. Nair (1981). Aravindakshan K K and C G R Nair; Ind. J. Chem; 20A (1981) 684. *Ind. J. Chem*; 20A, 684-687.
- Burger, K. (1973). Coordination Chemistry experimental methods. Edited by J M Millar– Butterworths, London, Publisher: Butterworth & Co Publishers Ltd, ISBN-10: 0408702052, ISBN-13: 978-0408702058.
- **Permareddi, J.R. (1969).** Electronic spectra of quadrate chromium(III) complexes *Coord Chem. Rev*; 4, 73.
- **Perumareddi, J. (1969).** Electronic spectra of quadrate chromium(III) complexes, *Coord. Chem. Rev;* 4 73-105.
- Davis, T.S., Fackler, J.P. and Weeks, M.J. (1968). Spectra of manganese(III) complexes. Origin of the low-energy bandInorg *Chem*, 7, 1994-2002.
- Lever, A.B.P. (1968). Inorganic Electronic Spectroscopy (Elsevier Publishing Co., Amsterdam), 290.
- **Boucher, L.J. (1974).** Manganese schiff's base complexes—II: Synthesis and spectroscopy of chlorocomplexes of some derivatives of (salicylaldehydeethylenediimato) manganese(III), *J Inorg. Nucl.*, 36, 531-536.
- Laxma Reddy, K., Lingaiah, P. and Veera Reddy, K. (1986). Ruthenium(II) complexes with 2-methyl-3-substituted (3H)-quinazolin-4-ones, Polyhedron, 5 (10), 1519-1523.
- Anita Rai, Soumitra Kumar Sengupta and Om Prakash Pandey (2000). Lanthanum(III) and praseodymium(III) complexes with bidentate and tetradentate schiff base ligands containing indole ring, 39A, 1198–1201.
- Bullock, J.I. (1967). Infrared spectra of some uranyl nitrate complexes, *J Inorg. Nucl. Chem*, 29, 2257-226.
- Hussain Reddy, K. and Sambasiva Reddy P. (2001). Mixed ligand zinc(II) and cadmium(II) complexes with alkyl xanthates and 2.2'-bipyridyl, 40A, 1118–1120.
- Hussain Reddy, K., Sambasiva Reddy, P. and Ravindra Babu, P. (2000). Nuclease activity of 2substituted heteroaromatic thiosemicarbazone and semicarbazone copper(II) complexesTrans-met Chem 25, 154-160.
- Hussain Reddy, K., Sambasiva Reddy, P. and Ravindra Babu, P. (1999). Synthesis, spectral studies and nuclease activity of mixed ligand copper(II) complexes of heteroaromatic semicarbazones/thiosemicarbazones and pyridine, J. Inorg Biochem, 77, 169.
- Habtemariam, A., Watchman, B., Potter, B.S., Palmer, R., Parsons, S., Parkin, A. and Sadler, P.J. (2001). Control of aminophosphine chelate ring-opening in Pt(ii) and Pd(ii) complexes: potential dual-mode anticancer agents, *J Chem. Soc, Dalton Trans* 8, 1306–1318.
- Anderson, J.C., Cubbon, R.J. and Harling, J.D. Investigation of the importance of nitrogen substituents in a N–P chiral ligand for enantioselective allylic alkylation *Tetrahedron: Asymmetry*. 12: 923-935.
- **Vogler, A. and Kunkely, H. (2002).** Outer-sphere charge transfer in ion pairs with hydridic, carbanionic, sulfidic and peroxidic anions as electron donors <sup>3</sup>/<sub>4</sub> spectroscopy and photochemistry. *Coordination Chemistry Reviews*, 229, 147-152.

Corresponding author:Dr. Aradhana Verma, Assistant Professor, ASPG College, Sikandrabad,Distt-Bulandshahar, UP, IndiaEmail: <a href="mailto:aradhanaverma25@gmail.com">aradhanaverma25@gmail.com</a>