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Synthesis and Structural Studies of Cr(III) Mn(III) and Fe(III) Mixed Ligand Complexes with 2;4- Dihydroxy Benzaldehyde Naphthalene-1-Acetic acid Hydrazide as Primary and Thiourea, N-Phenyl Thiourea and Thioacctamide as co-Ligands.

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ABSTRACT:

Through survey of the literature first of all we synthesis the mixed ligand complexes of Cr(III), Mn(III), and Fe(III), with 2,4-dyhydroxy benzaldehyde naphthalene - 1-acetic acid Hydrazide as as primary and Thiourea, N-phenyl Thiourea and thioacctamide as co-ligands here we report these complexes the structure and stoichiometry of the complexes have been established by various physiocochmical and spectral studies. Different ligand field parameters have also been calculated.

Key words : DHBNAAH, TU, co-ligands,spectral studies, IR, ligand field parameters.

INTRODUCTION:

There has been considerable interest in the synthetic(1-7) and Kinetic aspects of Cr(III) complexes of macrocyclic ligands. Much of the synthetic and characterization studies have been carried out on Cr(III) complexes towards a better understanding of their biological and technological importance(8). Kida(9) predicted that ternary Cr(III) complexes must be more stable than their corresponding binary complexes. Fe(III) is known to form high-spin (S=5/2), low-spin (S=1/2) and intermediate spin (S=3/2) complexes under influence of different ligand fields. Spin-crossover phenomenon is usually observed with Fe(III) compounds. Spectral and thermal characterization of mixed ligand coordination complexes of Fe(II & III) with 2-furan thiocarboxyhydrazide as primary and picolinic/ dipicolinic acid as co-ligand has been carried out. Fe(III) complexes of some azo days derived from antipyrine have been reported(10).

The importance of synthetic macrocyclic complexes is now well recognised due to their resemblance to the naturally occuringmacrocyclic(11-12) complexes. It is established that condensation of 1,2 diamino propane with acetone in presence of quantitative amount of perchloric acid yields only stereospecific 3,10-C meso-3,5,7,7,10,12,14, 14-octa methyl-1,4,8,11-tetraaza cyclotetradeca 4,11-diene, as dihydroperchlorate salt. Which has been assigned on the basis of ^{1}H-NMR-spectrum and X-ray crystallography. Its reduction with sodium(13-14) borohydride generated an isomeric mixture of three distinct diastereo isomers, which have been separated by fractional crystallization from xylene(15).

The structures of these have been established on the basis of spectral data and X-ray crystallography. These macrocycles give green cobalt(III) complexes, $[CoL'Cl_2]ClO_4$ (L'= isomeric $Me_8[14]$ anes(16) and orange to yellow nickel(II) complexes. $Ni[L]^{2+}$ and N-chiral diastereo isomers for these complexes have been separated and characterised. In principle due to the presence of four chiral nitrogen(17)centres on these macrocycles, each of the isomers can give 16-diastereo isomeric copper(II) complexes, $[CuL']^{2+}$. Out of the 16-theoretically possible diastereoisomers, only a few are stable and abundant enough to permit their isolation in the solid state(18-19).

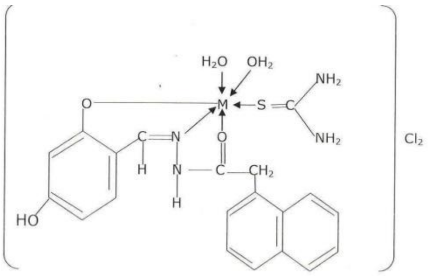
Complexes of Fe(III) with macrocyclic ligands derived from 2,3-butanedione and an aliphatic amine have been synthesised and characterised. Spectroscopic(20) studies on imidazole adducts of Fe(III) quardridentate Schiff base complexes have been reported by Choudhury and Medhi(21). pH-metric and thermodynamic studies on metal chelates of Cr(III) and Fe(III) ions with tridentate biprotic ligands have been carried out(22) by Sharma and Mathur.

Thorough survey of the literature revealed that no work seems to have been done on the mixed ligand complexes of Cr(III), Mn(III) and Fe(III) with 2;4-Dihydroxy benzaldehyde naphthalene-1-acetic acidhydrazide (DHBNAAH) as primary and thiourea (TU), N-phenyl thiourea (PTU) and thioacetamide (TA) as co-ligands. Here we report these complexes. The structures and stoichiometry of the complexes have been established by various physico-chemical and spectral studies. Different ligand field parameters have also been calculated.

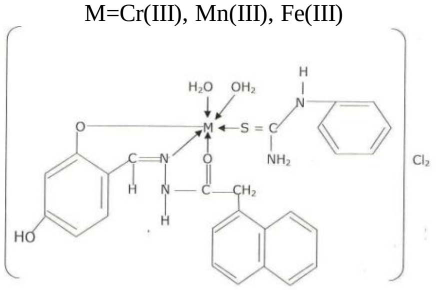
PREPARATION AND ISOLATION OF Cr(III), Mn(III) AND Fe(III) MIXED LIGAND COMPLEXES:

To a warm ethanolic solution of the metal(III) chloride (10 ml, 0.05 mol), dehydrated with 20 ml 2,2 dimethoxy propane, hot ethanolic solution (50 ml, 0.01 mol) of 2;4-dihydroxy benzaldehyde napththalene-1-acetic acid hydrazide was added dropwise. To this mixture, thiourea/N-phenyl thiourea/thioacetamide in ethanol (25 ml, 0.02 mol) was also added. The reaction mixture was thoroughly stirred and refluxed at 90^0C over water bath for about two hour. The pH of the reaction mixture was maintained to 6.8 by addition of sodium acetate buffer. The precipitated compounds were filtered, washed with ethanol, acetonitrile and dry ether. The complexes were recrystallised from chloroform and dried in vacuo over P_4O_{10}. Yield 52%.

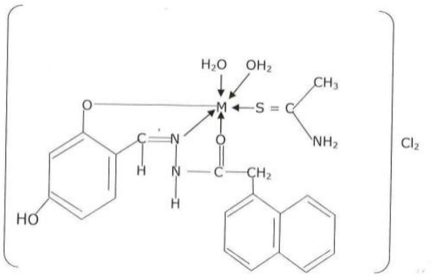
STRUCTURES OF Cr(III), Fe(III) AND Mn(III) MIXED LIGANDS COMPLEX:



Diaquo [(2;4-Dihydroxy benzaldehyde naphthalene-1-acetic acidhydrazido) (Thiourea)]-M(III) Chloride
M=Cr(III), Mn(III), Fe(III)



Diaquo [2;4-Dihydroxy benzaldehyde napthalene-1-acetic acidhydrozido) (N-Phenyl thiourea)]-M(III) Chloride
M=Cr(III), Mn(III), Fe(III)



Diaquo [2;4-Dihydroxy benzaldehyde napthalene-1-acetic acidhydrozido) (N-Phenyl thiourea)]-M(III) Chloride
Where M=Cr(III), Mn(III), Fe(III)

RESULTS AND DISCUSSION:

Analytical data recorded in Table-1 suggest 1:1:1 ($M:L:L_1/ L_2/L_3$) stoichiometry of the isolated mixed ligand complexes (where M= Cr^{3+}/Fe^{3+}, L=($C_{19}H_{15}N_2O_3$), L1=(CH_4N_2S), L_2=($C_7H_8N_2S$) &

$L_3=(C_2H_5NS)$. By the addition of alcoholic solution of silver nitrate to the solution of complexes, a white curdy precipitate obtained indicating the presence of ionic chlorine out side the coordination sphere. The compounds are stable and non-hygroscopic. The complexes are soluble in acetone benzene methanol. DMSO nitrobenzene & DMF. The conductance data (in acetone) reported in Table-1 correspond to 1-2 electrolytic nature of the complexes. Molecular weights were determined by cryoscopic method and recorded in Table-2. Colour and melting pots are also given in Table-2.

MAGNETIC STUDIES:

Cr(III) complexes are having magnetic moment of 3.80-3.86 B.M. (Table-2) corresponding to three unpaired electrons and sp^3d^2hybridisation. These values lie in the range expected for octahedral stereochemistry$^{(23)}$. The electronic spectra of acetonic solution of the complexes exhibit bands in the range 17200, 17840 cm^{-1} and 23200, 23600 $cm^{-1\ (24-27)}$.

TABLE-1

ANALYTICAL AND CONDUCTANCE DATA OF MIXED LIGAND COMPLEXES OF Cr(III), Mn(III) AND Fe(III)

S. No .	Complex	% Chemical analysis (Calculated) Found						$A_M(ohm^1)$ cm^1 mol^1
		C	H	N	S	Cl	Metal	
1	$[Cr(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$	42.60 (42.78)	3.96 (4.10)	9.0 (9.98)	5.55 (5.71)	12.50 (12.66)	10.38 (10.50)	142.40
2	$[Cr(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$	48.85 (48.98)	4.12 (4.24)	8.60 (8.79)	4.90 (5.03)	11.0 (11.15)	9.10 (9.25)	124.32
3	$[Cr(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	44.90 (45.00)	4.15 (4.29)	7.35 (7.50)	5.60 (5.73)	12.53 (12.68)	10.40 (10.52)	136.53
4	$[Fe(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$	42.86 (43.02)	4.0 (4.12)	9.90 (10.04)	5.60 (5.75)	12.60 (12.73)	9.90 (10.01)	138.92
5	$[Fe(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$	49.02 (49.22)	4.10 (4.26)	8.68 (8.83)	4.90 (5.60)	11.02 (11.20)	8.60 (8.81)	140.06
6	$[Fe(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	45.10 (45.25)	4.11 (4.31)	7.40 (7.54)	5.60 (5.76)	12.60 (12.75)	9.90 (10.03)	136.66
7	$[Mn(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$	42.90 (43.09)	4.02 (4.13)	9.90 (10.05)	5.60 (5.76)	12.65 (12.75)	9.70 (9.86)	102.0
8	$[Mn(C_{19}H_{15}N_2O_3)(C_7H_4N_2S)(H_2O)_2]Cl_2$	49.10 (45.20)	4.17 (4.27)	8.70 (8.85)	4.92 (5.06)	11.04 (11.22)	8.56 (8.68)	104.32
9	$[Mn(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	45.20 (45.32)	4.20 (4.32)	7.40 (7.55)	5.65 (5.77)	12.60 (12.77)	9.73 (9.88)	105.60

The values of B_{35} and B_{55} are reported in Table-3. The values of B_{35} are less than unity indicating type of interaction between Cr(III) and the ligands$^{(28)}$. The difference between B_{35} and B_{55} is supposed to be a function of bonding in the complexes. The covalency parameter B_{35}/B_{55} has been calculated $^{(29)}$ and recorded in the table. Spin-orbit coupling constant values of the compounds are also calculated. The spectral bands and calculated parameters support the octahedral stereochemistry for the Cr(III) complexes.

Fe(III) MIXED LIGAND COMPLEXES:

Magnetic moment values of Fe(III) complexes, under study, fall in the range 5.88-6.02 B.M. Slight deviation in magnetic moment values of the Fe(III) complexes than spin-only value (5.92 M.B.) may be due to some equilibrium between low-spin and high-spin states$^{(30,31)}$. These values of magnetic moment correspond to five unpaired electrons. The electronic spectra of Fe(III) complexes exhibit bands in the range 16600-17200, 21700-22400 and 24700-25200 cm^{-1}. These bands are tentatively assigned as:

$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
$^6A_{1g} \rightarrow {}^4T_{2g}(G)$

and $^6A_{1g} \rightarrow {}^4E_g(G)$

Table - 2

Magnetic Moments Molecular Weight and other physical data of Cr(III), Mn(III), and Fe(III), Mixed ligand complexes

S. No.	Complex	$\mu_{eff.}$ (B.M.)	Molecular Wt. Calcd. (Found)	M.P. (^0C)	Colour	Stereochemistry
1	$[Cr(C_{19}H_{15}N_2O_3)(CH_4N_2S)\ (H_2O)_2]Cl_2$	3.84	560.99 (201)	270	Greenish	Octahedral
2	$[Cr(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$	3.82	636.99 (230)	290	Grey	Octahedral
3	$[Cr(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	3.86	559.99 (196)	300	Grey	Octahedral
4	$[Fe(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$	6.02	557.90 (1951)	240	Dark Black	Distorted Octahedral
5	$[Fe(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$	5.92	633.90 (224)	265	Blackish	Distorted Octahedral
6	$[Fe(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	6.0	556.90 (196)	310	Dark Black	Distorted Octahedral
7	$[Mn(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$	4.85	556.99 (200)	280	Grey	Distorted Octahedral
8	$[Mn(C_{19}H_{15}N_2O_3)(C_7H_4N_2S)(H_2O)_2]Cl_2$	4.90	632.99 (234)	294	Grey	Distorted Octahedral
9	$[Mn(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	4.82	555.99 (198)	300	Grey	Distorted Octahedral

Table - 3

Electronic Spectral Bands and Structural Parameters of Mixed Ligand Complexes of Cr(III)

S.No.	Complex	Bands (cm^{-1})	B_{35} (cm^{-1})	B_{55} (cm^{-1})	β_{35}	β_{55}	β_{35}/β_{55}	λ (cm^{-1})	g
1	$[Cr(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$	17200 23200 13030	701	611	0.680	0.61	1.11	90.80	1.96
2	$[Cr(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$	17420 23530 13000	710	600	0.689	0.582	1.183	124.70	1.95
3	$[Cr(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	17820 23415 12680	730	580	0.708	0.57	1.242	48.12	1.97

$L=C_{19}H_{15}N_2O_3$

The band observed at about 27800 cm^{-1} expected to be the charge transfer band (L-M). The bands observed at around 17660 and 29815 cm^{-1} may possibly be due to split of $^4T_{1g}$ and thus the compounds possess distorted to D_{4h} symmetry, the values of D_{qz} Dt and are calculated with the help of the following equations(32-34).

$^6A_{1g} \longrightarrow {}^4T_{1g}(G)=10\ Dq\ (XY) - 35/Dt$ ....(1)

$Dt = 4/7\ (Dq\ E-D_{qz})$ .... (2)

$\delta\sigma = 3/8\ A - - 03/2\ Dt\ (K+5/4)$ .... (3)

$\delta\pi = \Delta/2 - -1/2\ Dt\ (K-5/3)$ .... (4)

Parameters 10 Dq.B and β for the complexes have been calculated and reported in Table-4.

Mn(II) COMPLEXES:

The room temperature magnetic moment values found for Mn(II) complexes are in agreement with high spin Oh-symmetry. The electronic spectra of Mn(III) complexes show bands around 14880, 16830 and 18350 cm^{-1} assignable to $^5B_{1g}$ $^5A_{1g}$; $^5B_{1g}$ $^5B_{2g}$ and $^5B_{1g}$ ^5E_g transitions$^{(35)}$.

IR SPECTRA:

On comparing the IR-spectra of free ligand and complexes, the following changes are noticed.

1.The absorption band at 3300 cm^1, characteristic of phenolic OH group is not present in the spectra of complexes, showing the deprotonation and subsequent replacement of proton of -OH by metal ion. The v(C-O) absorption frequency also get reduced from, 1320 cm^1 to 1300 cm^{-1}, further conform deprotonation of phenolic - OH group$^{(36)}$.

2.In the infra-red spectra, the ligand 2;4-dihydroxy benzaldehyde-naphthalene-1-acetic acid hydrazide showed amide band I (vC-O, 1648 cm^{-1}) and amide bands II and III (vC-N-1530, δ NH-1325). The metal complexes showed a lower frequency for amide band-I (vCO, 1610 cm^{-1}) while amide band II and III appeared in higher frequency (vCN, 1545, δ NH-1335) as compared to free ligand. Similarly all the metal complexes showed a lower frequency for amide-I and higher frequency for amide band II and III indicating coordination of metal to amide oxygen$^{(37)}$.

3.The bands at 1600-1620 cm^{-1} due to the azomethine group of the Schiff bases underwent a shift to lower frequency (1580-1590 cm^{-1}) after complexation indicating the coordination of azomethine nitrogen to metal ion and thus can be explained by the donation of electron from nitrogen to the empty d-orbitals of the metal atom$^{(38)}$.

TABLE-4
SPECTRAL BANDS AND STRUCTURAL PARAMETERS OF MIXED LIGAND COMPLEXES OF Fe(III)

S. No.	Complex	Bands (cm^{-1})	10 Dq (cm^{-1})	B (cm^{-1})	β	Dt (cm^{-1})	Dqz (cm^{-1})	$\delta\sigma$ (cm^{-1})	$\delta\pi$ (cm^{-1})
1	$[Fe(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$	17050 21845 26005	7810	725	0.56	-1.062	2630	294	-391
2	$[Fe(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$	16730 22240 25660	7690	862	0.61	-1.042	2571	288	-384
3	$[Fe(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	17136 22058 26110	7859	710	0.55	-1.055	2642	296	-394

L=($C_{19}H_{15}N_2O_3$); L1=CH_4N_2S; L_2= $C_7H_8N_2S$ and L_3=C_2H_5NS

4.In the spectra of thiourea, N-phenyl thiourea and thioacetamide, the characteristic bands due to vC-S seen at 1390-1400 and 820-825 cm^{-1} get shifted to 1360-1370 and 770-775 cm^{-1} bands in the complexes showing the participation of thiocarbonyl sulphur$^{(37)}$ in complex formation.

5.In the spectra of mixed ligand complexes, the N-H frequency bands are seen almost at the same position as in ligands suggesting the non-involvement of nitrogen of N-H or NH_2 group in coordination$^{(38)}$.

6.Some non-ligand medium intensity bands exist in the spectra of all the comlexes in the lower frequency region i.e. 470-490, 400-410 and 275-290 cm^{-1} which may tentatively assigned$^{(39-42)}$ as vM-O, vM-N and vM-S vibrations respectively.

7.The negative shift in the frequencies of v(C=O) v(OH) and v(C=N) found in the spectra of complexes reveals the coordination through carbonyl oxygen phenolic oxygen and azomethine nitrogen(43-44).

8.Presence of coordinated water molecule was confirmed by Karl-Fisher method(45-47) and IR. The band around 3410, 860 and 710 cm^{-1} are due to v(OH), *l*(OH) showing water molecule presence in coordination environment.

IR absorption bands are shown in table 5.

TABLE-5

DIAGNOSTATIC IR ABSORPTION BAND (cm^{-1}) AND THEIR ASSIGNMENTS IN MIXED LIGAND COMPLEXES OF Cr(III), Fe(III) AND Mn(III) COMPLEXES

S. No	Complex	(C=N)	v(N-N)	v(C=O) Amide-I	v(C=N$_{\delta}$ NH)Amide-II	vC-N Amide-III	vC=S	vM-O	vM-N	vM-s
1	$[Cr(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$	1590 m	945 m	1600st	1525w	1310sh	1360 w 770m	490 m	400 m	275 m
2	$[Cr(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$	1580 m	955 m	1610 st	1520 w	1310 sh	1370 w 775m	485 m	410 m	290 m
3	$[Cr(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	1600 m	925 m	600 st	1520 w	1310 sh	1365 w 775m	470 m	405 m	280 m
4	$[Fe(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$	1595 m	935 m	1610 st	1525 w	1310 sh	1360 w 770m	480 m	408 m	280 m
5	$[Fe(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$	1600 m	940 m	1610 st	1520 w	1310 sh	1365 w 775m	490 m	410 m	275 m
6	$[Fe(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	1590 m	930 m	1610 st	1525 w	1310 sh	1370 w 775m	485 m	405 m	290 m
7	$[Mn(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$	1600 m	225 m	1605 st	1520 w	1310 sh	1360 m 760m	480 m	400 m	270 m
8	$[Mn(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$	1605 m	230 m	1600 st	1515 w	1305 sh	1370 m 770m	490 m	410 m	270 m
9	$[Mn(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$	1595 m	240 m	1610 st	1525 w	1300 sh	1360 m 760w	480 m	400 m	280 m

SH= Sharp, m=median, w = weak and st-strong

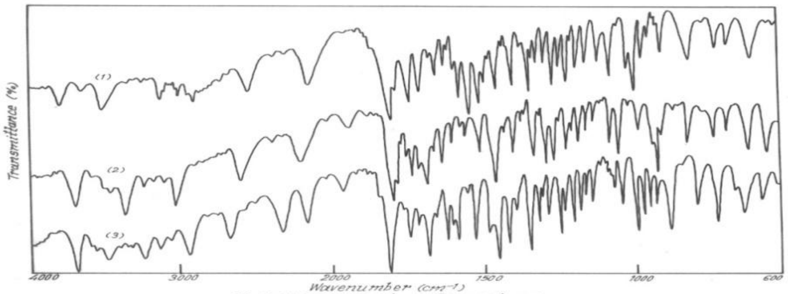


Fig.6.1 : I. R. Spectra of complexes.
(1): $[Cr(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$
(2): $[Cr(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$
(3): $[Cr(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$

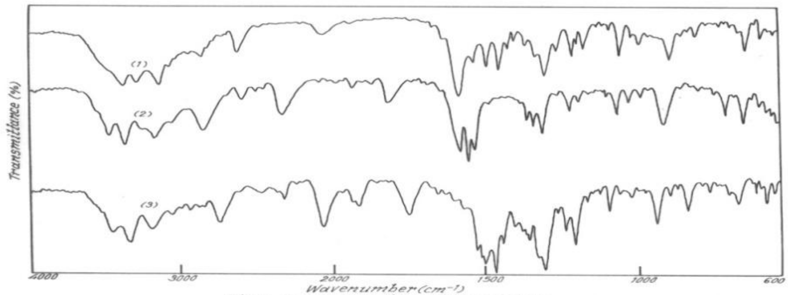


Fig.6.2: I.R. Spectra of complexes.
(1): $[Fe(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$
(2): $[Fe(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$
(3): $[Fe(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$

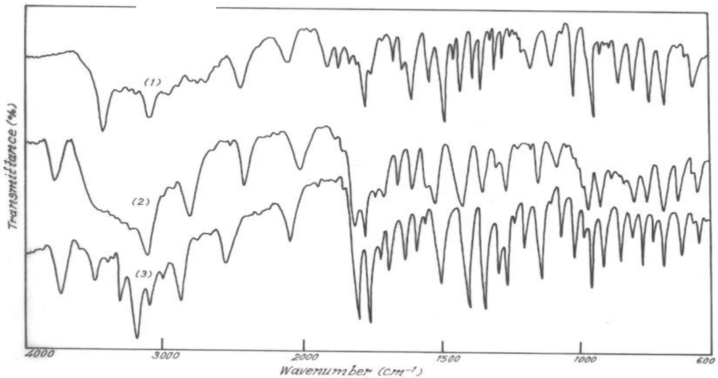


Fig.6.3: I.R. Spectra of complexes.
(1): $[Mn(C_{19}H_{15}N_2O_3)(CH_4N_2S)(H_2O)_2]Cl_2$
(2): $[Mn(C_{19}H_{15}N_2O_3)(C_7H_8N_2S)(H_2O)_2]Cl_2$
(3): $[Mn(C_{19}H_{15}N_2O_3)(C_2H_5NS)(H_2O)_2]Cl_2$

CONCLUSION:

Present work contain simple and mixed ligand complexes of Cr(III), Mn(III) and Fe(III) metal ions stoichiometry structure and geometry of the complexes have been established by chemical analysis, IR magnetic susceptibility measurements electronic spectral measurements. The work is helpful in many branches of chemistry and chemical industry due to a large number of applications they are employed in refineries and in fertilizer industry for gas sweetening's manufacturing intermeadiates for detergents pharmaceuticals paints and synthetic resins.

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