# Structural and Thermal decomposition Studies of Co (III)and Ni (II) metal complexes of Schiff Bases

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**Abstract :**In this paper two types of complexes of Co (III) and Ni (II) with Schiff bases are studied. The synthesis of complexes of above metal ion with 2;4 dihydroxy benzaldehyde isoicotinic acid hydrazide, 4-methyl-2, 6 diformyl phenol isonicotic acidhydrazide as primary and thiosalicylic acid (TSA), 2 aminothiophenol (2-ATP) and 2-thiophene acitic acid (2-TPA) as coligand have been reported. The mixed ligand complexes are characterized on basis andlytical spectral and thermal decomposition.

Key words: TSA ,2-ATP, 2-TPA and Schiff base.

**INTRODUCTION-** D-block elements (Transition metals) co-ordinate complexes and their derivative are very interesting in respect of biologically and chemically [1-4)]. Its striking structural aspects and unique stereo and magneto chemistry([5)] also have important role in chemistry. The complexes of Maganese play important role in photo chemical reaction (6-7). Several Manganese complexes are known to exhibit antifungal (8-9) and antileukemic activities. A lot of paper on these transition metal complexes of N and S/O donor ligands have been published. Maganese (II) complexes of biologically potent ligands hydrazinecarboxamide (HSCZ) or carbothioamide (HTSCZ) have been prepared. These are of the type [MnCl(Nx)$H_2O$] and [Mn$(NX)_3$] X is O or S and NX=donot system). Elemental analysis molecular weight determinations, molar conductance Magnetic moment, electronic, IR and ESR spectral studies have been employed to characterize these complexes magnetic data show that the ground state of these componds is the expected high spin state and the spectral data suggest that the coordination of ligand to the central metal atom takes place in a monobasic bidentate fashion through the thiolo sulphur or hydroxo oxygen and azomethine nitrogen.

The representative free ligands and their respective metal complexes were tested in vitro against different microorganisms to assess their antimicrobial properties(9).The literature survey indicate that no work have been done so far on the mixed ligand complexes of Co (III) and Ni (II) with substituted hydroxy aldehydes acidhydrazides as primary and sulphur donors as co-ligand Schiff bases are an important class of ligands in coordination chemistry and their completing ability containing different donor atom is widely reported (10-13). The ligands resulting from 4-amino 3-ethyl-5-mercapto-s-triazole and benzaldehyde, and 2-hydroxy -1- naphthldehyde have been reported to form the complexes with some metal ions(14). Here we report the synthesis of Co (III) and Ni (II) complexes with 2, 4-dihydroxy benzaldehyde isonicotinic acid hydrazide ($C_{13}H_{11}N_3O_3$), 4-methyl -2, 6-diformylphenol isonicotinic acid hydrazide ($C_{15}H_{13}N_3O_3$) and 2;4 dihydroxy benzaldhyde-2-furoic acidhydrazide

($C_{12}H_{10}N_2O_4$) as primary and thiosalicylic acid (TSA) 2-aminothiophenol (2-ATP) and 2-thiophene acetic acid (2-TPA) as co-ligand[15]. The mixed ligand complexes are characterized on the basis of analytical, electrolytic conductance, magnetic susceptibility electronic and IR spectral data. The molecular weights of the compounds have been determined cryoscopically. The thermal behavior of the mixed ligand complexes and ligand field parameters of the complexes viz. 10Dq are also investigated.

**Experimental : Preparation and isolation of complexes : Co (III) and Ni (II)mixed ligand complexes**

The acidhydrazide schiff base ($C_{13}H_{11}N_3O_3$) / ($C_{15}H_{13}N_3O_3$) / ($C_{12}H_{10}N_2O_2$) in ethanol (50ml, 0.01 mol) was mixed with the solution of Co $(No_3)$ $6H_2O/Ni(NO_3)_2$ $6H_2O/Cu(NO_3)_2$ $4H_2O/CoCl_2$ $6H_2O/Nicl_2$ $6H_2O$ / $Cucl_2 2H_2O$ (50 ml. 0.01 mol) dropwise with constant steering An aqueous ethanolic solution (50%, v/v) of thiosalicylic acid / 2-aminochiophenol/2-thiophene acctic acid (50ml 0.01 mol) was then added slowly and with constant stirring. The mixture having a 1:1:1 molar tatio was vigorously stired for 20 min at $60^0C$ on raising the pH to 6-7 with ditute ammonia solution, the whole content was then reflused for 1-1.5h on a water bath. The coloured complexes, reparated out on cooling, were filtered and washed subsequently with ethanol, hot water, and finally with dry ether and dried. The complexes were recryslally from chloroform and dried under vacuo over $P_4O_{10}$ yield 58-60%.

**RESULTS AND DISCUSSION :** Estimated data reported in Table-I suggested 1:1:1 (M: acid-hydrazide Schiff base: sulphur ligand) stoichiometry for the complexes. All the synthesised mixed ligand complexes are non-hygroscopic air stable and can be kept for a long time without change in colour.

TABLE-1

ANALYTICAL DATA OF MIXED LIGAND COMPLEXES OF Co (III) and Ni ( II)

| S. No. | Complex | % Chemical analysis; Found (Calculated) | | | | |
|---|---|---|---|---|---|---|
| | | Metal | C | H | N | S |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1 | $[Co(C_{13}H_{10}N_3O_3)(C_7H_6SO_2)NO_3]$ | 11.0<br>(11.10) | 45.03<br>(45.20) | 2.90<br>(3.01) | 10.40<br>(10.55) | 5.92<br>(6.04) |
| 2 | $[Co(C_{13}H_{10}N_3O_3)(C_6H_7NS)(H_2O)]NO_3$ | 11.20<br>(11.33) | 43.70<br>(43.85) | 3.49<br>(3.65) | 13.30<br>(13.46) | 6.0<br>(6.17) |
| 3 | $[Co(C_{13}H_{10}N_3O_3)(C_6H_6SO_2)(H_2O)]NO_3$ | 10.80<br>(10.97) | 42.30<br>(42.46) | 3.10<br>(3.35) | 10.20<br>(10.43) | 5.80<br>(5.97) |
| 4 | $[Co(C_{15}H_{12}N_3O_3)(C_7H_6NO_2)NO_3]$ | 10.40<br>(10.58) | 47.20<br>(47.40) | 3.15<br>(3.23) | 10.0<br>(10.05) | 5.60<br>(5.76) |
| 5 | $[Co(C_{15}H_{12}N_3O_3)(C_6H_7NS)(H_2O]NO_3$ | 10.60<br>(10.79) | 46.0<br>(46.15) | 3.70<br>(3.85) | 12.70<br>(12.82) | 5.70<br>(5.87) |
| 6 | $[Co(C_{15}H_{12}N_3O_3)(C_6H_6SO_2)(H_2O)]NO_3$ | 10.30 | 44.60 | 3.40 | 9.80 | 5.50 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | (10.47) | (44.76) | (3.55) | (9.95) | (5.69) | |
| 7 | $[Co(C_{12}H_9N_2O_4)(C_7H_6NO_2)NO_3]$ | 11.20<br>(11.30) | 43.70<br>(43.85) | 2.72<br>(2.88) | 7.90<br>(8.08) | 6.02<br>(6.17) | |
| 8 | $[Co(C_{12}H_9N_2O_4)(C_6H_7NS)(H_2O)]NO_3$ | 11.40<br>(11.58) | 42.30<br>(42.44) | 3.44<br>(3.54) | 10.90<br>(11.00) | 6.20<br>(6.30) | |
| 9 | $[Co(C_{12}H_9N_2O_4)(C_6H_6SO_2)(H_2O)]NO_3$ | 10.98<br>(11.20) | 41.0<br>(41.07) | 3.10<br>(3.23) | 7.90<br>(7.98) | 6.02<br>(6.10) | |
| 10 | $[Ni(C_{13}H_{10}N_3O_3)(C_6H_6SO_2)(H_2O)]NO_3$ | 10.80<br>(10.94) | 42.36<br>(42.48) | 3.23<br>(3.35) | 10.30<br>(10.43) | 5.80<br>(5.97) | |
| 11 | $[Ni(C_{15}H_{12}N_3O_3)(C_7H_6SO_2)NO_3]$ | 10.40<br>(10.54) | 47.30<br>(47.42) | 3.12<br>(3.23) | 10.0<br>(10.06) | 5.62<br>(5.76) | |
| 12 | $[Ni(C_{15}H_{12}N_3O_3)(C_6H_7NS)(H_2O]NO_3$ | 10.70<br>(10.76) | 46.10<br>(46.17) | 3.70<br>(3.85) | 12.47<br>(12.57) | 5.60<br>(5.76) | |
| 13 | $[Ni(C_{15}H_{12}N_3O_3)(C_6H_6SO_2)(H_2O)]NO_3$ | 10.30<br>(10.43) | 44.60<br>(44.78) | 3.42<br>(3.55) | 7.36<br>(7.46) | 5.60<br>(5.70) | |
| 14 | $[Ni(C_{12}H_9N_2O_4)(C_7H_6SO_2)NO_3]$ | 11.0<br>(11.30) | 43.72<br>(43.87) | 2.74<br>(2.89) | 8.0<br>(8.08) | 6.10<br>(6.17) | |
| 15 | $[Ni(C_{12}H_9N_2O_4)(C_6H_7NS)(H_2O)]NO_3$ | 11.40<br>(11.54) | 42.40<br>(42.45) | 3.40<br>(3.54) | 10.90<br>(11.01) | 6.20<br>(6.30) | |
| 16 | $[Ni(C_{12}H_9N_2O_4)(C_6H_6SO_2)(H_2O)]NO_3$ | 11.05<br>(11.17) | 40.90<br>(41.08) | 3.10<br>(3.23) | 7.82<br>(7.99) | 6.02<br>(6.10) | |

## ELECTRONIC SPECTRAL STUDIES :Co(III) MIXED LIGAND COMPLEXES

$[Co(C_7H_6SO_2)]\ NO_3$ where $L=C_{13}H_{10}N_3O_3/C_{15}H_{14}N_3O_3/C_{12}H_9N_2O_4$

Under the influence of tetrahedral field, the ground term of Co (III) ion i.e. $^4F$ gets split and consequently gives rise to these energy levels, $^4A_2$, $^4T_2$ and $^4T_1$ in the increasing order (16).

$^4T_1(P)>^4T_1(F)>^4T_2(F)>^4A_2(F)$

However, in a tetrahedral environment three spin-allowed bands are observed which may be assigned to:

$^4A_2(F) \rightarrow {}^4T_2(F)$ ($v_1$),

$^4A_2(F) \rightarrow {}^4T_1(F)$ ($v_2$),

and $^4A_2(F) \rightarrow {}^4T_2(P)$ ($v_3$)

Since $v_1$ band is very weak hence it seldom appears whereas the $v_2$ and $v_3$ bands being strong are invariably found in the spectra.

The absorption spectra of the solution of $[Co\ L\ (C_7H_6SO_2)]NO_3$ (where

$L=(C_{13}H_{10}N_3O_3)/(C_{15}H_{14}N_3O_3)/(C_{12}H_9N_2O_4)$ in DMF exhibit bands at 8.450-8, 520 and 15,600-15,650 $cm^{-1}$ assignable to $^4A_2(F)$ $^4T_1$ (F) and $^4A_2(F)$ $^4T_1$ (P) transitions respectively. A third band ($v_1$), though very weak, appears at 5,100-5,200 $cm^{-1}$. Using the method of Cotton and Goodgame, various ligand field parameters have been calculated. The mathematical equations for the above energy bands are as under:

$$v_1 = Dq. \quad (1)$$

$$v_2=1.5\ Dq+7.5\ B-Q \quad (2)$$

$$v_3=1.5\ Dq+7.5\ B+Q \quad (3)$$

$$Q=1/2\ [0.6\ Dq-15B)+0.64\ Dq^2]^{1/2} \quad (4)$$

Where B is the effective value of the Racah inter-electronic repulsion term in the complexes:

$\beta = B$ complex /B free ion

On solving these equations we get:

$$Dq=(v_2+v_3-15B)\ /3$$

$$Q=1/2(v_3-v_2)$$

$$4Q^2=Dq^2-18\ B\ Dq+225(B)^2$$

By making the use of the above equations, the values of different parameter have been calculated and tabulated in Table-2. The values of different parameters and magnetic moment show that the complexes $[CoL(C_7H_6SO_2]NO_3$ possess tetrahedral geometry. The spin-orbit coupling constant was calculated using the relation:

$L=(C_{13}H_{10}N_3O_3)/(C_{15}H_{14}N_3O_3)/(C_{12}H_9N_2O_4)$

$$\mu_{obs} = (\mu_{spin}\ only\ -31.12\ \lambda / \Delta)$$

**$[Co(C_{13}H_{10}N_3O_3)(C_6H_7NS)(H_2O)]NO_3$,$[Co(C_{13}H_{10}N_3O_3)(C_6H_6SO_2)(H_2O)]NO_3$$[Co(C_{15}H_{12}N_3O_3)(C_6H_7NS)(H_2O)]NO_3$,$[Co(C_{15}H_{12}N_3O_3)(C_6H_6SO_2)(H_2O)]NO_3$,$[Co(_{12}H_9N_2O_4)(C_6H_7NS)(H_2O)]NO_3$:$[Co(C_{12}H_9N_2O_4)(C_6H_6SO_2)(H_2O)]NO_3$:**

In octahedral Co(II) complexes three absorption transition are possible.

$$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)\ (v_1)$$

$$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)\ (v_2)$$

$$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(v_3)$$

band is generally broad and $v_3$ is a set of multiple bands and may be mixed with spin-forbidden transitions. The electronic spectra of Co(II) complexes, under study, show bands in the range 9,600-9,800, 17,800-18, 400 and 21,600-2,300 cm$^{-1}$ which may be assigned to the transition:

$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ($v_1$); $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ($v_2$); $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ($v_3$)

respectively characteristic of octahedral geometry(17) $v_1$ and $v_3$ bands are seen quite sharp $v_2$ band is very weak. The calculated values of the ligand field parameters are in conformity with the octahedral geometry of there ligand

## TABLE-2

## ELECTRONIC SPECTRAL BANDS, THEIR ASSIGNMENTS AND LIGAND FIELD PARAMETERS OF Co(III) MIXED LIGAND COMPLEXES

| S. No. | Complex | Bands (cm$^{-1}$) | 10 Dq (cm$^{-1}$) | B (cm$^{-1}$) | $\beta$ | L.F.S.E.(k. cal/mol) | $\lambda$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 | $[Co(C_{13}H_{10}N_3O_3)(C_7H_6SO_2)NO_3]$ | 5160 $^4A_2(F) \rightarrow {}^4T_2(F)$<br>8530$^4A_2(F) \rightarrow {}^4T_1(F)$<br>15620$^4A_2(F) \rightarrow {}^4T_1(P)$ | 5090 | 740 | 0.66 | 8.73 | -82.92 |
| 2 | $[Co(C_{15}H_{12}N_3O_3)(C_7H_6SO_2)NO_3]$ | 5220 $^4A_2(F) \rightarrow {}^4T_2(F)$<br>8470$^4A_2(F) \rightarrow {}^4T_1(F)$<br>15660$^4A_2(F) \rightarrow {}^4T_1(P)$ | 4760 | 760 | 0.68 | 8.16 | -78.77 |
| 3 | $[Co(C_{12}H_9N_2O_4)(C_7H_6SO_2)NO_3]$ | 5130$^4A_2(F) \rightarrow {}^4T_2(F)$<br>8545$^4A_2(F) \rightarrow {}^4T_1(F)$<br>15638$^4A_2(F) \rightarrow {}^4T_1(P)$ | 4850 | 810 | 0.73 | 8.31 | -96.04 |

**Ni(II) MIXED LIGAND COMPLEXES :** Stereochemistry of Ni(II) complexes of special interest from the spectrochemical point of view as it may form different types of the complexes viz. square-planar, tetrahedral, penta-coordinated and octahedral.

**$[Ni(C_{13}H_{10}N_3O_3)(C_7H_6SO_2)NO_3]$, $[Ni(C_{15}H_{12}N_3O_3)(C_7H_6SO_2)NO_3]$, $[Ni(C_{12}H_9N_2O_4)(C_7H_6SO_2)NO_3]$ :** The electronic spectra of these complexes are characteristic of square-planar geometry around the metal ion. The spectra exhibit a d-d band in the range 17,600-18,850 cm$^{-1}$ and $v_3$ band in 22,700-23m000 cm$^{-1}$ range. This second band has been observed(18-21) to be more intense. One weak band ($v_1$) also has been noticed at 12,200-12,350 cm$^{-1}$. The first two bands may be assigned to the following transition: $^1A_{1g}$ $^1A_{g2}$, $^1A_{1g}$ $^1B_{2g}$.(Table-3)

## TABLE-3

## PRINCIPAL BAND POSITIONS IN THE ELECTRONIC SPECTRA WITH POSSIBLE ASSIGMENTS AND THE LIGAND FIELD PARAMETERS OF MIXED LIGAND COMPLEXES OF Ni(II)

| S. No. | Complex | Observed Bands (cm-1) and their assignments | 10 Dq (cm$^{-1}$) | B (cm$^{-1}$) | $\beta$ | $v_2$ | $v_3$ | $v_2/v_1$ | L.F.S.E. (k.cal/ mol) | $\lambda$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| 1 | $[Ni(C_{13}H_{10}N_3O_3)(C_6H_7NS)(H_2O)NO_3$ | 9825 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>15136$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>24915$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ | 9825 | 712 | 0.69 | 15465 | 2464 | 1.54 | 33.66 | -266 |
| 2 | $[Ni(C_{13}H_{10}N_3O_3)(C_6H_6SO_2)(H_2O)NO_3$ | 9910$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>14922$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>25316$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ | 9910 | 702 | 0.68 | 15519 | 24610 | 1.60 | 33.97 | -310 |
| 3 | $[Ni(C_{15}H_{12}N_3O_3)(C_6H_7NS)(H_2O)NO_3$ | 9790$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ | 9790 | 765 | 0.74 | 15589 | 25166 | 1.55 | 35.0 | -204 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 15265 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>25334 $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ | | | | | | | | |
| 4 | $[Ni(C_{15}H_{12}N_3O_3)(C_6H_6SO_2)(H_2O)NO_3$ | 10040 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>16100 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>25973 $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ | 10040 | 685 | 0.66 | 15532 | 24334 | 1.60 | 34.42 | -322 |
| 5 | $[Ni(C_{12}H_9N_3O_3)(C_6H_7NS)(H_2O)NO_3$ | 9900 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>15310 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>24940 $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ | 9960 | 705 | 0.68 | 15563 | 24641 | 1.53 | 34.14 | -262 |
| 6 | $[Ni(C_{12}H_9N_3O_3)(C_6H_6SO_2)(H_2O)NO_3$ | 9740 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>15210 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>25140 $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ | 9740 | 756 | 0.73 | 15462 | 24862 | 1.56 | 33.39 | -240 |

**THERMAL BEHAVIOUR :** In investigated complexes the mode of coordination of the ligands is fully supported by their thermal behavior.In Co(III) complexes, it is observed that the water of hydration is eliminated at 70-290$^0$C which suggests the presence of water of hydration as coordinated water as well as crystal one. According to Nikolaev et.al(22-24) water eliminating below 150$^0$C can be considered as free crystal water and water eliminating above 150$^0$C may be due to its coordination to the metal ion. In case of the complexes of table-4 there is no mass-loss upto 260$^0$C suggesting the absence of lattice as well as coordinated water.

The Ni(II) complexes of table-4 showed two-step tree-step decomposition to produce stable residues. In Ni(II) complexes loss in weight corresponding to one water molecule takes place between 150-180$^0$C suggesting the presence of one molecule of coordinated water in them. All the Ni(II) complexes showed exothermic mass-losses in the temperature range 270-480$^0$C. On further heating, mass loss occurred gradually upto 680$^0$C. This is due to the oxidative decomposition of the ligands leading to the formation of stable metal oxide (NiO)(25,26).

## TABLE - 4

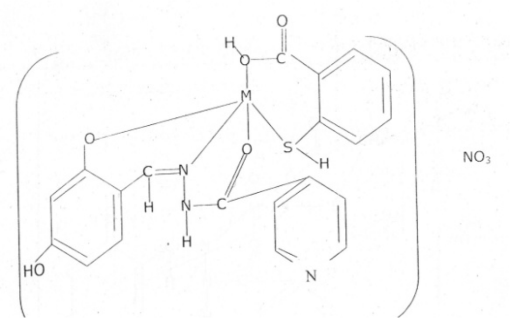
## THEROMOGRAVIMETRIC ANALYSIS OF Co (III) and Ni (II)MIXED LIGAND COMPLEXES

| S. No. | Complex | Dec. Temp. ($^0$C) | % Loss | | Species Formed | DTA Peak |
|---|---|---|---|---|---|---|
| | | | Observed | Calcd. | | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1 | $[Co(C_{13}H_{10}N_3O_3)(C_7H_6SO_2)NO_3]$ | 250-390<br>510-700 | 40.54<br>85.78 | 40.69<br>85.88 | $Co(C_{13}H_{10}N_3O_3)$<br>CoO | Exo. at 280-410$^0$C<br>Exo. at 480-700$^0$C |
| 2 | $[Co(C_{13}H_{10}N_3O_3)(C_6H_7NS)(H_2O)]NO_3$ | 150-190<br>260-410<br>510-720 | 3.30<br>39.30<br>85.40 | 3.46<br>39.44<br>85.59 | $[Co(C_{13}H_{10}N_3O_3)(C_6H_7SO_2)]NO_3$<br>$Co(C_{13}H_{10}N_3O_3)CoO$ | Exo. at 170$^0$C<br>Exo. at 270-400$^0$C<br>Exo. at 480-710$^0$C |
| 3 | $[Co(C_{13}H_{10}N_3O_3)(C_6H_6SO_2)(H_2O)]NO_3$ | 150-190<br>270-420<br>500-690 | 3.28<br>41.12<br>86.0 | 3.35<br>41.35<br>86.05 | $[Co(C_{13}H_{10}N_3O_3)(C_6H_6SO_2)]NO_3$<br>$Co(C_{13}H_{10}N_3O_3)CoO$ | Exo. at 190$^0$C<br>Exo. at 270-400$^0$C<br>Exo. at 470-700$^0$C |
| 4 | $[Co(C_{15}H_{12}N_3O_3)(C_7H_6SO_2)NO_3]$ | 250-410<br>500-690 | 38.70<br>86.40 | 38.79<br>86.55 | $Co(C_{15}H_{12}N_3O_3)$<br>CoO | Exo. at 280-400$^0$C<br>Exo. at 470-710$^0$C |
| 5 | $[Co(C_{15}H_{12}N_3O_3)(C_6H_7NS)(H_2O)]NO_3$ | 160-190<br>270-410 | 3.20<br>37.20 | 3.30<br>37.56 | $[Co(C_{15}H_{12}N_3O_3)(C_6H_7NS)]NO_3$ | Exo. at 180$^0$C<br>Exo. at 270-400$^0$C |

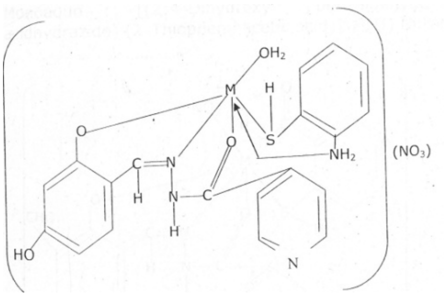
| | | | | | | |
|---|---|---|---|---|---|---|
| | | 500-680 | 85.10 | 86.28 | $Co(C_{13}H_{10}N_3O_3)CoO$ | Exo. at 480-700$^0$C |
| 6 | $[Co(C_{15}H_{12}N_3O_3)(C_6H_6SO_2)(H_2O)]NO_3$ | 150-180<br>250-410<br>500-680 | 3.10<br>39.30<br>86.50 | 3.20<br>39.44<br>86.69 | $[Co(C_{15}H_{12}N_3O_3)(C_6H_6SO_2)]NO_3$<br>$Co(C_{15}H_{12}N_3O_3)CoO$ | Exo. at 175$^0$C<br>Exo. at 270-400$^0$C<br>Exo. at 460-700$^0$C |
| 7 | $[Co(C_{12}H_9N_2O_4)(C_7H_6SO_2)NO_3]$ | 260-400<br>500-680 | 41.32<br>85.40 | 41.55<br>85.59 | $Co(C_{12}H_9N_2O_4)$<br>$CoO$ | Exo. at 270-400$^0$C<br>Exo. at 470-690$^0$C |
| 8 | $[Co(C_{12}H_9N_2O_4)(C_6H_7NS)(H_2O)]NO_3$ | 150-175<br>250-400<br>500-700 | 3.40<br>40.18<br>85.02 | 3.54<br>4.29<br>85.28 | $[Co(C_{12}H_9N_2O_4)(C_6H_7NS)]NO_3$<br>$Co(C_{13}H_{10}N_3O_3)CoO$ | Exo. at 175$^0$C<br>Exo. at 280-420$^0$C<br>Exo. at 490-700$^0$C |
| 9 | $[Ni(C_{13}H_{10}N_3O_3)(C_7H_6SO_2)NO_3]$ | 280-460<br>470-680 | 40.50<br>85.79 | 40.71<br>85.92 | $[Ni(C_{13}H_{10}N_3O_3)$<br>$NiO$ | Exo. at 280-470$^0$C<br>Exo. at 490-680$^0$C |
| 10 | $[Ni(C_{13}H_{10}N_3O_3)(C_6H_7NS)(H_2O)]NO_3$ | 160-180<br>280-480<br>480-680 | 3.36<br>38.50<br>85.30 | 3.46<br>38.63<br>85.63 | $[Ni(C_{13}H_{10}N_3O_3)(C_6H_7NS)]NO_3$<br>$Co(C_{13}H_{10}N_3O_3)CoO$ | Endo. at 170$^0$C<br>Exo. at 290-470$^0$C<br>Exo. at 460-670$^0$C |
| 11 | $[Ni(C_{13}H_{10}N_3O_3)(C_6H_6SO_2)(H_2O)]NO_3$ | 160-180<br>290-460<br>470-680 | 3.20<br>41.10<br>85.80 | 3.35<br>41.37<br>86.08 | $[Ni(C_{13}H_{10}N_3O_3)(C_6H_6SO_2)]NO_3$<br>$Co(C_{13}H_{10}N_3O_3)CoO$ | Endo. at 190$^0$C<br>Exo. at 300-470$^0$C<br>Exo. at 490-680$^0$C |
| 12 | $[Ni(C_{15}H_{12}N_3O_3)(C_7H_6SO_2)NO_3]$ | 270-470<br>480-680 | 38.60<br>86.40 | 38.81<br>86.58 | $[Ni(C_{15}H_{12}N_3O_3)$<br>$NiO$ | Exo. at 300-460$^0$C<br>Exo. at 450-680$^0$C |
| 13 | $[Ni(C_{15}H_{12}N_3O_3)(C_6H_7NS)(H_2O)]NO_3$ | 160-180<br>300-470<br>470-680 | 3.10<br>37.40<br>86.10 | 3.30<br>37.57<br>86.31 | $[Ni(C_{15}H_{12}N_3O_3)(C_6H_7NS)]NO_3$<br>$Co(C_{13}H_{10}N_3O_3)CoO$ | Endo. at 160$^0$C<br>Exo. at 310-490$^0$C<br>Exo. at 470-680$^0$C |
| 14 | $[Ni(C_{15}H_{12}N_3O_3)(C_6H_6SO_2)(H_2O)NO_3$ | 160-180<br>290-470<br>470-700 | 3.06<br>39.30<br>86.60 | 3.20<br>39.46<br>86.72 | $[Ni(C_{15}H_{12}N_3O_3)(C_6H_6SO_2)]NO_3$<br>$Ni(C_{15}H_{12}N_3O_3)$<br>$NiO$ | Endo. at 180$^0$C<br>Exo. at 300-490$^0$C<br>Exo. at 450-700$^0$C |
| 15 | $[Ni(C_{12}H_9N_2O_4)(C_7H_6SO_2) NO_3$ | 280-470<br>470-670 | 41.30<br>85.50 | 41.57<br>85.63 | $Ni(C_{12}H_9N_2O_4)$<br>$NiO$ | Exo. at 270-490$^0$C<br>Exo. at 460-670$^0$C |
| 16 | $[Ni(C_{12}H_9N_2O_4)(C_6H_7NS)(H_2O)NO_3$ | 160-180<br>290-460<br>470-670 | 3.24<br>40.20<br>85.10 | 3.54<br>40.31<br>85.32 | $[Ni(C_{15}H_{12}N_3O_3)(C_6H_7NS)]NO_3$<br>$Ni(C_{15}H_{12}N_3O_3)$<br>$NiO$ | Endo. at 175$^0$C<br>Exo. at 300-490$^0$C<br>Exo. at 490-670$^0$C |

**Conclusion :** The value of $\beta$ are less than unity suggesting considerably covalent character of the metal-ligand bond. The $\beta$ -value for these complexes are lower than those for free ion value indicating orbital overlap and delocalization of d-orbitals. The calculated value of the ligand field parameters are in conformity with the octahedral geometry of these complexes (35-37). The structural, spectral, and thermal studies of the metal complexes suggests the following structures:

### STRUCTURES OF Co (III) and Ni (II) MIXED LIGAND COMPLEXES

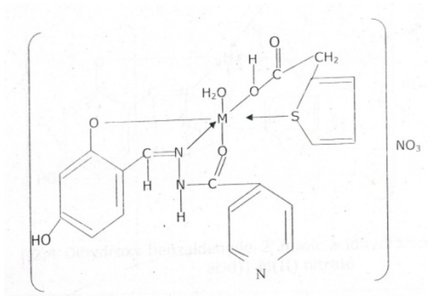


[2;4-Dihydroxy banzaldehyde Isonicotonic acidhydrazido) {Thiosalicylic acid)] - M(II) Nitrate

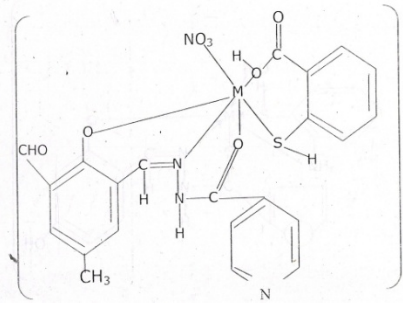


Monoaquo [2;4-Dihydroxy banzaldehyde Isonicotonic acidhydrazido) [Thiosalicylic acid)] - M(II) Nitrate

Where M= Co (III) and Ni (II)

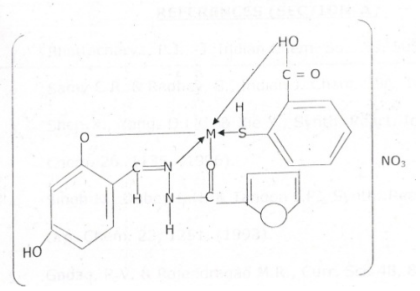


Monoaquo [2;4-Dihydroxy banzaldehyde Isonicotonic acidhydrazido) [Thiosalicylic acid)] - M(II) Nitrate

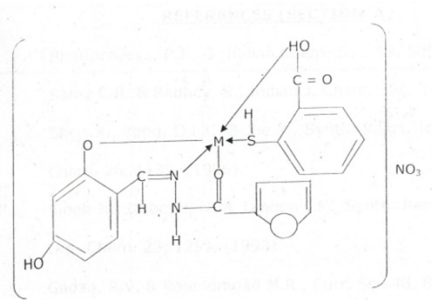


Nitrato-4-methyl-2;6-Diformyl phenol isonicotonic acidhydrazido) (2-Thiosalicylic acid)]-M(II)

Where M= Co (III) and Ni (II)



[2;4-Dihydroxy banzaldehyde Isonicotonic acidhydrazido) {Thiosalicylic acid)] - M(II) Nitrate



Monoaquo [2;4-Dihydroxy banzaldehyde Isonicotonic acidhydrazido) [Thiosalicylic acid)] - M(II) Nitrate

Where M=Co (III) and Ni (II)

## REFERENCES

1. Cleare M.N., Coord. Chem. Rev., 12, 349, (1974).
2. Haidcu I., Coord. Chem. Rev., 99, 253 and references therein (199).
3. Das, M. & Livingstone, S.E., Br. J. Chancer 37, 466 (1978).
4. Mohan, M., Sharma, P., Kumar M. & Jha N.K., Inorg. Chim. Acta 9, 125 (1986).
5. Singh B., Singh R.N. & Aggarwal, R.C, Polyhedron 4, 401, (1985).
6. Taozhang Hai & Brown T.L., J. Am. Chem. Soc. 115, 107 (1993).
7. Amesz J., Biochim. Biophys. Acta. 726, 1, (1983).
8. Nene Y.L. & Thapliyal P.N., Fungicides in plant disease control, 2nd Edn. (Oxford & IBH Publishing Co., New Delhi) 105, 1979.
9. Nighat Fahmi & Singh R.V., Indian Journal. Of Chemistry 36A, 805-808 (1997).

10. Bhattacharya, P.J., J. Indian Chem. Soc. 59, 505, (1982).
11. Samy C.R. & Radhey, S., Indian J. Chem. 35A, 1 (1996).
12. Shen X., Yang, Q.L.C. & Xie Y., Synth. React. Ionrg. Met. Org. Chem. 26, 1135, (1996).
13. Singh K., Dubey S.N. & Tandon J.P., Synth. React. Inorg. Met. Org. Chem. 23, 1251, (1993).
14. Gadag, R.V. & Rajendragad M.R., Curr. Sci. 48, 839 (1979).
15. Ashok K. Sen, Gurmit Singh, Kiran Singh, Raj K. Noreh, Ram N. Handa & Surendra N. Dubey, Indian Journal of Chemistry, 36A 891-894 (1997).
16. Holloway, C.E. & Melnik, M., J. Organometal. Chem. 495, 1 (1995).
17. Lever, A.B.P., "Inorganic Electronic Spectroscopy" Elsevier, New York, (1968).
18 Michael J. and Walton R.A. - J. Inorg. Nucl. Chem. 37, 71 (1975).
19. Movassagh B., Lakouraj M.M. and Ghodrati K., Indian J. Chem. 41B, 1293 (2002).
20. Norquist A.J., Heier K.R., Halsyamani P.S., Stern C.L. & Poeppelmeir K.R., Inorg. Chem. 40, 2015, (2001).
21. Laura Gagliardi and Bjorn O Rao S., Inorg. Chem. 42(5) 1599 (2003).
22. Nikolaev A.V., Logvinenko V.A. and Myachina L.I., "Thermal Analysis", Academic N.Y., 2, 779 (1969).
23. Seeney C.G., IIill J.O. and Magee R.J., Thermochimica Acta 11, 301 (1975).
24. Seeney C.G., Smith J.F., Hill J.O. and Magee R.J., J. Thermal Anal. 9, 415 (1979)
25. Fuchs R., Pumbee, D.S. (Jr.) and Rodewald F.F., Thermochim. Acta. 2, 515 (1971)
26. Nowicka B. and Osinska, Taniewska, S. Thermochim. Acta 115, 129 (1987)
27, Krishnan U, Iyer SK. Iminothiophenol Schiff base-based fluorescent probe for dual detection of Hg2+ and Cr3+ ions and its application in real sample analysis. Journal of Photochemistry and Photobiology A:Chemistry.2022;425:113663.
28. Bharali B, Talukdar H, Phukan P, Das DK. A new Schiff Base based fluorescent sensor for Al (III) based on 2-

Hydroxyacetophenone and o-Phenylenediamine. Journal of Fluorescence. 2020;30(4):751-757. DOI: 10.1007/s10895-020-02527-w J

29. Yuan C, Liu X, Wu Y, Lu L, Zhu M. A triazole Schiff base-based

selective and sensitive fluorescent probe for Zn2+: A combined

experimental and theoretical study. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2016;154:215-219. DOI: 10.1016/j.saa.2015.10.035

27. Fatima B, Hussain D, Bashir S, Hussain HT, Aslam R, Nawaz R, et al. Catalase immobilized antimonene quantum dots used as an electrochemical biosensor for quantitative determination of $H_2O_2$ from CA-125 diagnosed ovarian cancer samples. Materials Science and Engineering: C. 2020;117:111296. DOI: 10.1016/j.msec.2020.111296

28. Abou-Omar MN, Attia MS, Afify HG, Amin MA, Boukherroub R, Mohamed EH. Novel optical biosensor based on a nano-gold coated by Schiff base doped in sol/gel matrix for sensitive screening of oncomarker CA-125. ACS Omega. 2021;6(32):20812-20821. DOI: 10.1021/acsomega.1c01974

29. Sheta SM, Akl MA, Saad HE, El-Gharkawy ES. A novel cerium (iii)–isatin Schiff base complex: Spectrofluorometric and DFT studies and application as a kidney biomarker for ultrasensitive detection of human creatinine. RSC Advances. 2020;10(10):5853-5863. DOI: 10.1039/C9RA10133K

35. Horst Brombacher and Heinrich Vahrenkamp,Inorg. Chemistry

43(19),6054,(2004).

36. Hirayama, N.,Deguchi M.,Kawasumi H. and Honjo T., Talanta 65

(1) 225 (2005).

37. James W. canary, Shahab Mortezaie, Jian leang, coord. Chem. Rev.

254(19-20) 2249 (2010).

38. Kumari A, Meena R, Singh RV, Fahmi N. Synthesis, characterization, antimicrobial and DNA cleavage study of organoantimony (III) and organoarsenic (III) complexes with

monofunctional bidentate Schiff base. Indian Journal of Chemistry. 2021;60:341-347