

Structural and Thermal Decomposition Studies of Co(II), Ni(II) and Cu(II) Metal Complexes of Schiff Bases

Darpan Singh¹, Vishrut Chaudhary² and Meghraj Singh³

¹Lecturer, ²Assistant Professor, ³Lecturer

Department of Chemistry

¹DIET Meerut (U.P.), ²D.N. College Meerut (U.P.), ³ASIC Mawana Meerut (U.P.)

ABSTRACT:

Two types of complexes of Co(II), Ni(II) and Cu(II) with Schiff bases. Here we report the synthesis of complexes of above metal ion with 2;4-dihydroxybenzaldehydeisonicotinic acid hydrazide 4-methyl-2, 6 diformyl phenol isonicoticacidhydrazide as primary and thiosalicylic acid (TSA) 2-aminothiophenol (2-ATP) and 2-thiophene acetic acid (2-TPA) as coligand. The mixed ligand complexes are characterized on basis analytical spectral and thermal decomposition.

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

INTRODUCTION:

Transition metals and their derivative have evoked much interest due to their inherent biopotency⁽¹⁻⁴⁾ striking structural aspects and unique stereo and magneto chemistry⁵ The complexes of Maganese play important role in photo chemical reaction⁽⁶⁻⁷⁾. Several Magenesecomplexes are known to exhibit antifungal⁽⁸⁾ and antileukemic activities. Recently, a number of paper have appeared on transition metal complexes of N and S/O donor ligands.

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 compounds 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 thiolosulphur or hydroxo oxygen and azomethinenitrogen. The representative free ligands and their respective metal complexes were tested in vitro against different microorganisms to assess their antimicrobial properties⁽⁹⁾.

A perusal survey of the literature revealed that no work seems to have been done so far on the mixed ligand complexes of Co(II) Ni(II) and Cu(II) with substituted hydroxy aldehydes acidhydrazides as primary and sulphurdonors 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 metalions⁽¹⁴⁾. Here we report the synthesis of Co(II), Ni(II), and Cu(II) complexes with 2, 4-dihydroxy benzaldehydeisonicotinicacid hydrazide ($C_{13}H_{11}N_3O_3$), 4-methyl -2, 6-diformylphenolisonicotinic 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-ligand¹⁵. 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 behaviour of the mixed ligand complexes is also investigated ligand field parameters of the complexes viz. 10Dq, B, R have been calculated.

Experimental:

Preparation and Isolation of Complexes:

Co(II), Co(III), Ni(II) And Cu(II) Mixed Ligand Complexes:

The acidhydrazideschiff base (C₁₃H₁₁N₃O₃) / (C₁₅H₁₃N₃O₃) / (C₁₂H₁₀N₂O₂) in ethanol (50ml, 0.01 mol) was mixed with the solution of Co(NO₃)₂ 6H₂O/Ni(NO₃)₂ 6H₂O/Cu(NO₃)₂ 4H₂O/CoCl₂ 6H₂O/NiCl₂ 6H₂O / CuCl₂2H₂O (50 ml. 0.01 mol) dropwise with constant steering An aqueous ethanolic solution (50%, v/v) of thiosalicylic acid / 2-aminochiophenol/2-thiophene acetic acid (50ml 0.01 mol) was then added slowly and with constant stirring. The mixture having a 1:1:1 molar ratio was vigorously stirred for 20 min at 60°C on raising the pH to 6-7 with dilute ammonia solution, the whole content was then refluxed for 1-1.5h on a water bath. The coloured complexes, separated out on cooling, were filtered and washed subsequently with ethanol, hot water, and finally with dry ether and dried. The complexes were recrystallized from chloroform and dried under vacuum over P₄O₁₀ yield 58-60%.

RESULTS AND DISCUSSION

Analytical 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(II), Ni(II), AND Cu(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 ₃ O ₃)(C ₇ H ₆ SO ₂)NO ₃]	11.0 (11.10)	45.03 (45.20)	2.90 (3.01)	10.40 (10.55)	5.92 (6.04)
2	[Co(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	11.20 (11.33)	43.70 (43.85)	3.49 (3.65)	13.30 (13.46)	6.0 (6.17)
3	[Co(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	10.80 (10.97)	42.30 (42.46)	3.10 (3.35)	10.20 (10.43)	5.80 (5.97)
4	[Co(C ₁₅ H ₁₂ N ₃ O ₃)(C ₇ H ₆ NO ₂)NO ₃]	10.40 (10.58)	47.20 (47.40)	3.15 (3.23)	10.0 (10.05)	5.60 (5.76)
5	[Co(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	10.60 (10.79)	46.0 (46.15)	3.70 (3.85)	12.70 (12.82)	5.70 (5.87)
6	[Co(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	10.30 (10.47)	44.60 (44.76)	3.40 (3.55)	9.80 (9.95)	5.50 (5.69)
7	[Co(C ₁₂ H ₉ N ₂ O ₄)(C ₇ H ₆ NO ₂)NO ₃]	11.20 (11.30)	43.70 (43.85)	2.72 (2.88)	7.90 (8.08)	6.02 (6.17)
8	[Co(C ₁₂ H ₉ N ₂ O ₄)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	11.40 (11.58)	42.30 (42.44)	3.44 (3.54)	10.90 (11.00)	6.20 (6.30)
9	[Co(C ₁₂ H ₉ N ₂ O ₄)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	10.98 (11.20)	41.0 (41.07)	3.10 (3.23)	7.90 (7.98)	6.02 (6.10)
10	[Ni(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	10.80 (10.94)	42.36 (42.48)	3.23 (3.35)	10.30 (10.43)	5.80 (5.97)
11	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₇ H ₆ SO ₂)NO ₃]	10.40 (10.54)	47.30 (47.42)	3.12 (3.23)	10.0 (10.06)	5.62 (5.76)
12	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	10.70 (10.76)	46.10 (46.17)	3.70 (3.85)	12.47 (12.57)	5.60 (5.76)
13	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	10.30 (10.43)	44.60 (44.78)	3.42 (3.55)	7.36 (7.46)	5.60 (5.70)
14	[Ni(C ₁₂ H ₉ N ₂ O ₄)(C ₇ H ₆ SO ₂)NO ₃]	11.0 (11.30)	43.72 (43.87)	2.74 (2.89)	8.0 (8.08)	6.10 (6.17)
15	[Ni(C ₁₂ H ₉ N ₂ O ₄)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	11.40 (11.54)	42.40 (42.45)	3.40 (3.54)	10.90 (11.01)	6.20 (6.30)
16	[Ni(C ₁₂ H ₉ N ₂ O ₄)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	11.05	40.90	3.10	7.82	6.02

		(11.17)	(41.08)	(3.23)	(7.99)	(6.10)
17	[Cu(C ₁₅ H ₁₄ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	11.40 (11.50)	45.50 (45.60)	4.03 (4.16)	12.57 (12.67)	5.70 (5.80)
18	[Cu(C ₁₅ H ₁₄ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	11.02 (11.16)	44.14 (44.24)	3.76 (3.86)	9.70 (9.83)	5.53 (5.63)
19	[Cu(C ₁₂ H ₉ N ₂ O ₄)(C ₇ H ₆ SO ₂)NO ₃]	12.02 (12.11)	43.36 (43.46)	2.72 (2.86)	7.92 (8.01)	5.94 (6.09)
20	[Cu(C ₁₂ H ₉ N ₂ O ₄)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	12.22 (12.37)	41.90 (42.06)	3.33 (3.50)	10.80 (10.90)	6.12 (6.24)
21	[Cu(C ₁₂ H ₉ N ₂ O ₄)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	11.90 (11.98)	40.60 (40.71)	3.10 (3.20)	7.80 (7.92)	5.92 (6.04)
22	[Cu(C ₁₃ H ₁₀ N ₃ O ₃)(C ₇ H ₆ SO ₂)NO ₃]	11.72 (11.86)	44.70 (44.81)	2.82 (2.99)	10.36 (10.46)	5.83 (5.99)
23	[Cu(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)] NO ₃	12.02 (12.11)	43.36 (43.46)	3.50 (3.62)	13.22 (13.34)	6.02 (6.11)
24	[Cu(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)] NO ₃	11.62 (1.73)	42.0 (42.10)	3.20 (3.32)	10.24 (10.34)	5.80 (5.92)
25	[Cu(C ₁₅ H ₁₂ N ₃ O ₃)(C ₇ H ₆ SO ₂) NO ₃]	11.17 (11.27)	46.70 (46.84)	3.42 (3.55)	9.80 (9.94)	5.59 (5.69)

ELECTRONIC SPECTRAL STUDIES:

Co(II) MIXED LIGAND COMPLEXES:

[Co(C₇H₆SO₂)] NO₃ where L=C₁₃H₁₀N₃O₃/C₁₅H₁₄N₃O₃/C₁₂H₉N₂O₄

Under the influence of tetrahedral field, the ground term of Co(II) ion i.e. ⁴F gets split and consequently gives rise to these energy levels, ⁴A₂, ⁴T₂ and ⁴T₁ 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:

$${}^4A_2(F) \rightarrow {}^4T_2(F) (\nu_1),$$

$${}^4A_2(F) \rightarrow {}^4T_1(F) (\nu_2),$$

and
$${}^4A_2(F) \rightarrow {}^4T_2(P) (\nu_3)$$

Since ν_1 band is very weak hence it seldom appears whereas the ν_2 and ν_3 bands being strong are invariably found in the spectra.

The absorption spectra of the solution of [Co L (C₇H₆SO₂)]NO₃ (where L=(C₁₃H₁₀N₃O₃)/(C₁₅H₁₄N₃O₃)/(C₁₂H₉N₂O₄) in DMF exhibit bands at 8,450-8,520 and 15,600-15,650 cm⁻¹ assignable to ⁴A₂(F) ⁴T₁(F) and ⁴A₂(F) ⁴T₁(P) transitions respectively. A third band (ν_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:

$$\nu_1 = Dq. \tag{1}$$

$$\nu_2 = 1.5 Dq + 7.5 B - Q \tag{2}$$

$$\nu_3 = 1.5 Dq + 7.5 B + Q \tag{3}$$

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

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

$$\beta = B_{\text{complex}} / B_{\text{free ion}}$$

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 $[\text{CoL}(\text{C}_7\text{H}_6\text{SO}_2)\text{NO}_3]$ possess tetrahedral geometry. The spin-orbit coupling constant was calculated using the relation:

$$L = (\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3) / (\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}_3) / (\text{C}_{12}\text{H}_9\text{N}_2\text{O}_4)$$

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

$[\text{Co}(\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3)(\text{C}_6\text{H}_7\text{NS})(\text{H}_2\text{O})]\text{NO}_3$, $[\text{Co}(\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3)(\text{C}_6\text{H}_6\text{SO}_2)(\text{H}_2\text{O})]\text{NO}_3$, $[\text{Co}(\text{C}_{15}\text{H}_{12}\text{N}_3\text{O}_3)(\text{C}_6\text{H}_7\text{NS})(\text{H}_2\text{O})]\text{NO}_3$, $[\text{Co}(\text{C}_{15}\text{H}_{12}\text{N}_3\text{O}_3)(\text{C}_6\text{H}_6\text{SO}_2)(\text{H}_2\text{O})]\text{NO}_3$, $[\text{Co}(\text{C}_{12}\text{H}_9\text{N}_2\text{O}_4)(\text{C}_6\text{H}_7\text{NS})(\text{H}_2\text{O})]\text{NO}_3$, $[\text{Co}(\text{C}_{12}\text{H}_9\text{N}_2\text{O}_4)(\text{C}_6\text{H}_6\text{SO}_2)(\text{H}_2\text{O})]\text{NO}_3$:

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

$${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F}) (v_1)$$

$${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F}) (v_2)$$

$${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})(v_3)$$

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:

$${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F}) (v_1); {}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F}) (v_2); {}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P}) (v_3)$$

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

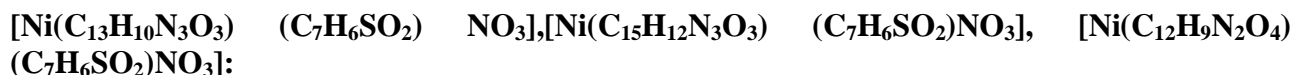
TABLE-2

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

S. No.	Complex	Bands (cm^{-1})	10 Dq (cm^{-1})	B (cm^{-1})	β	L.F.S.E.(k. cal/mol)	λ (cm^{-1})
1	$[\text{Co}(\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_3)(\text{C}_7\text{H}_6\text{SO}_2)\text{NO}_3]$	5160 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ 8530 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ 15620 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$	5090	740	0.66	8.73	-82.92
2	$[\text{Co}(\text{C}_{15}\text{H}_{12}\text{N}_3\text{O}_3)(\text{C}_7\text{H}_6\text{SO}_2)\text{NO}_3]$	5220 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ 8470 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ 15660 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$	4760	760	0.68	8.16	-78.77
3	$[\text{Co}(\text{C}_{12}\text{H}_9\text{N}_2\text{O}_4)(\text{C}_7\text{H}_6\text{SO}_2)\text{NO}_3]$	5130 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ 8545 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ 15638 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$	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.



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 v₃ band in 22,700-23m000 cm⁻¹ range. This second band has been observed⁽¹⁸⁻²¹⁾ to be more intense. One weak band (v₁) 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)	β	v ₂	v ₃	v ₂ /v ₁	L.F.S.E. (k.cal/mol)	λ (cm ⁻¹)
1	2	3	4	5	6	7	8	9	10	11
1	[Ni(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)NO ₃]	9825 ³ A _{2g} (F)→ ³ T _{2g} (F) 15136 ³ A _{2g} (F)→ ³ T _{2g} (F) 24915 ³ A _{2g} (F)→ ³ T _{1g} (P)	9825	712	0.69	15465	2464	1.54	33.66	-266
2	[Ni(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)NO ₃]	9910 ³ A _{2g} (F) → ³ T _{2g} (F) 14922 ³ A _{2g} (F)→ ³ T _{2g} (F) 25316 ³ A _{2g} (F)→ ³ T _{1g} (P)	9910	702	0.68	15519	24610	1.60	33.97	-310
3	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)NO ₃]	9790 ³ A _{2g} (F) → ³ T _{2g} (F) 15265 ³ A _{2g} (F)→ ³ T _{2g} (F) 25334 ³ A _{2g} (F)→ ³ T _{1g} (P)	9790	765	0.74	15589	25166	1.55	35.0	-204
4	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)NO ₃]	10040 ³ A _{2g} (F)→ ³ T _{2g} (F) 16100 ³ A _{2g} (F)→ ³ T _{2g} (F) 25973 ³ A _{2g} (F)→ ³ T _{1g} (P)	10040	685	0.66	15532	24334	1.60	34.42	-322
5	[Ni(C ₁₂ H ₉ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)NO ₃]	9900 ³ A _{2g} (F) → ³ T _{2g} (F) 15310 ³ A _{2g} (F)→ ³ T _{2g} (F) 24940 ³ A _{2g} (F)→ ³ T _{1g} (P)	9960	705	0.68	15563	24641	1.53	34.14	-262
6	[Ni(C ₁₂ H ₉ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)NO ₃]	9740 ³ A _{2g} (F) → ³ T _{2g} (F) 15210 ³ A _{2g} (F)→ ³ T _{2g} (F) 25140 ³ A _{2g} (F)→ ³ T _{1g} (P)	9740	756	0.73	15462	24862	1.56	33.39	-240

THERMAL BEHAVIOUR:

The mode of coordination of the ligands in the complexes has been further supported by their thermal behavior. Thermogravimetric analysis opens up new possibilities for the investigation of metal complexes.

Co(II) COMPLEXES:

It is observed that the water of hydration is eliminated at 70-290⁰C which suggests the presence of water of hydration as coordinated water as well as crystal one. According to Nikolaevet.al⁽²²⁻²⁴⁾ water eliminating below 150⁰C can be considered as free crystal water and water eliminating above 150⁰C may be due to its coordination to the metal ion. In case of the complexes.

(Table-4), there is no mass-loss upto 260⁰C 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 150-180⁰C suggesting the presence of one molecule of coordinated water in them. All the Ni(II) complexes showed exothermic mass-losses in the temperature range 270-480⁰C. On further

heating, mass loss occurred gradually upto 680^oC. This is due to the oxidative decomposition of the ligands leading to the formation of stable metal oxide (NiO)^(25,26).

The thermograms of the Cu(II) complexes show that the weight of the⁽²⁷⁻³¹⁾ complexes remains constant up to 270^oC in case of up to 190^oC in case of rest of the complexes. The complexes except show weight loss in the temperature range 190-210^oC corresponding to one molecule of water. Further, the loss in weight at this temperature range shows that the water molecule is in the coordinated form. The TG curves of all the Cu(II) complexes shows continuous loss in mass 260-550^oC temperature range due to the elimination of sulphur ligand, NO₂, O₂ etc. The on further heating further decomposition takes place in 540-660^oC temperature range. Ultimately complexes changes into oxide.

The DTA curves of the complexes containing coordinated water showed a broad endothermic peak in the temperature range 170-210^oC. Further, in DTA curves of all the complexes, the appearance of a broad multiple exothermic peak at 280-540^oC following by a sharp exothermic peak at 580-660^oC indicated the removal or both the ligands leading to the formation of CuO⁽³²⁻³⁴⁾.

TABLE - 4
THEROMOGRAVIMETRIC ANALYSIS OF Co(II), Ni(II)AND Cu(II) MIXED LIGAND COMPLEXES

S. No.	Complex	Dec. Temp. (°C)	% Loss		Species Formed	DTA Peak
			Observed	Calcd.		
1	2	3	4	5	6	7
1	[Co(C ₁₃ H ₁₀ N ₃ O ₃)(C ₇ H ₆ SO ₂)NO ₃]	250-390 510-700	40.54 85.78	40.69 85.88	Co(C ₁₃ H ₁₀ N ₃ O ₃) CoO	Exo. at 280-410 ^o C Exo. at 480-700 ^o C
2	[Co(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	150-190 260-410 510-720	3.30 39.30 85.40	3.46 39.44 85.59	[Co(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₇ S O ₂)]NO ₃ Co(C ₁₃ H ₁₀ N ₃ O ₃)CoO	Exo. at 170 ^o C Exo. at 270-400 ^o C Exo. at 480-710 ^o C
3	[Co(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	150-190 270-420 500-690	3.28 41.12 86.0	3.35 41.35 86.05	[Co(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₆ S O ₂)]NO ₃ Co(C ₁₃ H ₁₀ N ₃ O ₃)CoO	Exo. at 190 ^o C Exo. at 270-400 ^o C Exo. at 470-700 ^o C
4	[Co(C ₁₅ H ₁₂ N ₃ O ₃)(C ₇ H ₆ SO ₂)NO ₃]	250-410 500-690	38.70 86.40	38.79 86.55	Co(C ₁₅ H ₁₂ N ₃ O ₃) CoO	Exo. at 280-400 ^o C Exo. at 470-710 ^o C
5	[Co(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	160-190 270-410 500-680	3.20 37.20 85.10	3.30 37.56 86.28	[Co(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₇ N S)]NO ₃ Co(C ₁₃ H ₁₀ N ₃ O ₃) CoO	Exo. at 180 ^o C Exo. at 270-400 ^o C Exo. at 480-700 ^o C
6	[Co(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	150-180 250-410 500-680	3.10 39.30 86.50	3.20 39.44 86.69	[Co(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₆ S O ₂)]NO ₃ Co(C ₁₅ H ₁₂ N ₃ O ₃)CoO	Exo. at 175 ^o C Exo. at 270-400 ^o C Exo. at 460-700 ^o C
7	[Co(C ₁₂ H ₉ N ₂ O ₄)(C ₇ H ₆ SO ₂)NO ₃]	260-400 500-680	41.32 85.40	41.55 85.59	Co(C ₁₂ H ₉ N ₂ O ₄) CoO	Exo. at 270-400 ^o C Exo. at 470-690 ^o C
8	[Co(C ₁₂ H ₉ N ₂ O ₄)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	150-175 250-400 500-700	3.40 40.18 85.02	3.54 4.29 85.28	[Co(C ₁₂ H ₉ N ₂ O ₄)(C ₆ H ₇ N S)]NO ₃ Co(C ₁₃ H ₁₀ N ₃ O ₃)CoO	Exo. at 175 ^o C Exo. at 280-420 ^o C Exo. at 490-700 ^o C
9	[Ni(C ₁₃ H ₁₀ N ₃ O ₃)(C ₇ H ₆ SO ₂)NO ₃]	280-460 470-680	40.50 85.79	40.71 85.92	[Ni(C ₁₃ H ₁₀ N ₃ O ₃) NiO	Exo. at 280-470 ^o C Exo. at 490-680 ^o C
10	[Ni(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	160-180 280-480 480-680	3.36 38.50 85.30	3.46 38.63 85.63	[Ni(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₇ N S)]NO ₃ Co(C ₁₃ H ₁₀ N ₃ O ₃)CoO	Endo. at 170 ^o C Exo. at 290-470 ^o C Exo. at 460-670 ^o C
11	[Ni(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	160-180 290-460 470-680	3.20 41.10 85.80	3.35 41.37 86.08	[Ni(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₆ S O ₂)]NO ₃ Co(C ₁₃ H ₁₀ N ₃ O ₃)CoO	Endo. at 190 ^o C Exo. at 300-470 ^o C Exo. at 490-680 ^o C
12	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₇ H ₆ SO ₂)NO ₃]	270-470 480-680	38.60 86.40	38.81 86.58	[Ni(C ₁₅ H ₁₂ N ₃ O ₃) NiO	Exo. at 300-460 ^o C Exo. at 450-680 ^o C
13	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)]NO ₃	160-180 300-470 470-680	3.10 37.40 86.10	3.30 37.57 86.31	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₇ N S)]NO ₃ Co(C ₁₃ H ₁₀ N ₃ O ₃) CoO	Endo. at 160 ^o C Exo. at 310-490 ^o C Exo. at 470-680 ^o C
14	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	160-180	3.06	3.20	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₆ S O ₂)]NO ₃ Co(C ₁₃ H ₁₀ N ₃ O ₃) CoO	Endo. at 180 ^o C

	NO ₃	290-470 470-700	39.30 86.60	39.46 86.72	O ₂)]NO ₃ Ni(C ₁₅ H ₁₂ N ₃ O ₃) NiO	Exo. at 300-490 ⁰ C Exo. at 450-700 ⁰ C
15	[Ni(C ₁₂ H ₉ N ₂ O ₄)(C ₇ H ₆ SO ₂) NO ₃	280-470 470-670	41.30 85.50	41.57 85.63	Ni(C ₁₂ H ₉ N ₂ O ₄)NiO	Exo. at 270-490 ⁰ C Exo. at 460-670 ⁰ C
16	[Ni(C ₁₂ H ₉ N ₂ O ₄)(C ₆ H ₇ NS) (H ₂ O)NO ₃	160-180 290-460 470-670	3.24 40.20 85.10	3.54 40.31 85.32	[Ni(C ₁₅ H ₁₂ N ₃ O ₃)(C ₆ H ₇ N S)]NO ₃ Ni(C ₁₅ H ₁₂ N ₃ O ₃) NiO	Endo. at 175 ⁰ C Exo. at 300-490 ⁰ C Exo. at 490-670 ⁰ C
17	[Cu(C ₁₃ H ₁₀ N ₃ O ₃)(C ₇ H ₆ SO ₂)NO ₃]	270-540 560-640	40.0 85.0	40.34 85.15	Cu(C ₁₃ H ₁₀ N ₃ O ₃) CuO	Exo. at 290-520 ⁰ C Exo. at 580-630 ⁰ C
18	[Cu(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)] NO ₃	190-210 260-550 540-660	3.34 38.92 84.70	3.43 39.09 84.84	[Cu(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₇ N)] NO ₃ CuO	Endo at 170-210 ⁰ C Exo. at 280-540 ⁰ C Exo. at 660 ⁰ C
19	[Cu(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₆ SO ₂)(H ₂ O)]NO ₃	190-200 270-550 560-660	3.10 40.85 85.08	3.32 41.00 85.31	[Cu(C ₁₃ H ₁₀ N ₃ O ₃)(C ₆ H ₆ S O ₂)] NO ₃ CuO	Endo at 170-210 ⁰ C Exo. at 280-540 ⁰ C Exo. at 640 ⁰ C
20	[Cu(C ₁₅ H ₁₄ N ₃ O ₃)(C ₇ H ₆ SO ₂)]NO ₃	270-540 560-660	38.05 85.60	38.34 85.89	Cu(C ₁₅ H ₁₄ N ₃ O ₃) CuO	Exo. at 170-210 ⁰ C Exo. at 280-520 ⁰ C
21	[Cu(C ₁₅ H ₁₄ N ₃ O ₃)(C ₆ H ₇ NS)(H ₂ O)] NO ₃	190-200 270-530 560-650	3.12 36.96 85.15	3.26 37.11 85.61	[Cu(C ₁₅ H ₁₄ N ₃ O ₃)(C ₆ H ₇ N S)]NO ₃ Cu(C ₁₅ H ₁₄ N ₃ O ₃) CuO	Endo at 180-200 ⁰ C Exo. at 290-520 ⁰ C Exo. at 580 ⁰ C
22	[Cu(C ₁₅ H ₁₄ N ₃ O ₃)(C ₆ H ₇ SO ₂)(H ₂ O)]NO ₃	190-200 270-530 560-650	3.04 38.70 85.78	3.16 38.99 86.08	[Cu(C ₁₅ H ₁₄ N ₃ O ₃)(C ₆ H ₇ SO ₂)]NO ₃ Cu(C ₁₅ H ₁₄ N ₃ O) CuO	Endo at 180-210 ⁰ C Exo. at 290-540 ⁰ C Exo. at 600 ⁰ C

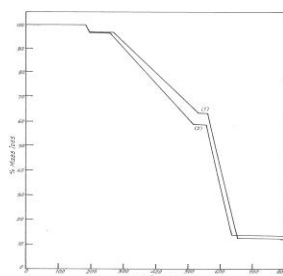


Fig. 2: Thermo gravimetric curves of Cu(II) complexes:
(I): [Cu(C₁₅H₁₄N₃O₃)(C₇H₆SO₂)]NO₃ (166g)
(II): [Cu(C₁₅H₁₄N₃O₃)(C₆H₇NS)(H₂O)]NO₃ (166g)

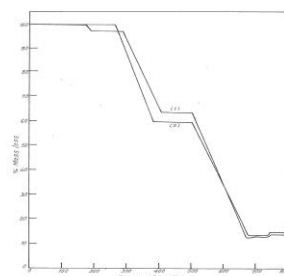


Fig. 1: Thermo gravimetric curves of Co(II) complexes:
(I): [Co(C₁₅H₁₄N₃O₃)(C₇H₆SO₂)]NO₃ (166g)
(II): [Co(C₁₅H₁₄N₃O₃)(C₆H₇NS)(H₂O)]NO₃ (166g)

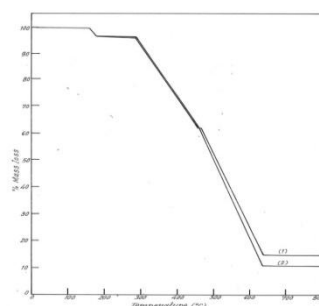
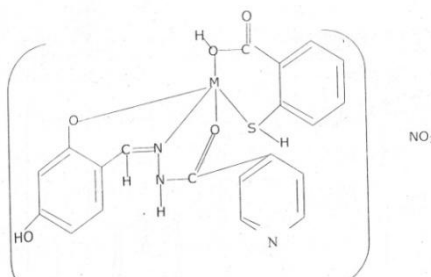


Fig. 3: Thermo gravimetric curves of Ni(II) complexes:
(I): [Ni(C₁₅H₁₄N₃O₃)(C₇H₆SO₂)]NO₃ (166g)
(II): [Ni(C₁₅H₁₄N₃O₃)(C₆H₇NS)(H₂O)]NO₃ (166g)

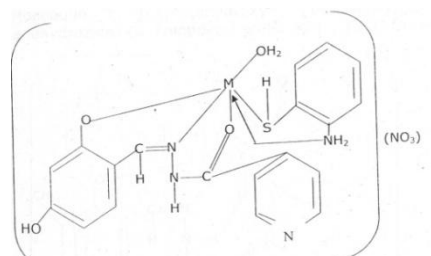
CONCLUSION:

The B-value for these complexes are lower than those for free ion value indicating orbital overlap and delocalization of d-orbitals. The value of β are less than unity suggesting considerably covalent character of the metal-ligand bond. The calculated value of the ligand field parameters are in conformity with the octahedral geometry of these complexes⁽³⁵⁻³⁷⁾. On the studies of structural, spectral and thermal the structural of the metal complexes are given below:

STRUCTURES OF Co(II), Co(III), Ni(II), Cu(II) AND Mn(II) MIXED LIGAND COMPLEXES

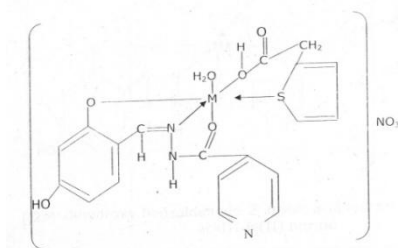


[2;4-Dihydroxy benzaldehydeisonicotonicacidhydrazido) {Thiosalicylic acid}] - M(II) Nitrate

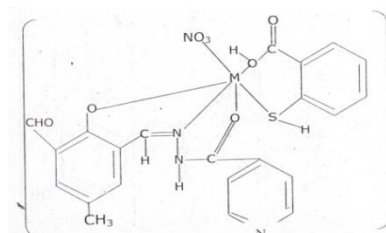


Monoaquo [2;4-Dihydroxy benzaldehydeisonicotonicacidhydrazido) [Thiosalicylic acid]] - M(II) Nitrate

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

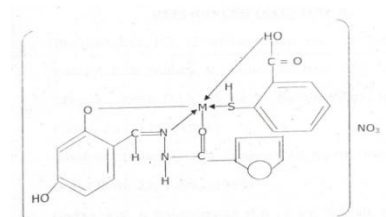


Monoaquo [2;4-Dihydroxy benzaldehydeisonicotonicacidhydrazido) [Thiosalicylic acid]] - M(II) Nitrate

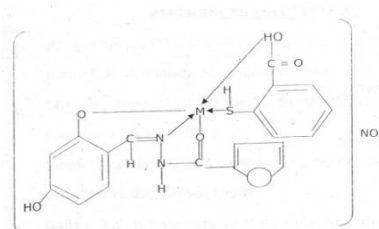


Nitrato-4-methyl-2;6-Diformyl phenol isonicotonicacidhydrazido) (2-Thiosalicylic acid)]-M(II)

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



[2;4-Dihydroxy benzaldehydeisonicotonicacidhydrazido) {Thiosalicylic acid}] - M(II) Nitrate



Monoaquo [2;4-Dihydroxy banzaldehydeIsonicotonicacidhydrazido) [Thiosalicylic acid]] - M(II)
Nitrate

Where M=Co(II), Ni(II) and Cu(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. & Poepelmeir 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., Hill 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. Piekarski, H. and Waiszewski D., *Thermochim. Acta.* 190, 299 (1991).
28. Piekarska A. and Osinska, Taniewska S., *Thermochim. Acta* 194, 109 (1992).
29. Piekarska A. and Osinska, Taniewska, S., *Thermochim Acta* 170, 189 (1999).
30. Moreau C. & Douheret G., *Thermo Chim. Acta*, 13, 385 (1975).
31. Moreau C. & Douheret G., *J. Chem. thermodyn.* 8, 403 (1976).
32. Pal A. and Singh Y.P., *J. Chem. Thermodyn.* 26, 1063 (1994).
33. Davis M.I. and Chacon M., *Thermo Chem. Acta*, 190, 259 (1991).
34. Chandrasekhar S., Takhi M. & Mahapatra S., *Synth. Commun.* 26, 3947 (1996).
35. Horst Brombacher and Heinrich Vahrenkamp, *Inorg. Chemistry* 43(19), 6054, (2004).
36. Hirayama, N., Deguchi M., Kawasumi H. and Honjo T., *Talanta* 65225 (2005).
37. James W. canary, Shahab Mortezaie, Jianleang, *coord. Chem. Rev.* 254(19-20) 2249 (2010).