Synthesis, Spectroscopic and Physicochemical Characterization and Biological Activity of Co(II) and Ni(II) Coordination Compounds with 4-Aminoantipyrine Thiosemicarbazone

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ABSTRACT

We describe the synthesis and characterization of cobalt(II) and nickel(II) coordination compounds of 4[N-(furan-2'-aldimine)amino]antipyrine thiosemicarbazone (FFAPTS) and 4[N-(4'-nitro-benzalidene)amino]antipyrine thiosemicarbazone (4'-NO₂BAAPTS). All the isolated compounds have the general composition MX₂(L)(H₂O) (M = Co²⁺ or Ni²⁺; X = Cl, Br, NO₃, NCS or CH₃COO; L = FFAPTS or 4'-NO₂BAAPTS) and M(ClO₄)₂(L)₂ (M = Co²⁺ or Ni²⁺; L = FFAPTS or 4'-NO₂BAAPTS). Infrared spectral studies indicate that both the thiosemicarbazones coordinate in their neutral form and they act as {N,N,S} tridentate chelating ligands. Room temperature magnetic measurements and electronic spectral studies suggest the distorted octahedral geometries of the prepared complexes. Thermogravimetric studies are also reported and the possible structures of the complexes are proposed. Antibacterial and antifungal properties of these metal-coordination compounds have also been studied.

Key Words: Cobalt(II), Nickel(II), Complexes, Thiosemicarbazone, Biological Activity.

INTRODUCTION

Of the sulfur donor ligands, thiosemicarbazones have perhaps not been given as much attention as dithiophosphate /1/, dithiocarbamates /2,3/, dithiolates /4/, dithio-β-diketonates /5/, dithiooxamide /6/ or

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xanthates /3/. Although many thiosemicarbazones possess a wide spectrum of medicinal properties, including activity against influenza /7/, protozoa /8/, smallpox /9/, certain kinds of tumor /10/, tuberculosis /11/, leprosy /12/, bacterial /13/ and viral infections /14/, psoriasis /15/, rheumatism and tripanosomiasis /16/, coccidiosis /17/, malaria /18/, and have been suggested as possible pesticides /19/ and fungicides /20/, their activity has frequently been thought to be due to their ability to chelate trace metals. Liebermeister /21/ showed that copper ions enhance the antitubercular activity of *p*-acetamidobenzaldehyde thiosemicarbazone. Similarly, Petering *et al.* /22/ showed that the active intermediate in the antitumour activity of 3-ethoxy-2-oxobutylaldehyde bis-(thiosemicarbazone) (H_2KTS) was the chelate $Cu(KTS)$. These findings have continuously led to an increased interest in the chemistry of metal chelates of thiosemicarbazones. A number of review articles /23-28/ have appeared on various metal-coordination complexes of thiosemicarbazones. In recent years a number of workers have also reported some transition metal coordination complexes of thiosemicarbazones. /29-36/. Comparatively less is known about transition metal coordination complexes of thiosemicarbazones having a pyrazolone ring. In view of this, in the present work we describe the synthesis, spectral, magnetic, thermal and biological properties of Co^{2+} and Ni^{2+} complexes of 4 [N-(furan-2'-aldimine)amino]antipyrine thiosemicarbazone (FFAPTS) (I) and 4[N-(4'-nitrobenzalidene)amino]antipyrine thiosemicarbazone (4'-NO₂BAAPTS) (II).

FFAPTS (I)

4'-NO₂BAAPTS (II)

EXPERIMENTAL

$MX_2 \cdot nH_2O$ ($M = Co^{2+}$ or Ni^{2+} ; $X = Cl, Br, NO_3$ or CH_3COO) were obtained from BDH and were used as such. $M(NCS)_2$ ($M = Co^{2+}$ or Ni^{2+}) were prepared by mixing metal chloride (in ethanol) and ethanolic solution of potassium thiocyanate in 1:2 molar ratio. Precipitated KCl was filtered off and filtrate having respective metal thiocyanate was used immediately for complex formation. $M(ClO_4)_2$ ($M = Co^{2+}$ or Ni^{2+})

were prepared by the addition of an ethanolic solution of sodium perchlorate into respective metal chloride solutions. White precipitate of NaCl was filtered off and the filtrate containing $M(\text{ClO}_4)_2$ was used as such for complex formation. Both the thiosemicarbazones ligands, *i.e.* FFAAPTS and 4'-NO₂BAAPTS, were synthesized in the laboratory as described previously /37/.

Synthesis of the complexes

Co²⁺ complexes of FFAAPTS or 4'-NO₂BAAPTS

All the complexes were prepared by mixing ethanolic solution of ligand and metal salts in required molar ratio (1:1/1:2 where both the ligands were in 10% excess). The reaction mixture was refluxed on a water bath for 2-3 hrs and then concentrated to a small volume on a hot plate at ~50°C. After cooling, desired crystals of the complexes obtained were filtered, recrystallized and washed in the ethanol and dried in vacuum over P₄O₁₀.

Ni²⁺ complexes of FFAAPTS or 4'-NO₂BAAPTS

A general method was used for the preparation of the complexes. A hot ethanolic solution of the corresponding nickel(II) salt was mixed with a hot ethanolic solution of the respective ligand (in 1:1 or 1:2 molar ratios where both the ligands were in 10% excess). The reaction mixture was refluxed on a water bath for ~2 hrs. On cooling at room temperature, the desired complexes were precipitated out in each case. They were filtered, recrystallized, washed with ethanol and diethyl-ether and finally dried over P₄O₁₀ under vacuum.

Physical measurements and analytical estimations

The cobalt(II) and nickel(II) in their metal complexes were estimated complexometrically with EDTA using murexide and erichrome black-T as indicators respectively after decomposing the complexes with conc. H₂SO₄ and H₂O₂ /38/. The halogens and pseudo halogens were estimated by Volhard's method /39/. The perchlorate was estimated by the method suggested by Kurz *et al.* /40/. The percentage of sulfur was estimated gravimetrically as BaSO₄. The nitrogen content was determined by the Kjeldahl method.

The molecular weight of the complexes was determined in the laboratory cryoscopically in freezing nitrobenzene using a Beckmann thermometer of $\pm 0.01^\circ\text{C}$ accuracy. The conductivity measurements were carried out, at room temperature in nitrobenzene, using a conductivity bridge and dip type cell operated at 220 volts A.C. mains. The magnetic measurements on powder form of the complexes were carried out at room temperature on Evans's balance using anhydrous copper(II) sulfate as calibrant. The infrared spectra of the complexes were recorded on a Perkin Elmer infrared spectrophotometer model Spectrum 1000 in CsI pellets in the range of 4000-200 cm⁻¹. Diffused reflectance spectra of the solid compounds were recorded on a Beckmann DK-2A spectrophotometer at C.D.R.I, Lucknow, India. Thermogravimetric studies of the complexes were carried out on Santon Red Craft Thermobalance Model TG-750 in static air with open sample holder and a small boat, the heating rate was 6°C/min.

RESULTS AND DISCUSSION

The reaction of Co^{2+} and Ni^{2+} with FFAPTS and 4'- NO_2 BAPTS yielded the $\text{MX}_2(\text{L}) (\text{H}_2\text{O})$; [$\text{M} = \text{Co}^{2+}$ or Ni^{2+} ; $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{NCS}$ or CH_3COO] and $\text{M}(\text{ClO}_4)_2(\text{L})_2$ [$\text{M} = \text{Co}^{2+}$ or Ni^{2+} ; $\text{L} = \text{FFAPTS}$ or 4'- NO_2 BAPTS]. The analytical data of these complexes showed that the solids are stable and can be stored for months without any significant change in their formulae. These complexes are generally soluble in common organic solvents. The molar conductance values of the complexes in nitrobenzene reveal that the halo, nitrate, isothiocyanato and acetato complexes are essentially non-electrolytes, while the perchlorato complexes dissociate in nitrobenzene and behave as 1:2 electrolytes /41/. The cryoscopic molecular weights and conductivity data are presented in Tables 1 and 2. The molecular weight results are in broad agreement with the conductance data suggesting monomeric formulations.

Magnetic susceptibility

The magnetic measurements of the cobalt(II) complexes (4.8-5.4 BM) (Table 1) show that all are paramagnetic and have three unpaired electrons indicating a high-spin octahedral configuration. The paramagnetism observed for the present series of Ni^{2+} complexes ranges from 2.6-3.2 BM (Table-2), which is consistent with the octahedral stereochemistry of these complexes.

Infrared spectra

A study and comparison of infrared spectra of both thiosemicarbazone ligands (FFAPTS and 4'- NO_2 BAPTS) and their Co^{2+} and Ni^{2+} complexes (Tables 3-6) imply that these ligands behave as neutral tridentate and the metals are coordinated through N and N of two azomethine groups and of S of thio-keto group. The strong bands observed at $3440\text{-}3270\text{ cm}^{-1}$ region in both thiosemicarbazones have been observed due to N-H vibrations. Practically no effect on these frequencies after complexation preclude the possibility of complexation at this group. The absorptions at $\sim 1600\text{ cm}^{-1}$ in free ligands may be attributed to C=N stretching vibrations of imine-nitrogen which is in agreement with the previous observations[42,43]. On complexation FFAPTS and 4'- NO_2 BAPTS with Co^{2+} and Ni^{2+} these frequencies are shifted to lower energies (Tables 3-6). These observations suggest involvement of unsaturated nitrogen atoms of the two azomethine groups in bonding with the metal ions.

In substituted thioureas, the C=S stretching vibrations contributed greatly to some other vibrations as C-N stretching and bending as well as N-C-S bending modes /44/. In the spectra of the present ligands, the bands observed in the region $1300\text{-}1125\text{ cm}^{-1}$, $1125\text{-}1095\text{ cm}^{-1}$ and $840\text{-}730\text{ cm}^{-1}$ regions are assigned to [$\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \nu(\text{C}-\text{N})$], $\delta(\text{N}-\text{C}-\text{S}) + \delta(\text{C}=\text{S})$ bending and $\nu(\text{C}=\text{S})$ stretching, respectively, which are in line with the observations of previous researchers /45,46/. Coordination of sulfur with the metal ions results in the displacement of electrons towards the latter, thus resulting in the weakening of C=S bond. Hence on complexation C=S stretching vibrations should decrease and those of C-N should increase. In all the present complexes of Co^{2+} and Ni^{2+} with FFAPTS and 4'- NO_2 BAPTS, frequencies in the range $1300\text{-}1125\text{ cm}^{-1}$

Table 1

Analytical, conductivity, molecular weight and magnetic moment data of Co^{2+} complexes of FFAAPTS and 4'-NO₂BAAPTS.

Complex	Yield (%)	Analysis: found (calcd.) %				m.w. Found (Calcd.)	$\Omega\text{m (ohm}^{-1}\text{cm}^2\text{ mole}^{-1})$	μ_{eff} (B.M.)
		Co	N	S	Anion			
$\text{CoCl}_2(\text{H}_2\text{O})(\text{FFAAPT})$	72	11.70 (11.75)	16.63 (16.73)	6.30 (6.37)	14.03 (14.14)	496 (502)	3.1	3.1
$\text{CoBr}_2(\text{H}_2\text{O})(\text{FFAAPT})$	70	9.92 (9.98)	14.10 (14.21)	5.32 (5.41)	26.97 (27.07)	587 (591)	3.7	2.9
$\text{Co}(\text{NO}_3)_2(\text{H}_2\text{O})(\text{FFAAPT})$	75	10.57 (10.63)	20.06 (20.18)	5.70 (5.76)	-	551 (555)	3.9	3.2
$\text{Co}(\text{NCS})_2(\text{H}_2\text{O})(\text{FFAAPT})$	70	10.70 (10.78)	20.33 (20.47)	17.49 (17.55)	21.04 (21.20)	544 (547)	4.0	2.6
$\text{Co}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})(\text{FFAAPT})$	68	10.67 (10.74)	15.20 (15.30)	5.76 (5.82)	-	546 (549)	3.4	3.2
$\text{Co}(\text{ClO}_4)_2(\text{FFAAPT})_2$	70	6.05 (6.10)	17.27 (17.39)	6.55 (6.62)	20.50 (20.60)	318 (966)	52.3	3.0
$\text{CoCl}_2(\text{H}_2\text{O})(4'\text{-NO}_2\text{BAAPTS})$	70	10.52 (10.59)	17.46 (17.59)	5.69 (5.74)	12.63 (12.74)	553 (557)	3.7	5.1
$\text{CoBr}_2(\text{H}_2\text{O})(4'\text{-NO}_2\text{BAAPTS})$	70	9.06 (9.13)	15.08 (15.17)	4.91 (4.95)	24.63 (24.76)	641 (646)	3.4	4.9
$\text{Co}(\text{NO}_3)_2(\text{H}_2\text{O})(4'\text{-NO}_2\text{BAAPTS})$	72	9.61 (9.67)	20.79 (20.93)	5.17 (5.24)	-	607 (610)	2.7	5.0
$\text{Co}(\text{NCS})_2(\text{H}_2\text{O})(4'\text{-NO}_2\text{BAAPTS})$	65	9.72 (9.80)	20.50 (20.65)	15.83 (15.94)	19.17 (19.26)	597 (602)	3.1	4.8
$\text{Co}(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})(4'\text{-NO}_2\text{BAAPTS})$	60	9.69 (9.76)	16.14 (16.22)	5.23 (5.29)	-	599 (604)	2.9	5.2
$\text{Co}(\text{ClO}_4)_2(4'\text{-NO}_2\text{BAAPTS})_2$	60	5.40 (5.48)	18.13 (18.21)	5.87 (5.94)	18.30 (18.49)	356 (1076)	51.9	5.4

Table 2Analytical, conductivity, molecular weight and magnetic moment data of Ni²⁺ complexes of FFAAPTS and 4'-NO₂BAAPTS.

Complex	Yield (%)	Analysis : Found (Calcd.) %				m.w. Found (Calcd.)	Ωm (ohm ⁻¹ cm ² mole ⁻¹)	μ_{eff} (B.M.)
		Ni	N	S	Anion			
NiCl ₂ (H ₂ O)(FFAAPS)	75	11.71 (11.75)	16.62 (16.73)	6.29 (6.37)	14.04 (14.14)	497 (502)	3.1	3.1
NiBr ₂ (H ₂ O)(FFAAPS)	70	9.90 (9.98)	14.10 (14.21)	5.32 (5.41)	26.95 (27.07)	597 (591)	3.7	2.9
Ni(NO ₃) ₂ (H ₂ O)(FFAAPS)	75	10.55 (10.63)	20.06 (20.18)	5.70 (5.76)	-	551 (555)	3.9	3.2
Ni(NCS) ₂ (H ₂ O)(FFAAPS)	72	10.69 (10.78)	20.35 (20.47)	17.47 (17.55)	21.06 (21.20)	543 (547)	4.0	2.6
Ni(CH ₃ COO) ₂ (H ₂ O)(FFAAPS)	70	10.64 (10.74)	15.19 (15.30)	6.76 (5.82)	-	545 (549)	3.4	3.2
Ni(ClO ₄) ₂ (FFAAPS) ₂	70	6.03 (6.10)	17.26 (17.39)	6.55 (6.62)	20.48 (20.60)	319 (966)	52.3	3.0
NiCl ₂ (H ₂ O)(4'-NO ₂ BAAPTS)	70	10.51 (10.59)	17.47 (17.59)	5.68 (5.74)	12.63 (12.74)	553 (557)	3.9	2.9
NiBr ₂ (H ₂ O)(4'-NO ₂ BAAPTS)	68	9.06 (9.13)	15.07 (15.17)	4.90 (4.95)	24.64 (24.76)	642 (646)	4.1	3.0
Ni(NO ₃) ₂ (H ₂ O)(4'-NO ₂ BAAPTS)	72	9.62 (9.67)	20.80 (20.93)	5.18 (5.24)	-	606 (610)	2.9	3.2
Ni(NCS) ₂ (H ₂ O)(4'-NO ₂ BAAPTS)	70	9.71 (9.80)	20.52 (20.65)	15.82 (15.94)	19.15 (19.26)	598 (602)	3.6	2.8
Ni(CH ₃ COO) ₂ (H ₂ O)(4'-NO ₂ BAAPTS)	70	9.67 (9.76)	16.13 (16.22)	5.23 (5.29)	-	599 (604)	3.9	2.7
Ni(ClO ₄) ₂ (4'-NO ₂ BAAPTS) ₂	65	5.41 (5.48)	18.13 (18.21)	5.85 (5.94)	18.32 (18.49)	355 (1076)	52.9	2.9

Table 3
Infrared Absorption frequencies (cm^{-1}) of Co^{2+} complexes of FFAAPTS.

Assignments	FFAAPTS	CoCl_2 (FFAAPTS). H_2O	CoBr_2 (FFAAPTS). H_2O	$\text{Co}(\text{NO}_3)_2$ (FFAAPTS). H_2O	$\text{Co}(\text{NCS})_2$ (FFAAPTS). H_2O	$\text{Co}(\text{CH}_3\text{COO})_2$ (FFAAPTS). H_2O	$\text{Co}(\text{ClO}_4)_2$ (FFAAPTS). H_2O
$\nu(\text{N-H})$	3440 s 3280 s	3442 s 3280 m	3440 s 3282 m	3445 s 3282 m	3442 s 3285 m	3440 s 3282 m	3442 m 3280 m
$\nu(\text{C=N})$	1600 s	1570 s	1550 s	1550 s	1542 s	1552 s	1550 m
$\nu(\text{C=S}) +$ $\nu(\text{C=N}) +$ $\nu(\text{C-N})$	1315 s 1185 m	1350 s 1220 m	1335 m 1210 m	1330 m 1215 m	1332 m 1220 m	1330 m 1222 m	1335 m 1215 m
$\delta(\text{N-C-S}) +$ C-S bending	1122 m 1095 m	1162 m 1110 m	1155 m 1112 m	1150 m 1115 m	1152 m 1112 m	1155 m 1115 m	1150 m 1120 m
$\nu(\text{N-N})$	1040 m	1052 m	1055 m	1058 m	1050 m	1052 m	1055 m
$\nu(\text{C=S})$	840 s 820 m 780 s	810 m 795 m	812 m 790 m	815 m 792 m	825 m 795 m	815 m 775 m	812 m 780 m
$\nu(\text{Co-N})$ $\nu(\text{Co-S})$	-	410 m 345 w	405 m 340 w	412 m 342 w	408 m 340 w	410 m 350 w	405 m 345 w
$\nu(\text{Co-Cl})$	-	342 w	-	-	-	-	-

Table 4
Infrared absorption frequencies (cm^{-1}) of Co^{2+} complexes of 4'- NO_2 BAAPTS.

Assignments	4'- NO_2 BAAPTS	CoCl_2 4'- (NO_2) BAAPTS). H_2O	CoBr_2 (4'- NO_2 BAAPTS). H_2O	$\text{Co}(\text{NO}_3)_2$ (4'-BAAPTS). H_2O	$\text{Co}(\text{NCS})_2$ (4'- NO_2 BAAPTS). H_2O	$\text{Co}(\text{CH}_3\text{COO})_2$ (4'- NO_2 BAAPTS). H_2O	$\text{Co}(\text{ClO}_4)_2$ 2(4'- NO_2 BAAPTS).
$\nu(\text{N-H})$	3355 s 3330 m	3350 m 3330 m	3358 s 3335 w	3360 m 3332 m	3360 s 3332 m	3358 m 3330 m	3360 m 3332 w
$\nu(\text{C=N})$	1600 s	1578 m	1575 m	1565 m	1570 m	1565 m	1570 m
$\nu(\text{C=S}) +$ $\nu(\text{C=N}) +$ $\nu(\text{C-N})$	1310 m 1290 m	1360 m 1315 m	1370 m 1320 m	1375 m 1322 m	1370 m 1340 m	1372 m 1340 m	1365 m 1335 m
$\delta(\text{N-C-S}) +$ C-S bending	1115 m 1095 w	1150 m 1130 m	1160 m 1130 m	1162 m 1138 m	1165 m 1142 m	1155 m 1135 m	1160 m 1135 m
$\nu(\text{N-N})$	1052 m	1062 m	1065 m	1062 m	1065 m	1068 m	1065 m
$\nu(\text{C=S})$	832 s 730 m	780 s 740 m	770 s 745 m	755 s 735 m	772 s 745 m	770 m 742 m	765 s 732 m
$\nu(\text{Co-N})$ $\nu(\text{Co-S})$	-	410 m 342 w	410 m 332 w	405 m 330 w	412 m 332 w	410 m 340 w	408 m 335 w
$\nu(\text{Co-Cl})$	-	325 w	-	-	-	-	-

Table 5
Infrared Absorption frequencies (cm⁻¹) of Ni²⁺ complexes of FFAAPTS.

Assignments	FFAAPTS	NiCl ₂ (FFAAPTS). H ₂ O	NiBr ₂ (FFAAPTS). H ₂ O	Ni(NO ₃) ₂ (FFAAPTS). H ₂ O	Ni(NCS) ₂ (FFAAPTS). H ₂ O	Ni(CH ₃ COO) ₂ (FFAAPTS). H ₂ O	Ni(ClO ₄) ₂ (FFAAPTS) ₂
v(N-H)	3440 s 3280 s	3445 s 3280 m	3442 s 3282 m	3445 s 3285 m	3442 s 3280 m	3442 m 3282 m	3440 s 3282 m
v(C=N)	1600 s	1552 s	1565 s	1555 s	1560 s	1562 s	1555 s
v(C=S) + v(C=N) + v(C-N)	1315 s 1185 m	1330 s 1216 m	1350 s 1220 m	1335 m 1210 m	1330 m 1215 m	1332 m 1222 m	1335 m 1215 m
δ(N-C-S)+ C-S bending	1122 m 1095 m	1152 m 1115 m	1162 m 1112 m	1155 m 1115 m	1152 m 1112 m	1155 m 1115 m	1150 m 1122 m
v(N-N)	1040 m	1058 m	1055 m	1060 m	1058 m	1055 m	1052 m
v(C=S)	840 s 820 m 780 s	820 m 795 m	815 m 792 m	825 m 795 m	815 m 775 m	812 m 782 m	812 m 792 m
v(Ni-N)/ v(Ni-S)	-	410 m 345 w	405 m 352 w	408 m 348 w	412 m 345 w	408 m 348 w	410 m 345 w
v(Ni-Cl)	-	345 w	-	-	-	-	-

Table 6
Infrared Absorption frequencies (cm⁻¹) of Ni²⁺ complexes of 4'-NO₂BAAPTS.

Assignments	4'-NO ₂ BAAPTS	NiCl ₂ 4'-(NO ₂ BAAPTS). H ₂ O	NiBr ₂ (4'-NO ₂ BAAPTS). H ₂ O	Ni(NO ₃) ₂ (4'-NO ₂ BAAPTS). H ₂ O	Ni(NCS) ₂ (4'-NO ₂ BAAPTS). H ₂ O	Ni(CH ₃ COO) ₂ (4'-NO ₂ BAAPTS). H ₂ O	Ni(ClO ₄) ₂ (4'-NO ₂ BAAPTS) ₂
v(N-H)	3355 s 3330 m	3365 m 3332 m	3360 m 3332 w	3362 m 3335 w	3365 s 3330 m	3358 m 3332 m	3335 m 3330 w
v(C=N)	1600 s	1568 m	1570 s	1565 m	1550 m	1545 m	1552 m
v(C=S)+ v(C=N)+ v(C-N)	1310 m 1290 m	1370 m 1340 m	1373 m 1335 m	1370 m 1342 m	1372 m 1335 m	1378 m 1340 m	1375 m 1335 m
δ(N-C-S)+ C-S bending	1115 m 1095 w	1160 m 1120 w	1165 m 1130 w	1168 m 1135 w	1170 m 1125 w	1172 m 1128 w	1168 m 1130 w
v(N-N)	1052 m	1062 m	1065 m	1068 m	1065 m	1060 m	1065 m
v(C=S)	832 s 730 m	772 s 705 m	775 m 715 m	780 m 710 m	778 m 718 m	780 m 712 m	770 s 715 m
v(Ni-N)/ v(Ni-S)	-	410 m 345 w	408 m 352 w	412 m 340 w	408 m 355 w	412 m 350 w	410 m 348 w
v(Ni-Cl)	-	342 w	-	-	-	-	-

increased by 50-60 cm^{-1} . Similarly, bending modes of N-C-S and C=S also increased but to a lesser extent. On the other hand, on complexation the frequencies in region 840-730 cm^{-1} were shifted to lower wave numbers and intensity of the bands were also reduced. The changes described are not peculiar and they suggest (C=S) coordination.

The possibility of thione-thiol tautomerism ($\text{H-N-C=S} \rightleftharpoons \text{C=N-SH}$) in these ligands has been ruled out for no bands around 2700-2500 cm^{-1} , which is characteristic of thiol groups displayed in the infrared absorption /47,48/. In the far infrared spectral region, some new bands with medium to weak intensity in region 410-350 cm^{-1} were assigned to $\nu(\text{M-N})$ and $\nu(\text{M-S})$. Thus the infrared spectral suggested the tridentate nature of the thiosemicarbazones and pointed out the N,N,S sites as possible donor atoms. In these complexes, the presence of coordinated water was suggested by the very broad absorption centered around 3450 cm^{-1} in their infrared spectra. Bands at ~ 930 and 770 cm^{-1} may be attributed to rocking and wagging modes of the coordinated water /49,50/.

In all the perchlorato complexes, the presence of the ν_3 (1100-1080 cm^{-1}) and ν_4 (625-620 cm^{-1}) bands showed that the T_d symmetry of ClO_4^- is maintained in all the complexes. This suggested the presence of ClO_4^- outside the coordination sphere in these complexes /51,52/. In thiocyanato complexes, the three fundamental absorption C-N stretch (ν_1), C-S stretch (ν_3) and N-C-S bending (ν_2) were identified in regions 2045-2030, 845-840 and 475-460 cm^{-1} respectively. These frequencies are associated with the terminal N-bonded isothiocyanate ions /53/.

In nitrate complexes, the infrared data indicated the occurrence of two strong absorption bands in 1560-1520 cm^{-1} and 1310-1300 cm^{-1} regions, which were attributed to ν_4 and ν_1 modes of vibrations of the covalently bonded nitrate groups, respectively /54/. If the $(\nu_4-\nu_1)$ is taken as an approximate measure of the covalency of nitrate group /55,56/, a value of $\sim 220 \text{ cm}^{-1}$ for these complexes suggested strong covalency for the metal-nitrate bonding. Lever *et al.* /57/ have shown that the number and relative energies of nitrate combination frequencies ($\nu_1+\nu_4$) in the region 1800-1700 cm^{-1} of the infrared spectrum, may be used as an aid to distinguish the various coordination modes of the nitrate group. Lever *et al.* /57/ have suggested that bidentate coordination of the nitrate group involves a greater distortion from D_{3h} symmetry than unidentate coordination, therefore, bidentate nitrate groups should show a larger separation of $(\nu_1+\nu_4)$. After an investigation of the spectra of a number of compounds of known crystal structure, Lever *et al.* /57/ showed this to be true; the separation for monodentate nitrate groups appeared to be 5-26 cm^{-1} and that for bidentate groups 25-66 cm^{-1} . In the present complexes, a separation of 15-25 cm^{-1} in the combination bands ($\nu_1+\nu_4$) in the 1800-1700 cm^{-1} region concluded the monodentate nitrate coordination. In acetato complexes, the $\nu_{\text{asym}}(\text{COO}^-)$ of free acetate ions are at ~ 1560 and 1415 cm^{-1} respectively. In the unidentate complex, $\nu(\text{C=O})$ is higher than $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu(\text{C-O})$ is lower than $\nu_{\text{sym}}(\text{COO}^-)$. As a result, the separation between the two $\nu(\text{C-O})$ is much larger in unidentate complexes than free ion. The opposite trend is observed in the bidentate complex, *i.e.* the separation between the $\nu(\text{C-O})$ is smaller than that of free ion in this case. In the bridging complexes, however, two $\nu(\text{C-O})$ are closed to the free ion values. The present complexes showed infrared absorption frequency bands corresponding to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ at ~ 1610 and 1370 cm^{-1} , respectively. These observations indicated that both the acetate groups in the present complexes are unidentate /58,59/.

Electronic spectra

The electronic spectra of all the Co^{2+} complexes recorded were very similar to each other and consist of two bands in the regions $18500\text{--}18000\text{ cm}^{-1}$ and $21000\text{--}20000\text{ cm}^{-1}$, which clearly indicated the octahedral stereochemistry of the complexes. The band maxima and their assignments are presented in Table 7. In the present work the ligand field parameters were calculated by the methods given by Reedijk *et al.* /60/ for the ligand field spectra of octahedral Co^{2+} complexes. The energy of ν_1 corresponds to $10 D_q$ for weak field and the value of D_q is obtained from it. With these assignments, the calculated ligand field parameters B and D_q have also been calculated and given in Table 7. The existence of distortion from a regular octahedral structure was revealed by appreciable intensity enhancement in all the Co^{2+} complexes studied. Apart from this, no differences in the spectra of regular and pseudo octahedral complexes of Co^{2+} were observed.

The absorption spectra of the Ni^{2+} complexes studied displayed bands (Table 8) in $11000\text{--}8200\text{ cm}^{-1}$ (ν_1), $17500\text{--}15400\text{ cm}^{-1}$ (ν_2) and $27500\text{--}24500\text{ cm}^{-1}$ (ν_3) suggested the octahedral stereochemistry of these complexes /61,62/. The calculated $10 D_q$ values are also included in Table 8. In the corresponding $[\text{NiCl}_6]^{2-}$, $[\text{NiBr}_6]^{2-}$ or $[\text{Ni}(\text{NCS})_6]^{2-}$, the $10 D_q$ values are of the order of 7200, 7000 and 9700 cm^{-1} respectively. Comparing these values with our results, we can say that there is a weakening effect of axial ligand strength in the complexes. This weakening effect of the axial ligands is expected because the equatorial ligands exert a strong steric hinderance preventing axial ligands from approaching the central metal as closely as would be required for optimum covalent bonding /63/.

Thermogravimetric studies

The thermogravimetric results of cobalt(II) complexes of FFAAPTS (L_1) are presented in Table 9. The thermogravimetric data indicated that the complexes were stable up to 85°C and non-hygroscopic in nature. At temperature range of $80\text{--}125^\circ\text{C}$, one coordinated water molecule is lost, after which decomposition and deligation processes started. Finally, at $\sim 600^\circ\text{C}$, Co_3O_4 was obtained as final residue. The thermal decomposition may be represented by the following equations:

Table 7Electronic spectral data (cm^{-1}) and ligand field parameters of Co(II) complexes of FFAAPTS.

Complex	ν_2 ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$	N_3 ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	D_Q (cm^{-1})	B (cm^{-1})	β	D_Q/β	ν_1 (cm^{-1})
$\text{CoCl}_2(\text{FFAAPTS}) \cdot \text{H}_2\text{O}$	18520	20000	1115	1070	0.96	1.04	8770
$\text{CoBr}_2(\text{FFAAPTS}) \cdot \text{H}_2\text{O}$	18180	20000	1104	1060	0.95	1.04	8700
$\text{Co}(\text{NO}_3)_2(\text{FFAAPTS}) \cdot \text{H}_2\text{O}$	18000	20835	1104	1060	0.95	1.04	8690
$\text{Co}(\text{NCS})_2(\text{FFAAPTS}) \cdot \text{H}_2\text{O}$	18100	20835	1105	1061	0.95	1.04	8700
$\text{Co}(\text{CH}_3\text{COO})_2(\text{FFAAPTS}) \cdot \text{H}_2\text{O}$	18520	20000	1105	1070	0.96	1.04	8772
$\text{Co}(\text{ClO}_4)_2(\text{FFAAPTS})_2$	18000	20833	1104	1060	0.95	1.04	8690
$\text{CoCl}_2(4'\text{-NO}_2\text{BAAPTS}) \cdot \text{H}_2\text{O}$	18000	20833	1104	1060	0.95	1.04	8690
$\text{Co}(\text{NO}_3)_2(4'\text{-NO}_2\text{BAAPTS}) \cdot \text{H}_2\text{O}$	18180	20000	1104	1060	0.95	1.04	8700
$\text{Co}(\text{NCS})_2(4'\text{-NO}_2\text{BAAPTS}) \cdot \text{H}_2\text{O}$	18520	20835	1104	1060	0.95	1.04	8696
$\text{Co}(\text{CH}_3\text{COO})_2(4'\text{-NO}_2\text{BAAPTS}) \cdot \text{H}_2\text{O}$	18180	20000	1115	1070	0.96	1.04	8772
$\text{Co}(\text{ClO}_4)_2(4'\text{-NO}_2\text{BAAPTS})_2$	18180	20835	1105	1061	0.95	1.04	8700

Table 8Electronic spectral data (cm^{-1}) and ligand field parameters of Ni(II) complexes of FFAAPTS.

Complex	ν_1	ν_2	ν_3	D_q (cm^{-1})	B (cm^{-1})	β
$\text{NiCl}_2(\text{FFAAPTS}) \cdot \text{H}_2\text{O}$	9600	16200	24400	960	1043	0.96
$\text{Ni}(\text{NO}_3)_2(\text{FFAAPTS}) \cdot \text{H}_2\text{O}$	9900	16600	24390	990	1076	0.99
$\text{Ni}(\text{NCS})_2(\text{FFAAPTS}) \cdot \text{H}_2\text{O}$	9800	16700	24500	980	1065	0.98
$\text{Ni}(\text{CH}_3\text{COO})_2(\text{FFAAPTS}) \cdot \text{H}_2\text{O}$	9600	15380	25640	960	1093	0.96
$\text{Ni}(\text{ClO}_4)_2(\text{FFAAPTS})_2$	9090	15150	25000	910	988	0.91
$\text{NiCl}_2(4'\text{-NO}_2\text{BAAPTS}) \cdot \text{H}_2\text{O}$	8240 10870	17540	27500	1087	829	0.79
$\text{Ni}(\text{NO}_3)_2(4'\text{-NO}_2\text{BAAPTS}) \cdot \text{H}_2\text{O}$	8270 10930	17700	27200	1093	794	0.76
$\text{Ni}(\text{NCS})_2(4'\text{-NO}_2\text{BAAPTS}) \cdot \text{H}_2\text{O}$	8200 10810	17540	26950	1081	804	0.77
$\text{Ni}(\text{CH}_3\text{COO})_2(4'\text{-NO}_2\text{BAAPTS}) \cdot \text{H}_2\text{O}$	10990	16950	27400	1099	750	0.73
$\text{Ni}(\text{ClO}_4)_2(4'\text{-NO}_2\text{BAAPTS})_2$	10930	17700	27000	1093	794	0.76

Table 9

Thermoanalytical results obtained for the Co(II) complexes of FFAAPTS.

Complex	Decomp, Temp. (°C)		Decomp. Products	Weight loss (%)	
	Initial	Final		Found	Calcd.
CoCl ₂ (FFAAPTS).H ₂ O	85	120	CoCl ₂ (FFAAPTS)	3.66	3.58
	200	280	CoCl ₂ (FFAAPTS) _{0.5}	39.98	38.84
	320	360	CoCl ₂	75.20	74.10
	520	600	Co ₃ O ₄	85.10	83.99
Co(NO ₃) ₂ (FFAAPTS).H ₂ O	80	120	Co(NO ₃) ₂ (FFAAPTS)	3.40	3.24
	190	260	Co(NO ₃) ₂ (FFAAPTS) _{0.5}	36.10	35.13
	320	370	Co(NO ₃) ₂	68.00	67.02
	530	605	Co ₃ O ₄	86.70	85.52
Co(NCS) ₂ (FFAAPTS).H ₂ O	85	125	Co(NCS) ₂ (FFAAPTS)	3.46	3.29
	180	275	Co(NCS) ₂ (FFAAPTS) _{0.5}	36.32	35.64
	315	365	Co(NCS) ₂	68.86	68.00
	530	610	Co ₃ O ₄	86.20	85.31
NiBr ₂ (4'-NO ₂ BAAPTS).H ₂ O	80	125	NiBr ₂ (4'-NO ₂ BAAPTS)	2.86	2.78
	175	260	NiBr ₂ (4'-NO ₂ BAAPTS) _{0.5}	35.02	34.44
	300	360	NiBr ₂	66.80	66.09
	505	590	NiO	89.10	88.39
Ni(NO ₃) ₂ (4'-NO ₂ BAAPTS).H ₂ O	85	120	Ni(NO ₃) ₂ (4'-NO ₂ BAAPTS)	3.10	2.95
	190	265	Ni(NO ₃) ₂ (4'-NO ₂ BAAPTS) _{0.5}	37.10	36.47
	300	380	Ni(NO ₃) ₂	70.90	70.00
	535	610	NiO	88.20	87.70
Ni(NCS) ₂ (4'-NO ₂ BAAPTS).H ₂ O	85	125	Ni(NCS) ₂ (4'-NO ₂ BAAPTS)	3.10	2.99
	185	260	Ni(NCS) ₂ (4'-NO ₂ BAAPTS) _{0.5}	37.50	36.96
	280	370	Ni(NCS) ₂	71.80	70.93
	525	605	NiO	88.30	87.54

The thermal results of Ni(II) complexes of 4'-NO₂BAAPTS (L₂) are also presented in Table 9. The careful analysis of thermogravimetric curves showed the following thermal equations:

Biological properties

A number of workers /27,31,64-67/ were interested in investigating the biological and medicinal properties of transition metal complexes of thiosemicarbazones. Thomas and Parmeswaran /31/ studied the antitumour activities of Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺ chelates of anthracene-9-carboxaldehyde thiosemicarbazone. Murthy and Dharmaraja /64/ reported the cytotoxic activity of phenylglyoxal bis(thiosemicarbazone) against *Ehrlich ascites* carcinoma cells. These compounds were also screened for antimicrobial activity on *B.subtilis* and *E.coli*. They inhibited the bacterial growth considerably. In the present studies, the antibacterial activities of the cobalt(II) complexes and standard drugs (ampicillin and tetracycline) were screened by agar-cup method in DMF solvent at a concentration of 50 µg/ml; the results were checked against gram positive bacteria *B.subtilis* and *S.aureus* and gram negative bacteria *E.coli* and *S.typhi* (Table 10). The diameters of zone of inhibition (in mm) of the standard drug ampicillin against gram positive bacteria *B.subtilis* and *S.aureus* and gram negative bacteria *E.coli* and *S.typhi* were found to be 24, 22, 17 and 16 respectively, while tetracycline gave 18, 17, 21 and 22 respectively. Under identical conditions, Table 10 shows that all the cobalt(II)-thiosemicarbazone complexes have moderate antibacterial activities against these bacteria. Both thiosemicarbazones and their cobalt(II) complexes were screened for their antifungal activities against two fungi (*A.niger* and *C.albicans*). The results (Table-10) showed that almost all complexes showed nearly the same extent of activity, but they are less active compared to salicylic acid. It is interesting to note that due to presence of furan ring and comparatively faster diffusion of FFAAPTS complexes showed increased antifungal activity than that of 4'-NO₂BAAPTS complexes. These compounds were found to be efficient antifungal agents.

Table 10Antifungal and antibacterial activities of cobalt(II) complexes of FFAAPTS and 4'-NO₂BAAPTS.

Complex	Antibacterial activity				Antifungal Action	
	Zone of inhibition in numbers					
	B. s	S.a	E.c.	S.t	A niger	albicans ^c
CoCl ₂ (H ₂ O)(FFAAPTS)	14	15	13	14	++	++
CoBr ₂ (H ₂ O)(FFAAPTS)	12	10	11	10	++	++
Co(NO ₃) ₂ (H ₂ O)(FFAAPTS)	11	10	10	11	++	++
Co(NCS) ₂ (H ₂ O)(FFAAPTS)	15	14	16	15	+++	++
Co(CH ₃ COO) ₂ (H ₂ O)(FFAAPTS)	11	10	12	10	++	++
Co(ClO ₄) ₂ (FFAAPTS) ₂	11	10	11	11	++	++
CoCl ₂ (H ₂ O)(4'-NO ₂ BAAPTS)	12	10	11	12	+	+
CoBr ₂ (H ₂ O)(4'-NO ₂ BAAPTS)	11	11	10	09	+	+
Co(NO ₃) ₂ (H ₂ O)(4'-NO ₂ BAAPTS)	10	09	11	10	+	+
Co(NCS) ₂ (H ₂ O)(4'-NO ₂ BAAPTS)	12	11	10	08	+	+
Co(CH ₃ COO) ₂ (H ₂ O)(4'-NO ₂ BAAPTS)	10	09	11	10	+	+
Co(ClO ₄) ₂ (4'-NO ₂ BAAPTS) ₂	11	10	09	10	+	+
Ampicillin	24	22	17	16	-	-
Tetracycline	18	17	21	22	-	-
Salicylic acid	-	-	-	-	++++	++++

CONCLUSION

The type of complexes isolated during the present study demonstrate that interactions of Co^{2+} and Ni^{2+} salts with thiosemicarbazones lead to complexes with 1:1 and 1:2 stoichiometries. Co(II) complexes of both the thiosemicarbazones showed moderate antibacterial activities against *E.coli* and *S.typhi*. The compounds have antifungal activity against *A.niger* and *C.albicans*. FFAPTS complexes showed increased antifungal activity than that of 4'-NO₂BAPTS complexes. The overall experimental evidence shows that these metal ions display a coordination number six and presumably have a distorted octahedral environment around the metal ion as shown in Figures 1 and 2.

Fig. 1: Probable structure of Ni and Co metal complexes of thiosemicarbazone:
 $[\text{MX}_2(\text{H}_2\text{O})(\text{L})]$; ($\text{M} = \text{Co}^{2+}$ or Ni^{2+} ; $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{NCS}$ or OAc and $\text{L} = \text{FFAPTS}$ or 4'-NO₂BAPTS).

Fig. 2: Probable structure of Ni and Co metal complexes of thiosemicarbazone:
 $[\text{M}(\text{ClO}_4)_2(\text{L})_2]$; ($\text{M} = \text{Co}^{2+}$ or Ni^{2+} and $\text{L} = \text{FFAPTS}$ or 4'-NO₂BAPTS).

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