

## Synthesis and characterization of complexes of 2-hydroxy-3 nitro acetophenyl amino guanidine with 3d-series transition metals

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### Abstract

Synthesis, analysis and IR Spectra of 2- Hydroxy – 3 – nitroacetophenyl amino guanidine have been discussed. Complexes of Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Co(III), Ni(II) and Cu(II) with this ligand have been synthesized, their magnetic and electrical properties have been studied, structure of the complexes have been assigned on the basis of elemental analysis and IR spectral data.

*Key words* : Synthesis, 2- Hydroxy – 3 – nitroacetophenyl amino guanidine, Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Co(III), Ni(II), Cu(II), Elemental analysis IR spectra, Electronic spectra.

### Introduction

In recent years metal complexes with Schiff's bases received attention due to their diverse range of applications<sup>1-5</sup> Schiff's bases are organic compounds having azomethine groups ( $>C=N-$ ) and various studies<sup>6-7</sup> have shown that  $>C=N-$  group has numerous biological importance.<sup>8-10</sup> Schiff's base

becomes more useful chelating agent when a suitable functional group such as  $-OH$ ,  $-SH$ ,  $-NH_2$  etc is present sufficiently close to azomethine group in the molecule. This is why we have undertaken the title project.

### Experimental

(A) *Preparation of ligand:*

Aminoguanidine bicarbonate (3 gm)

was dissolved in dilute hydrochloric acid. It was treated with methanolic solution of 2 – hydroxy – 3 – nitroacetophenone (6 gm). The mixture is refluxed for about half an hour. On cooling yellowish coloured precipitate appeared. It was filtered and washed with water. The crude product was recrystallised from alcohol. The pure and dry crystals was obtained. (m.pt.  $210^{\circ}\text{C}$ )

The ligand was soluble in methanol and ethanol but insoluble in acetone and water.

*(B) Preparation of complexes :*

Aqueous solution of chromium (III) chloride (0.521g), ferrous ammonium sulphate (0.745g), Iron (III) chloride, Cobalt (II), Cobalt (III) chloride (0.403 g), nickel (II) chloride (0.475g) and copper (II) chloride, Managanese (II) chloride was separately mixed with methanolic solution of the ligand 2 – hydroxy – 3 – nitro acetophenyl aminoguanidine in the ratio of 1:2. The mixture was refluxed for about 2 hrs and cooled. Now few drops of ammonium hydroxide were added. The black colored precipitate separated was again digested on water bath for an hour and then cooled. The solid crystal of complexes was dried and analyzed chemically<sup>11</sup>.

Iron gives green precipitate, cobalt give faint red brown ppt, Ni give red ppt, Cu give brown ppt.

The colored solid complexes were purified by recrystallisation. Chromium, iron complexes are insoluble in water, slightly soluble in alcohol but dissolves fairly in DMF. Copper complex is insoluble in water, dissolves slightly in ehanol but fairly in DMF.

The metal contents of all the complexes were analyzed using standard method.

The IR spectra of the ligand and complex were recorded on Beckman IR-20 spectrophotometer using KBr pallet technique. The electronic spectra of the complexes were recorded on a Cary 2390 spectrophotometer. Magnetic moment were measured by Guoy method using mercury tetrathiocyanato cobalt (II) as a callibrant. The molar conductance measurement were done on Toshniwal conductivity bridge using DMF as a solvent. Analytical data, colour, molar conductivity, electronic and spectral data magnetic moment and decomposition temperature are recorded in table I and salient feature of IR spectral data are recorded in Table 2

### 3. Result and Discussion

*Electronic spectra of complexes :*

- (a) The reflectance spectra of the Cr(III) complexes shows bands at  $17290$  and  $22730\text{ cm}^{-1}$  which are assigned to  ${}^4\text{A}_{2g}$  (F)  $\rightarrow {}^4\text{T}_{2g}$  (F) and to  ${}^4\text{A}_{2g}$  (F)  $\rightarrow {}^4\text{T}_{1g}$  (P) transitions in octahedral stereochemistry.<sup>23</sup>
- (b) A band is observed in the spectrum of Fe(II) complex at  $11600\text{ cm}^{-1}$  which may be attributed to  ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$  transition characteristic to octahedral stereochemistry.
- (c) The reflectance spectra of Fe(III) complex gives three bands at  $14710\text{ cm}^{-1}$   $19050\text{ cm}^{-1}$  and  $25000\text{ cm}^{-1}$  which correspond to  ${}^6\text{A}_{1g} \rightarrow {}^6\text{T}_{1g}$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$  transitions assuming idealized octahedral symmetry.<sup>12</sup>
- (d) The diffused reflectance spectra of Co(II)

- complexes gives three d-d transition bands at  $9505\text{ cm}^{-1}$ ,  $19500\text{ cm}^{-1}$  and  $22320\text{ cm}^{-1}$  assigned as  ${}^4T_{1g}$   ${}^4T_{2g}(F)$ ,  ${}^4T_{1g}$   ${}^4A_{2g}(F)$  and  ${}^4T_{1g}$   ${}^4T_{1g}(p)$  also suggest an octahedral geometry.<sup>13</sup>
- (e) The diffused reflectance spectra of Co(III) complexes gives two bands at  $11500\text{ cm}^{-1}$  and  $19050\text{ cm}^{-1}$  assigned to  ${}^1A_g$   ${}^1T_{1g}$  and  ${}^1A_g$   ${}^1T_{2g}$  transitions respectively which suggest octahedral geometry.<sup>14</sup>
- (f) Ni(II) complex shows four band in their reflectance spectra at  $11245\text{ cm}^{-1}$ ,  $16000\text{ cm}^{-1}$ ,  $24680\text{ cm}^{-1}$  and  $10752\text{ cm}^{-1}$  out of which first three are assigned to spin allowed d-d transition as  ${}^3A_{2g}(F)$   ${}^3A_{2g}$ ,  $(F)$ ,  ${}^3T_{2g}(F)$   ${}^3T_{1g}(F)$  and  ${}^3A_{2g}(F)$   ${}^3T_{1g}(P)$  transitions respectively and the last one is a spin forbidden transitions and may be assigned to  ${}^2B_{1g} - {}^2E_g$  transition.
- (g) Ni(II) complex shows two bands at  $15625\text{ cm}^{-1}$  and  $20,000\text{ cm}^{-1}$  which are due to  ${}^1A_{1g}$   ${}^1A_{2g}$  and  ${}^1A_{1g}$   ${}^1B_{1g}$  transitions which suggest square planar geometry.<sup>15</sup>
- (h) The visible spectra of Cu(II) complex show a broad band at  $13850\text{ cm}^{-1}$  to  $15000\text{ cm}^{-1}$  due to  ${}^3E_g$   ${}^3T_{2g}$  transitions. The broadness of band and its position indicate distorted octahedral geometry for this complex.
- (i) The Cu (II) complex show one broad bond at  $20,000\text{ cm}^{-1}$  which may be assigned to the overlap of  ${}^3B_{1g}$   ${}^3A_{1g}$ ,  ${}^3B_{2g}$   ${}^3E_g$  transition and suggest square planar geometry.<sup>16</sup>
- (j) The Mn (II) Complex exhibits three bands at  $11910\text{ cm}^{-1}$ ,  $16660\text{ cm}^{-1}$  and  $32810\text{ cm}^{-1}$  indicating hexa co-ordinated structure.

### IR Spectra of ligand and complexes :

2 – Hydroxy – 3 – nitro acetophenyl aminoguanidine, (HNAPAG)

The Interpretation of I.R. spectra is quite complicated due to the presence of various similar groups and hence many absorption bands. However, comparison of the spectral bands of the ligand (HNAPAG), with those of its complexes gives some important informations regarding the nature of the ligand as well as the co-ordination sites through which metal ion co-ordinate with the ligand.

The broad band at  $3200\text{ cm}^{-1}$  in the ligand assignable to phenolic O - H (hydrogen bonded) stretching frequency<sup>13</sup> disappears in the Ni (II), Co (II), Co(III), Cr(III), Fe (II), and Fe (III) complexes showing deprotonation of phenolic protons through complexation. The ligand also shows strong bands near  $1265\text{ cm}^{-1}$  which may be attributed to the phenolic  $\nu C - O$  vibration. A shift of this band to higher frequency ( $\sim 1300\text{ cm}^{-1}$ ) in the complexes indicated chelation of the ligand to metal ion through phenolic oxygen. The presence of a band near  $(3545)\text{ cm}^{-1}$  in Cu (II) and Mn (II) complexes may be due to O - H of water molecule associated with the complexes. This is further justified by the presence of a band around  $1600\text{ cm}^{-1}$  as deformation band of water molecule.

The ligand exhibit a band near  $3425\text{ cm}^{-1}$  and  $3085\text{ cm}^{-1}$  which are assigned to  $NH_2$  and  $>N - H$  stretching<sup>12</sup> respectively, does not change appreciably in the complexes indicating non - involvement of  $>N - H$  and

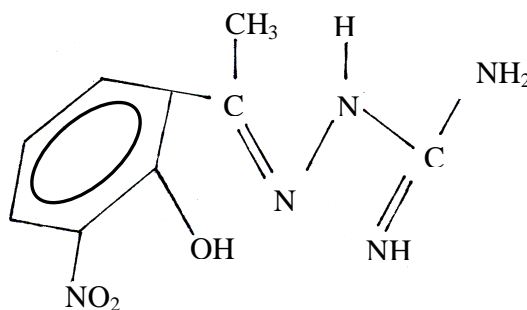
NH<sub>2</sub> nitrogen atom in chelate formation. Bands at 2465 cm<sup>-1</sup>, 2205 cm<sup>-1</sup>, 1905 cm<sup>-1</sup>, 925 cm<sup>-1</sup>, 845 cm<sup>-1</sup> and 785 cm<sup>-1</sup> are the characteristic bands of the compound which remain unaffected on complex formation. In this cases of metal complexes, the most interesting feature noted is about the doublet band<sup>13</sup> observed in the I.R. spectrum of the ligand near 1625 cm<sup>-1</sup>. The higher one goes upto 1655 cm<sup>-1</sup> to 1685 cm<sup>-1</sup> probably due to the bending mode of the NH<sub>2</sub> group which remain practically unaffected and shows that the NH<sub>2</sub> and >N - H mostly does not take part in the co-ordination. The other component which is due to C=NH group stretching frequency shifts to the lower frequencies about (~ 1570 cm<sup>-1</sup>) in complexes, indicating the co-ordination through C = N (imine) group. In the case of Ni (II) and Cu (II) it has been observed that as the reaction is carried out at pH 9, the band assigned to C = NH group, disappears. It suggests that at higher pH co-ordination of Ni (II) and Cu (II) through C = N group, takes place by deprotonation. Martin and co-workers<sup>14</sup> have also reported the same thing.

A sharp band at 1595 cm<sup>-1</sup> observable in the free ligand is assigned to C = N vibration of Schiff's base residue. This band shifts to the lower frequencies in the complexes, which indicates that azomethine nitrogen of C = N takes part in co-ordination.<sup>17-18</sup>

The  $\nu$ C-N due to nitro group, appearing in the region 1400 cm<sup>-1</sup> in the free ligand,<sup>22</sup> remains unaltered in all the complexes, suggesting non-participation of nitro group in co-ordination.

Thus 2-Hydroxy-3-nitro acetophenyl amidoguanidine (HNAPAG) behaves as a tridentate ligand co-ordinating through phenolic oxygen (C - O), ; nitrogen atom of C = N, of azomethine group and nitrogen atom of C = NH, of imine group). It is further confirmed by work of Hovorka.

It is noteworthy that the ligand behaves as monoprotic for all the metal ions under investigation except for Ni (II) and Cu (II) when complexation is carried out at higher pH (pH = 9). In the latter cases ligand behaves like biprotic involving the deprotonation of C = NH (imine) proton. Thus the structure of ligand may be represented as



3 - Nitro - 2 - hydroxyl acetophenyl amino guanidine.

#### *Magnetic properties :*

The  $\mu_{eff}$  value of Cr(III) complex (3.8 BM) fall in the range required for octahedral stereochemistry<sup>19</sup> of Fe(II) (5.3 BM) consistent with high spin octahedral geometry. Fe(III) (5.9 BM) also supports octahedral geometry<sup>20</sup> Co(II) (5.0 BM) suggest an octahedral

structure Co(III) is diamagnetic which suggest low spin octahedral geometry, Ni(II) (2.9 BM) is in good agreement with an octahedral geometry. Diamagnetism of another Ni(II) complex suggest square planar geometry,  $\mu_{eff} = 1.7$  BM for both Cu complex<sup>21</sup> is in very good agreement with spin only value of Cu(II) complexes which correspond presence of one unpaired electron. The magnetic moment value of Mn(II) complex (1.08 BM) looks sub normal. It may be due to metal-metal interaction<sup>22</sup>. This suggest that the complex may be binuclear.

#### *Electrical conductivity :*

The molar conductance values of the complexes in  $10^{-3}$  M solution in DMF was found to be  $89.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  for Cr(III) complex, 98.3 for Fe(III) complex, 93.5 for Co(III) indicating its 1:1 electrolytic nature. Co(II) 18.34, Ni(II) 20.7 and 8.7, Cu(II) = 17.9 and  $21.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  indicating their non-electrolytic nature.

#### *Decomposition Temperature :*

Decomposition temperature of complexes varies from  $160^{\circ}\text{C}$  to  $300^{\circ}\text{C}$  indicating complexes are thermally stable.

Table – 1 .A Decomposition temperature, electrical conductivity and magnetic moment value of complexes.

		DT	EC	$\mu_{eff}$
<b>a.</b>	[Cr(HNAPAG) <sub>2</sub> ] Cl	$210^{\circ}\text{C}$	89.4	3.83
<b>b.</b>	[Fe(HNAPAG) <sub>2</sub> ]	$160^{\circ}\text{C}$	---	5.2
<b>c.</b>	[Fe (HNAPAG) <sub>2</sub> ] Cl	$240^{\circ}\text{C}$	98.3	5.94
<b>d.</b>	[Co(HNAPAG) <sub>2</sub> ]	$300^{\circ}\text{C}$	18.34	5.1
<b>e.</b>	[Co(HNAPAG) <sub>2</sub> ] Cl	$210^{\circ}\text{C}$	93.5	0.0
<b>f.</b>	[Ni(HNAPAG) <sub>2</sub> ]	$240^{\circ}\text{C}$	20.7	2.99
<b>g.</b>	[Ni(HNAPAG) NH <sub>3</sub> ]	$240^{\circ}\text{C}$	8.7	0.0
<b>h.</b>	[Cu(HNAPAG) Cl.2H <sub>2</sub> O]	$250^{\circ}\text{C}$	17.9	1.78
<b>i.</b>	[Cu(HNAPAG) NH <sub>3</sub> ]	$230^{\circ}\text{C}$	21.2	1.84
<b>j.</b>	[Mn(HNAPAG) Cl.2H <sub>2</sub> O]	$240^{\circ}\text{C}$	---	1.08

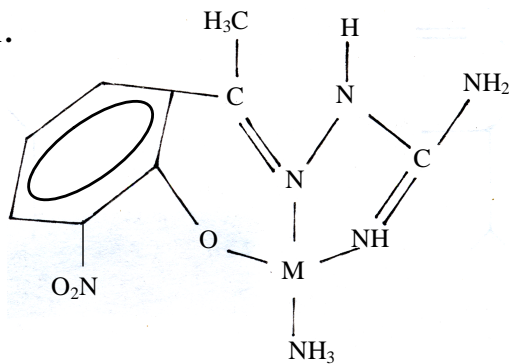
Table 1.B. Elemental analysis data of ligand and metal complexes

Compounds	Colour	Elemental analysis				
		% observed (Calculated)				
		M	C	H	N	Cl
HNAPAG	Yellow		45.23 (45.76)	5.08 (4.24)	29.07 (29.66)	
[Cr(HNAPAG) <sub>2</sub> ] Cl	black	8.76 (9.33)	37.47 (38.74)	4.44 (3.23)	26.26 (25.11)	6.11 (6.37)
[Fe(HNAPAG) <sub>2</sub> ]	Green	10.17 (10.61)	40.17 (40.08)	4.73 (3.42)	25.93 (26.63)	
[Fe (HNAPAG) <sub>2</sub> ] Cl	Dark green	9.09 (9.94)	37.83 (38.48)	4.67 (3.21)	23.36 (24.94)	6.01 (6.33)
[Co(HNAPAG) <sub>2</sub> ]	Red	10.03 (11.14)	39.37 (40.82)	4.93 (3.40)	25.31 (26.47)	
[Co(HNAPAG) <sub>2</sub> ] Cl	Faint red	10.13 (10.44)	37.17 (38.27)	4.72 (3.11)	24.05 (24.80)	6.02 (6.29)
[Ni(HNAPAG) <sub>2</sub> ]	Red brown	11.32 (11.10)	40.15 (40.85)	4.71 (3.40)	25.57 (26.48)	
[Ni(HNAPAG) NH <sub>3</sub> ]	Red	18.19 (18.89)	34.07 (34.76)	4.78 (3.86)	26.38 (27.04)	
[Cu(HNAPAG) Cl.2H <sub>2</sub> O]	Bluish red	16.70 (17.16)	28.34 (29.19)	4.72 (3.51)	18.22 (18.92)	8.37 (9.59)
[Cu(HAAPAG) NH <sub>3</sub> ]	Red	19.36 (20.13)	34.12 (24.23)	5.09 (3.80)	25.27 (26.62)	
[Mn(HNAPAG) Cl.2H <sub>2</sub> O]	Yellow	14.38 (15.19)	27.89 (29.88)	4.99 (3.60)	18.76 (19.37)	8.32 (9.82)

	HNAPAG	Cu(HNAPAG)2	Fe(HNAPAG)2	[Fe(HNAPAG)2]Cl	Co(HNAPAG)2	[Co(HNAPAG)2]Cl	Ni(HNAPAG)2	Ni(HNAPAG)2NH3	[Cu(HNAPAG)2]Cl.2H2O	[Cu(HNAPAG)2]Cl.2H2O	[Mn(HNAPAG)2]Cl.2H2O
- NH <sub>2</sub> Stretching	3425	3420	3390	3410	3395	3405	3405	3395	3405	3405	3405
- O - H Hydrogen bond	3200										
- C - H Stretching	3145	3145	3145	3145	3145	3145	3145	3145	3145	3145	3145
> N - H Stretching	3085	3085	3085	3085	3085	3085	3085	3085	3085	3085	3085
C - H Aromatic Stretching	2985	2985	2985					2985	2985	2985	2985
C - H Stretching	2755	2755	2755								
Skeletalvibrations	2465, 2205, 1905	2465, 2205, 1905	2465, 2205, 1905	2465, 2205, 1905	2465, 2205, 1905	2465, 2205, 1905	2465, 2205, 1905	2465, 2205, 1905	2465, 2205, 1905	2465, 2205, 1905	2465, 2205, 1905
-NH <sub>2</sub> , > N-H bending	1655, 1626	1665, 1625	1675, 1625	1675, 1625	1670, 1625	1680, 1625	1675, 1625		1670, 1625	1665, 1625	
C = N Stretching	1595	1580	1570	1590	1580	1570	1580	1580	1580	1575	1580
C - N Stretching	1400	1400	1400	1400	1400	1400	1400	1400	1400	1400	1400
C - O Phenolic	1265	1285	1200	1275	1305	1285	1295	1280	1300	1285	1300
Characteristic vibration of 1,2,4, substituted benzene ring	925, 845, 785			925, 845, 785	925, 845, 785	925, 845, 785			925, 845, 785	925, 845, 785	925, 845, 785
M - N Bond		525	515	525	585	515	515	525	515	525	515
M - O Bond		425	435	495	495	485	480	475	415	485	410
M - NH <sub>3</sub>								645		645	
			[Cu (HNAPAG) Cl. 2H <sub>2</sub> O]			[Mn(HNAPAG)Cl.2H <sub>2</sub> O]					
O - H stretching of water molecule			3545			3545					
Deformation band of water molecule			1600			1600					

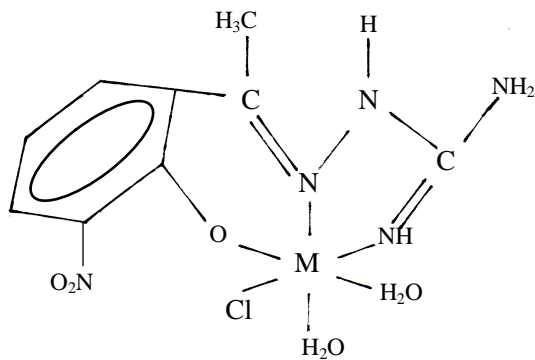
## Structure of metal complexes

1.



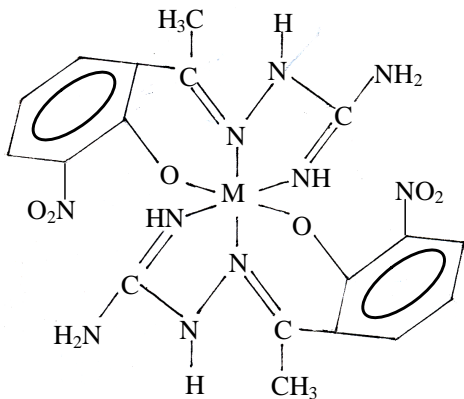
Where, M = Cu(II), Ni(II)

4.



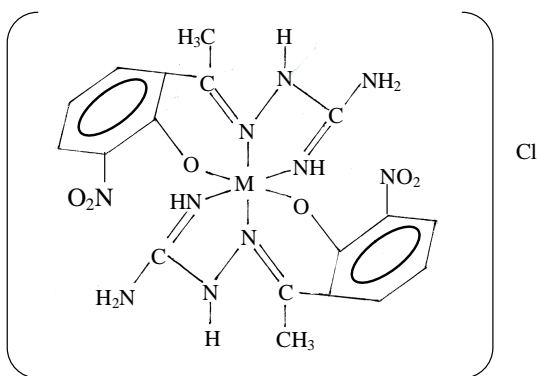
Where M = Mn (II), Cu(II)

2.

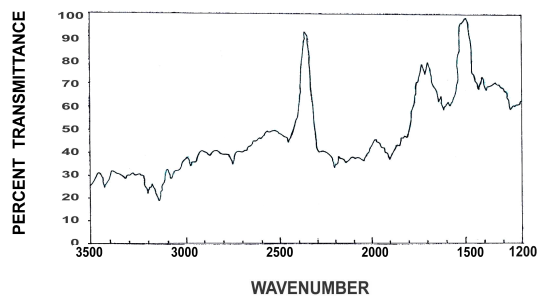


Where, M = Fe (II), Co(II), Ni(II)

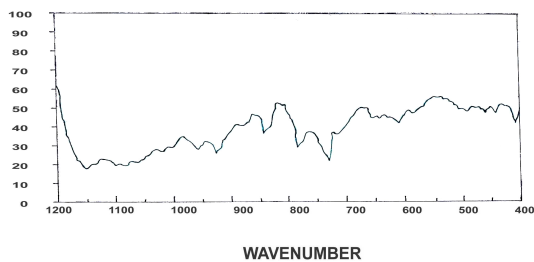
3.



Where, M = Cr(III), Fe(III), Co(III)



a (HNAPAG)



b (HNAPAG)

Fig. 1(a,b) IR Spectra of  
2 - HYDROXY - 3 - NITRO  
ACETOPHENYL AMIDOGUANIDINE  
( HNAPAG )

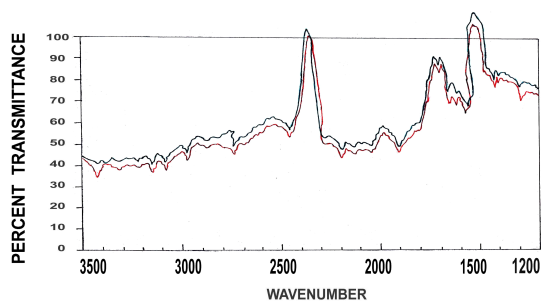
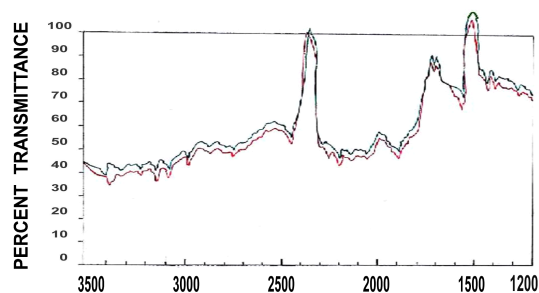
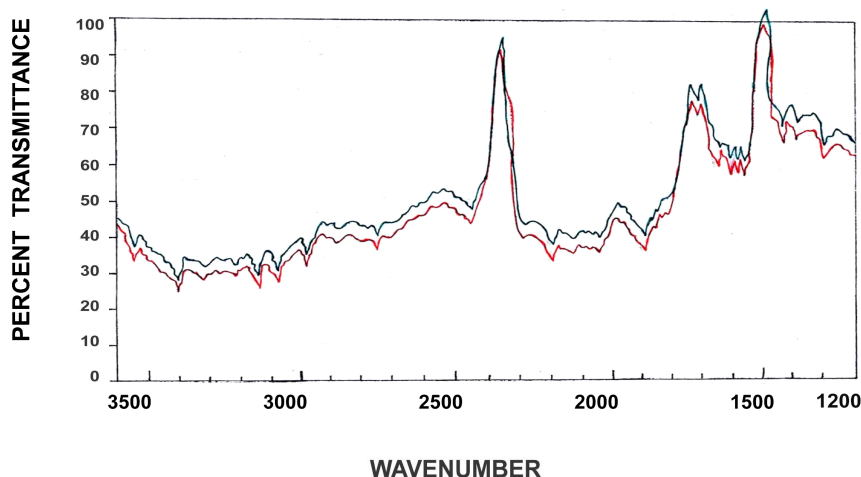


Fig. 2 :

[Cr ( HNAPAG )<sub>2</sub> ] Cl , and  
2 . [ Fe ( HNAPAG )<sub>2</sub> ] Cl,  
[Co(HNAPAG)<sub>2</sub>] Cl

Fig 3: [ Ni ( HNAPAG )NH<sub>3</sub> ] and  
2 . [ Cu ( HNAPAG )NH<sub>3</sub> ]Fig. 4 [ Cu (HNAPAG)Cl.2H<sub>2</sub>O] and 2. [ Mn (HNAPAG)Cl. 2H<sub>2</sub>O]

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