

Thiosemicarbazones의 몇 가지 코발트(II) 및 니켈(II) 착물에 대한 합성, 항박테리아 및 항균 활성

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Synthesis, Antibacterial and Antifungal Activities of Some Cobalt(II) and Nickel(II) Complexes of Thiosemicarbazones

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요약. 두 가지 새로운 thiosemicarbazone으로, 예를 들면, 4[N-(4'-ethylbenzalidene)amino]antipyrine thiosemicarbazone(EBAAPTS) 및 4[N-(2',4'-dimethylbenzalidene)amino]antipyrine thiosemicarbazone(DMBAAPTS)를 합성하여 그 특성을 규명하였다. 이들 thiosemicarbazone(EBAAPTS 및 DMBAAPTS)의 코발트(II) 및 니켈(II)에 대한 착물화 특성을 조사하였다. EBAAPTS 및 DMBAAPTS와 코발트(II) 및 니켈(II) 염과의 반응을 뜨거운 에탄올 용액에서 수행한 결과, 일반적 조성으로 $[MX_2(L)H_2O]$ ($M=Co^{2+}$ 또는 Ni^{2+} ; $X=Cl^-$, Br^- , NO_3^- , NCS^- 또는 CH_3COO^- ; $L=EBAAPTS$ 또는 $DMBAAPTS$)을 갖는 새로운 착물의 형성을 확인하였다. 새롭게 합성한 이들 착물에 대해 원소분석, 분자량, 몰전도도, 자기수자율, 적외선 및 자외선 분광학 등의 방법으로 특성을 규명하였다. 니트로벤젠 용액에서 이들 착물의 몰전도도를 측정된 결과, 비전해질 성질을 가짐을 알았다. 또한, 모든 착물은 높은-스핀 형태였다. 분광학적 연구로부터 $[MX_2(L)H_2O]$ 형의 코발트(II) 및 니켈(II) 착물은 팔면체의 기하구조를 갖는 것으로 확인되었다. 이들 착물을 이용하여 항박테리아 및 항균 활성을 여러 종류의 병원균, 세균 및 박테리아에 대해 조사하여 생물학적 활성을 고찰하였다.

주제어: 코발트(II), 니켈(II), Thiosemicarbazones, 코발트(II) thiosemicarbazone 착물, 니켈(II) thiosemicarbazone 착물, 생물학적 성질

ABSTRACT. In the present paper two new thiosemicarbazones *i.e.*, 4[N-(4'-ethylbenzalidene)amino]antipyrine thiosemicarbazone (EBAAPTS) and 4[N-(2',4'-dimethylbenzalidene)amino]antipyrine thiosemicarbazone (DMBAAPTS) have been synthesized and characterized. The complexing abilities of these thiosemicarbazones *i.e.* EBAAPTS and DMBAAPTS towards cobalt(II) and nickel(II) salts have been explored. The reactions of the hot ethanolic solutions of cobalt(II) and nickel(II) salts with EBAAPTS and DMBAAPTS led to the formation of the novel complexes of general composition $[MX_2(L)H_2O]$ ($M=Co^{2+}$ or Ni^{2+} ; $X=Cl^-$, Br^- , NO_3^- , NCS^- or CH_3COO^- ; $L=EBAAPTS$ or $DMBAAPTS$). The newly synthesized complexes have been characterized by elemental analyses, molar mass, molar conductance, magnetic susceptibility, infrared and electronic spectral studies. The molar conductance measurements of the complexes in nitrobenzene correspond to their non-electrolytic nature. All the complexes are of high-spin type. On the basis of spectral studies an octahedral geometry has been assigned for Co(II) and Ni(II) complexes of the type $[MX_2(L)H_2O]$. These complexes were screened for their antibacterial and antifungal activities on different species of pathogens, fungi and bacteria and their biopotency has been discussed.

Keywords: Cobalt(II), Nickel(II), Thiosemicarbazones, Cobalt(II) thiosemicarbazones complexes, Nickel(II) thiosemicarbazones complexes, Biological properties

INTRODUCTION

Many thiosemicarbazones possess a wide spectrum of medicinal properties including activity against influenza, protozoa, small pox, certain kinds of tumour, tuberculosis, leprosy, bacterial and viral infections, psoriasis, rheumatism and tripanosomiasis, coccidiosis, malaria and have been suggested as possible pesticides and fungicides. Their activity has frequently been thought to be due to their ability to chelate trace metals. Thus the metal chelates with ligands of biological importance have been playing an important role in the development of new coordination chemistry. Complexes containing chelating ligands, which show promising biological activity, have been recently studied by ourselves¹⁻¹¹ and others.¹²⁻²² We have investigated the synthesis and characterization of cobalt(II),¹⁻² nickel(II),²⁻³ oxovanadium(IV),⁴⁻⁵ platinum(II)⁶ and some lanthanide(III)⁷ complexes that contain a range of ancillary ligands such as semicarbazones,⁷ thiosemicarbazones.^{1,2,4-6} Recently, we focused our attention to the investigation on transition metal complexes of N and O donor ligands.^{3,8,9} Very recently we reported the synthesis, characterization and biological activities of nickel(II) and cobalt(II) complexes of N and O donor of hydrazones derived from isonicotinic acid hydrazide *viz.*, N-isonicotinamido-furfural-2'-aldimine (INH-FFL), N-isonicotinamido cinnamalidine (INH-CIN) and N-isonicotinamido-3',4',5'-trimethoxybenzalaldimine (INH-TMB) ligands.^{3,10,11} Although many thiosemicarbazones possess a wide spectrum of medicinal and biological properties²³⁻²⁶ still the metal complexes of the sulphur donor thiosemicarbazones have not been given as much attention as dithiophosphate, dithiocarbamates, dithiolates, dithio- β -diketonates, dithioamide or xanthates. Thus herein we present our studies on two new thiosemicarbazones N, N and S donor ligands *i.e.*, 4[N-(4'-ethylbenzalidene)amino]antipyrine thiosemicarbazone (EBAAPTS) (*Fig. 1*) and 4[N-(2',4'-dimethylbenzalidene)amino]antipyrine thiosemicarbazone (DMBAAPTS) (*Fig. 2*)

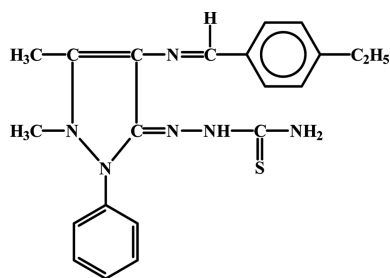


Fig. 1. 4[N-(4'-Ethylbenzalidene)amino]antipyrine thiosemicarbazone (EBAAPTS) [Mol. formula $C_{21}H_{24}N_6S$].

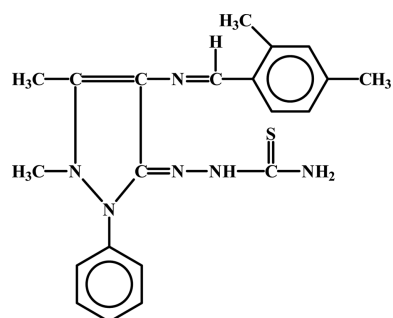


Fig. 2. 4[N-(2',4'-Dimethylbenzalidene)amino]antipyrine thiosemicarbazone (DMBAAPTS) [Mol. formula $C_{21}H_{24}N_6S$].

(*Fig. 2*) have been synthesized and their coordination behaviour towards Co(II) and Ni(II) are reported.

EXPERIMENTAL

Materials

$MX_2 \cdot nH_2O$ ($M = Co^{2+}$ or Ni^{2+} ; $X = Cl^-$, Br^- , NO_3^- , NCS^- or CH_3COO^-) were obtained from SD Fine Chemicals Ltd. (Mumbai, India) and were used as received. $M(NCS)_2$ was prepared by mixing metal chloride (in ethanol) and ethanolic solution of potassium thiocyanate in 1:2 molar ratio. The precipitated KCl was filtered off and the filtrate having respective metal thiocyanate was used immediately for complex formation. The ligands EBAAPTS and DMBAAPTS were synthesized in the laboratory by our reported method.²⁶

Synthesis of the complexes

A general method has been used for the preparation of all the complexes. A hot ethanolic solution of the corresponding cobalt(II) or nickel(II) salt was mixed with a hot ethanolic solution of the ligand (EBAAPTS or DMBAAPTS) in 1:1 molar ratio.^{1,2,10,11} The reaction mixture was refluxed on water bath for *ca.* 2 h. On cooling in ice cold water, the coloured complexes precipitated out in each case. The products were filtered, washed with ethanol, re-crystallized and dried over P_4O_{10} under vacuum.

Instrumentation, physico-chemical measurements and analytical estimations

The cobalt(II) and nickel(II) in their metal complexes were estimated complexometrically with EDTA using murexide and eriochrome black-T as indicators respectively after decomposing the complexes with conc. H_2SO_4 and H_2O_2 .² The halogens and pseudohalogen were estimated by reported method.^{1,2,10,11} The sulfur content in the complexes was estimated gravimetrically as precipitated

BaSO₄ while the nitrogen content in the complexes was determined by the Kjeldahl method.

The molecular weight determination of the present complexes was carried out cryoscopically in freezing PhNO₂ using a Beckmann thermometer of ± 0.01 °C accuracy. A Toshniwal conductivity bridge and dip type cell was used for the conductivity measurements of the complexes in PhNO₂ at room temperature. The magnetic susceptibility measurements on powder form of the complexes were carried out at 25 °C on Evan's balance using anhydrous CuSO₄ as calibrant. The infrared spectra of the complexes were recorded on a Perkin Elmer infrared spectrophotometer model 521 KBr 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 analyses of the complexes were carried out on Perkin-Elmer Pyris Diamond in static air with an unlined platinum boat sample holder, at the heating rate of 6 °C/min. The antibacterial and antifungal activities of some representative cobalt(II) complexes and standards ampicillin, tetracycline and salicylic acid were screened by following our reported methods.^{1,2,10,11}

RESULTS AND DISCUSSION

The reaction of Co(II) and Ni(II) with EBAAPTS and DMBAAPTS yielded the complex, [MX₂(L)(H₂O)] where M=Co²⁺ or Ni²⁺; X=Cl⁻, Br⁻, NO₃⁻, NCS⁻ or CH₃COO⁻ and L=EBAAPTS or DMBAAPTS. The analytical data of these complexes showed that they are stable and can be stored for months without any significant change. These complexes are generally soluble in common organic solvents. The molar conductance values of the complexes in nitrobenzene reveal that all the halo, nitrate, isothiocyanato and acetato complexes are essentially non-electrolytes.²⁷ The cryoscopically determined molecular weights and conductivity data are presented in Table 1. In general, the molecular weight results are good agreement with the conductance data suggesting monomeric formulations.

Magnetic susceptibility

The calculated magnetic moment based on magnetic susceptibility measurements of the cobalt(II) and nickel(II) complexes are given in Table 1. The observed values of magnetic moment for cobalt(II) complexes are generally diagnostic of the coordination geometry about the metal ion.^{1,2,11} The low spin square planar cobalt(II) complexes

may be readily identified by values of μ_{eff} in the range 2.1-2.9 B.M., arising from one unpaired electron plus an apparently large orbital contribution. Both tetrahedral and high-spin octahedral cobalt(II) complexes possess three unpaired electrons but may be distinguished by the magnitude of the deviation of μ_{eff} from the spin only value¹. The magnetic moment of the tetrahedral cobalt(II) complexes with an orbitally non-degenerate ground state is increased above the spin only value via contribution from higher orbitally degenerate terms and occurs in the range 4.2-4.7 B.M.^{1,2} The octahedral cobalt(II) complexes however maintain a large contribution due to ⁴T_g ground term and exhibit μ_{eff} in the range 4.8-5.6 B.M.¹ Few data are available for high spin five-coordinate complexes, however, the range has been given as 4.5-4.8 B.M. The magnetic moments of the present cobalt(II) complexes are in the range of 4.8-5.1 BM (Table 1) which show that all cobalt(II) complexes are paramagnetic and have three unpaired electrons indicating a high-spin octahedral configuration.

Magnetic behavior of the octahedral nickel(II) complexes is relatively simple. Nickel(II) has the electronic configuration 3d⁸ and exhibit a magnetic moment higher than expected for two unpaired electrons in the octahedral environment (2.8-3.2 B.M.) and the tetrahedral (3.4-4.2 B.M.) complexes whereas its square-planar complexes would be diamagnetic.^{2,11} The paramagnetism observed for the present series of nickel(II) complexes ranges from 2.9-3.2 BM (Table 1), which is consistent with the octahedral stereochemistry of these complexes.

Infrared spectra

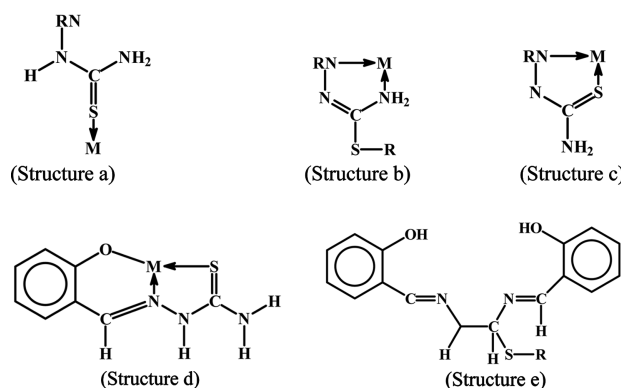
It is known that the thiosemicarbazide molecule itself exists in the *trans* configuration (Structure a) and while complexing in this configuration it behaves as a monodentate ligand, bonding only through the sulphur atom.^{1,2,4,6,11} It is also known that bonding can also occur through the hydrazinic nitrogen and the amide nitrogen (Structure b), if the sulphur centre is substituted.^{1,2,4} On re-investigating the crystal structure of thiosemicarbazide hydrochloride, these conformation changes on the basis of protonated deprotonated isomeric forms and steric effects. In most of the complexes studied, the thiosemicarbazone function coordinates to the metal ion in the *cis*-configuration (Structure c) as a bidentate ligand bonding through the thione/thiol sulphur atom and the hydrazine nitrogen atom in a bidentate manner.^{1,2,6,11}

When an additional coordinating functionality is present in the proximity of the N,S-donating centres, the ligands are

Table 1. Analytical, conductivity and molecular weight data of Co(II) and Ni(II) complexes of EBAAPTS and DMBAAPTS

Complex	Yield (%)	Analysis: Found (Calcd.) (%)						Mol.wt.: Found (Calcd.)	Ω_m (ohm ⁻¹ cm ² mol ⁻¹)	μ_{eff} (BM)
		M (Co or Ni)	C	H	N	S	Anion			
[CoCl ₂ (EBAAPTS)H ₂ O]	80	10.84 (10.92)	46.56 (46.66)	4.77 (4.81)	15.44 (15.55)	5.87 (5.92)	12.99 (13.14)	535 (540)	1.7	4.8
[CoBr ₂ (EBAAPTS)H ₂ O]	82	9.30 (9.37)	39.96 (40.06)	4.08 (4.13)	13.25 (13.35)	5.02 (5.08)	25.21 (25.43)	626 (629)	2.0	5.1
[Co(NO ₃) ₂ (EBAAPTS)H ₂ O]	79	9.86 (9.95)	42.38 (42.49)	4.33 (4.38)	18.77 (18.88)	5.35 (5.39)	-	589 (593)	1.4	4.9
[Co(NCS) ₂ (EBAAPTS)H ₂ O]	80	9.99 (10.08)	47.08 (47.18)	4.39 (4.44)	19.02 (19.14)	5.42 (5.47)	19.39 (19.82)	581 (582)	1.6	4.8
[Co(CH ₃ COO) ₂ (EBAAPTS)H ₂ O]	76	9.93 (10.05)	50.93 (51.10)	5.40 (5.45)	14.17 (14.31)	5.41 (5.45)	-	582 (587)	1.3	4.9
[NiCl ₂ (EBAAPTS)H ₂ O]	78	10.85 (10.92)	46.52 (46.66)	4.76 (4.81)	15.43 (15.55)	5.87 (5.92)	12.96 (13.14)	536 (540)	1.9	3.1
[NiBr ₂ (EBAAPTS)H ₂ O]	75	9.30 (9.37)	39.93 (40.06)	4.08 (4.13)	13.23 (13.35)	5.02 (5.08)	25.19 (25.43)	625 (629)	1.8	2.9
[Ni(NO ₃) ₂ (EBAAPTS)H ₂ O]	80	9.87 (9.95)	42.36 (42.49)	4.33 (4.38)	18.76 (18.88)	5.33 (5.39)	-	588 (593)	1.7	3.2
[Ni(NCS) ₂ (EBAAPTS)H ₂ O]	81	10.00 (10.08)	46.98 (47.18)	4.38 (4.44)	18.98 (19.14)	5.43 (5.47)	19.40 (19.82)	581 (585)	2.0	3.0
[Ni(CH ₃ COO) ₂ (EBAAPTS)H ₂ O]	82	9.98 (10.05)	50.96 (51.10)	5.40 (5.45)	14.17 (14.31)	5.40 (5.45)	-	583 (587)	1.9	3.1
[CoCl ₂ (DMBAAPTS)H ₂ O]	79	10.85 (10.92)	46.58 (46.66)	4.77 (4.81)	15.42 (15.55)	5.87 (5.92)	12.95 (13.14)	535 (540)	1.8	4.9
[CoBr ₂ (DMBAAPTS)H ₂ O]	78	9.30 (9.37)	39.95 (40.66)	4.09 (4.13)	13.00 (13.35)	5.03 (5.08)	25.17 (25.43)	624 (629)	2.0	5.0
[Co(NO ₃) ₂ (DMBAAPTS)H ₂ O]	78	9.86 (9.95)	42.35 (42.49)	4.35 (4.38)	18.76 (18.88)	5.33 (5.39)	-	587 (593)	2.1	4.8
[Co(NCS) ₂ (DMBAAPTS)H ₂ O]	80	9.99 (10.08)	46.98 (47.18)	4.39 (4.44)	19.01 (19.14)	5.42 (5.47)	19.49 (19.82)	580 (585)	1.8	4.9
[Co(CH ₃ COO) ₂ (DMBAAPTS)H ₂ O]	82	9.96 (10.05)	50.92 (51.10)	5.40 (5.45)	14.19 (14.31)	5.40 (5.45)	-	582 (587)	1.9	5.1
[NiCl ₂ (DMBAAPTS)H ₂ O]	80	10.87 (10.92)	46.50 (46.66)	4.76 (4.81)	15.42 (15.55)	5.87 (5.92)	12.96 (13.14)	535 (540)	1.7	2.9
[NiBr ₂ (DMBAAPTS)H ₂ O]	79	9.28 (9.37)	39.96 (40.66)	4.08 (4.13)	13.21 (13.35)	5.03 (5.08)	25.26 (25.43)	626 (629)	1.8	3.0
[Ni(NO ₃) ₂ (DMBAAPTS)H ₂ O]	76	9.86 (9.95)	42.37 (42.49)	4.33 (4.38)	18.75 (18.85)	5.36 (5.39)	-	587 (593)	1.6	3.1
[Ni(NCS) ₂ (DMBAAPTS)H ₂ O]	78	10.00 (10.08)	46.89 (47.18)	4.40 (4.44)	18.95 (19.14)	5.42 (5.47)	19.67 (19.82)	580 (585)	2.0	2.9
[Ni(CH ₃ COO) ₂ (DMBAAPTS)H ₂ O]	79	9.96 (10.05)	50.87 (51.10)	5.40 (5.45)	14.18 (14.31)	5.40 (5.45)	-	582 (587)	1.7	3.2

found to act as tridentate species (Structure d) yielding a polymeric compounds in some cases. It is also shown that alkylation of the thiocarbonyl sulphur of thiosemicarbazone derivatives induces not only complexation through the terminal amino group, but also has enough acidic character for it to function as a mono acidic ligand. In the presence of various transitions metal ions, the ligands (EBAAPTS and DMBAAPTS) are capable of condensing at the terminal amino nitrogen atom through another aldehyde or ketone to yield quadridentate ligands, as shown in Structure e, using such template reactions.



Relevant to the bonding in thiosemicarbazone complexes is the ability to locate the various groups infra red (IR) frequencies corresponding to typical linkages. Although there have been many attempts to assign empirically a few infrared bands of metal complexes of thiosemicarbazone ligands,^{1,2,4,6,11} no complete assignment of their IR spectra have been available. A study and comparison of infrared spectra of EBAAPTS and DMBAAPTS and their [MX₂(L)(H₂O)] type complexes with Co(II) and Ni(II) are shown in Table 2 and 3 which imply that these ligands behave as neutral tridentate and coordinated through N and N of two azomethine groups and of S of thio-keto group. The strong bands observed at 3322-3200 cm⁻¹ region in both thiosemicarbazones have been observed due to N-H vibrations. Practically, there is no effect on these frequencies after complexation exclude the possibility of complexation by this group in ligands; EBAAPTS and DMBAAPTS. The absorptions in 1622-1610 cm⁻¹ range in free ligands (EBAAPTS and DMBAAPTS) may be attributed to C=N stretching vibrations of imine-nitrogen which is in agreement with the previous observations.²⁸ On complexation of EBAAPTS (Table 2) and DMBAAPTS (Table 3) with Co(II) and Ni(II) these frequencies are shifted to lower energies. These observations suggest involvement of unsaturated nitrogen atoms

of the two azomethine groups in bonding with the Co(II) and Ni(II) ions.

In substituted thioureas, the C=S stretching vibrations contributed markedly to CN stretching and bending as well as N-C-S bending modes of vibrations. In the spectra of the present ligands (EBAAPTS and DMBAAPTS), the bands observed in the region 1290-1255 cm⁻¹, 1130-1075 cm⁻¹ and 840-760 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.²⁹ The coordination of sulfur with Co(II) and Ni(II) ions results in donation of electrons towards the metal ions. This results in the weakening of C=S bond. Hence on complexation C=S stretching vibrations should decrease and those of C-N should increase. In the present complexes of Co(II) and Ni(II) with EBAAPTS and DMBAAPTS, frequencies in the range 1290-1260 cm⁻¹ increased by 40-50 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 840-760 cm⁻¹ were shifted to lower wave numbers and intensity of the bands were also reduced. The changes described suggest coordination through S of C=S.

As there were no bands around 2700-2500 cm⁻¹, in the

Table 2. Key infrared bands (cm⁻¹) of EBAAPTS and Co(II) and Ni(II) complexes of EBAAPTS

Compound	Assignments						
	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \nu(\text{C}-\text{N})$	$\delta(\text{NCS}) + \text{CS}$ bending	$\nu(\text{N}-\text{N})$	$\nu(\text{C}=\text{S})$	$\nu(\text{M}-\text{N})/\nu(\text{M}-\text{S})$
EBAAPTS	3300s 3200s	1622s	1285s 1255s	1130s 1075m	1045	840m 765m	-
[CoCl ₂ (EBAAPTS)H ₂ O]	3300s 3202s	1580s	1305m	1172m 1130m	1055	805m 712m	450m 340w
[CoBr ₂ (EBAAPTS)H ₂ O]	3303s 3201s	1570s	1310m	1185m 1132m	1052	808m 705m	452m 345w
[Co(NO ₃) ₂ (EBAAPTS)H ₂ O]	3301s 3200s	1565s	1320m	1180m 1132m	1060	812m 732m	430m 350w
[Co(NCS) ₂ (EBAAPTS)H ₂ O]	3302s 3201s	1545s	1315m	1175m 1130m	1058	812m 715m	3445m 335w
[Co(CH ₃ COO) ₂ (EBAAPTS)H ₂ O]	3305s 3202s	1550s	1312m	1182m 1105m	1055	810m 740m	455m 352m
[NiCl ₂ (EBAAPTS)H ₂ O]	3303s 3200s	1572s	1313m	1180m 1135m	1056	809m 725m	445m 338w
[NiBr ₂ (EBAAPTS)H ₂ O]	3305s 3202s	1660s	1315m	1178m 1132m	1052	811m 737m	450m 350w
[Ni(NO ₃) ₂ (EBAAPTS)H ₂ O]	3303s 3200s	1552s	1310m	1182m 1110m	1062	810m 735m	455m 352w
[Ni(NCS) ₂ (EBAAPTS)H ₂ O]	3300s 3205s	1548s	1312m	1182m 1138m	1058	812m 730m	440m 340w
[Ni(CH ₃ COO) ₂ (EBAAPTS)H ₂ O]	3305s 3200s	1550s	1321m	1182m 1115m	1055	815m 742m	442m 342m

Table 3. Key infrared bands (cm^{-1}) of DMBAAPTS and Co(II) and Ni(II) complexes of DMBAAPTS

Compound	Assignments						
	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \nu(\text{C}-\text{N})$	$\delta(\text{NCS}) + \text{CS bending}$	$\nu(\text{N}-\text{N})$	$\nu(\text{C}=\text{S})$	$\nu(\text{M}-\text{N})/\nu(\text{M}-\text{S})$
DMBAAPTS	3320s 3250s	1610vs	1290s 1260vs	1125s 1080m	1050m	840s 760vs	-
[CoCl ₂ (DMBAAPTS)H ₂ O]	3322s 3250s	1572s	1355s 1285m	1170m 1110m	1065m	870m 725m	445m 342m
[CoBr ₂ (DMBAAPTS)H ₂ O]	3320s 3252s	1578s	1340s 1282m	1190m 1152m	1060m	872m 730m	440m 340w
[Co(NO ₃) ₂ (DMBAAPTS)H ₂ O]	3320s 3250s	1575s	1350s 1285m	1170m 1132m	1062m	885m 735m	445m 335w
[Co(NCS) ₂ (DMBAAPTS)H ₂ O]	3322s 3252s	1560s	1342s 1290m	1175m 1130m	1065m	890m 735m	442m 342w
[Co(CH ₃ COO) ₂ (DMBAAPTS)H ₂ O]	3320s 3250s	1565s	1345m 1285m	1178m 1135m	1060m	894m 725m	445m 338w
[NiCl ₂ (DMBAAPTS)H ₂ O]	3318s 3252m	1570s	1345m 1292m	1180m 1132m	1065m	892m 730m	448m 350w
[NiBr ₂ (DMBAAPTS)H ₂ O]	3321s 3250s	1575s	1340s 1285m	1175m 1138m	1062m	894m 715m	452m 340w
[Ni(NO ₃) ₂ (DMBAAPTS)H ₂ O]	3320s 3252s	1572s	1352s 1280m	1180m 1135m	1067m	892m 720m	447m 342w
[Ni(NCS) ₂ (DMBAAPTS)H ₂ O]	3322s 3250s	1575s	1342s 1292m	1182m 1140m	1065m	890m 725m	445m 348w
[Ni(CH ₃ COO) ₂ (DMBAAPTS)H ₂ O]	3321s 3250s	1578s	1345m 1290m	1175m 1138m	1062m	892m 730m	448m 340w

infrared spectra, the possibility of thione-thiol tautomerism ($\text{H}-\text{N}-\text{C}=\text{S} \rightleftharpoons \text{C}=\text{N}-\text{SH}$) in the ligands, EBAAPTS and DMBAAPTS, has been ruled out. In the far infrared spectral region, some new bands with medium to weak intensity in region $450-335 \text{ cm}^{-1}$ were assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$. Thus the infrared spectral suggested the tridentate nature of the thiosemicarbazones and pointed out the N, N, S sites as possible donor atoms. The presence of coordinated water was confirmed by very broad absorptions around 3400 cm^{-1} in the infrared spectra of the complexes. Also the bands at ~ 930 and 770 cm^{-1} may be due to rocking and wagging modes of the coordinated water.³⁰

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 $475-460 \text{ cm}^{-1}$, respectively. These frequencies are associated with the terminal N-bonded isothiocyanate ions.³¹ The appearance of two strong absorption bands in $1560-1520 \text{ cm}^{-1}$ and $1310-1300 \text{ cm}^{-1}$ region for nitrate complexes were attributed to ν_4 and ν_1 modes of vibrations, respectively, of the covalently bonded nitrate groups.³² The $(\nu_4-\nu_1)$ values of $\sim 220 \text{ cm}^{-1}$ for these complexes suggested strong covalency for the metal-nitrate bonding.² Lever *et al.* have shown that the number and relative ener-

gies of nitrate combination frequencies ($\nu_1+\nu_4$) in the region $1800-1700 \text{ cm}^{-1}$ of the infrared spectrum, may be used as an aid to distinguish the various coordination modes of the nitrate group.³³ It has been demonstrated 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 $(\nu_1+\nu_4)$.³³ Lever *et al.* confirmed that the separation for monodentate nitrate appeared to be $5-26 \text{ cm}^{-1}$ and for bidentate nitrate $25-66 \text{ cm}^{-1}$.³³ A separation of $15-25 \text{ cm}^{-1}$ in the combination bands ($\nu_1+\nu_4$) in the $1800-1700 \text{ cm}^{-1}$ region in the present complexes confirmed the monodentate nitrate coordination. The acetate 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} , respectively² confirming that both the acetate groups in the present complexes are unidentate.³⁴

Electronic spectra

The electronic spectra of all the Co(II) complexes recorded were quite similar to each other and consist of two bands in the regions $18520-18000 \text{ cm}^{-1}$ and $20840-20000 \text{ cm}^{-1}$, which clearly indicated the octahedral stereochemistry of the complexes. The band maxima and their assignments

Table 4. Electronic spectral data and ligand field parameters of Co(II) complexes of EBAAPTS and DMBAAPTS

Complex	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)	Dq (cm ⁻¹)	B (cm ⁻¹)	β	Dq/B
[CoCl ₂ (EBAAPTS)H ₂ O]	8690	18000	20833	1104	1060	0.95	1.04
[CoBr ₂ (EBAAPTS)H ₂ O]	8700	18180	20835	1105	1061	0.95	1.04
[Co(NO ₃) ₂ (EBAAPTS)H ₂ O]	8700	18100	20835	1105	1061	0.95	1.04
[Co(NCS) ₂ (EBAAPTS)H ₂ O]	8772	18180	20000	1115	1070	0.96	1.04
[Co(CH ₃ COO) ₂ (EBAAPTS)H ₂ O]	8770	18520	20000	1115	1070	0.96	1.04
[CoCl ₂ (DMBAAPTS)H ₂ O]	8690	18000	20835	1104	1060	0.95	1.04
[CoBr ₂ (DMBAAPTS)H ₂ O]	8690	18000	20835	1104	1060	0.95	1.04
[Co(NO ₃) ₂ (DMBAAPTS)H ₂ O]	8700	18100	20840	1105	1060	0.95	1.04
[Co(NCS) ₂ (DMBAAPTS)H ₂ O]	8396	18180	20835	1104	1060	0.95	1.04
[Co(CH ₃ COO) ₂ (DMBAAPTS)H ₂ O]	8690	18000	20835	1104	1060	0.95	1.04

Table 5. Electronic spectral data and ligand field parameters of Ni(II) complexes of EBAAPTS and DMBAAPTS

Complex	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)	Dq (cm ⁻¹)	B (cm ⁻¹)	β
[NiCl ₂ (EBAAPTS)H ₂ O]	8200 10810	17540	26950	1081	804	0.77
[NiBr ₂ (EBAAPTS)H ₂ O]	8270 10900	17700	27200	1093	795	0.76
[Ni(NO ₃) ₂ (EBAAPTS)H ₂ O]	9600	16200	24400	960	1043	0.96
[Ni(NCS) ₂ (EBAAPTS)H ₂ O]	9800	16700	24500	980	1065	0.98
[Ni(CH ₃ COO) ₂ (EBAAPTS)H ₂ O]	10900	17700	27000	1093	794	0.76
[NiCl ₂ (DMBAAPTS)H ₂ O]	9090	15150	25000	910	988	0.91
[NiBr ₂ (DMBAAPTS)H ₂ O]	9800	16700	24600	982	1065	0.98
[Ni(NO ₃) ₂ (DMBAAPTS)H ₂ O]	9900	16600	24390	990	1076	0.99
[Ni(NCS) ₂ (DMBAAPTS)H ₂ O]	8240 10870	17540	27500	1087	829	0.79
[Ni(CH ₃ COO) ₂ (DMBAAPTS)H ₂ O]	10999	16950	27400	1099	750	0.73

are presented in Table 4. The energy of ν_1 corresponds to $10D_q$ for weak field. The ligand field parameters, D_q , B and nephelauxetic effect (β) have also been calculated, using first order perturbation theory, from the ligand field spectra of octahedral Co(II) complexes, and reported in Table 4. The appreciable intensity enhancement in all the Co(II) complexes studied confirmed the distortion from a regular octahedral structure.

The band maxima, their assignments, the calculated nephelauxetic effect (β) and the ligand field parameters B and D_q for some representative Ni(II) complexes are listed in Table 5. The absorption spectra of the Ni(II) complexes studied displayed bands in 10999-8200 cm⁻¹ (ν_1), 17700-15150 cm⁻¹ (ν_2) and 27500-24400 cm⁻¹ (ν_3) (Table 5) suggested the octahedral stereochemistry of these complexes.³⁵ The comparison of the $10D_q$ values 7200, 7000 and 9700 cm⁻¹ for [NiCl₆]⁴⁻, [NiBr₆]⁴⁻ or [Ni(NCS)₆]⁴⁻ complexes, respectively with our results for

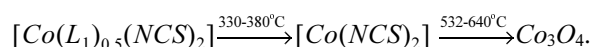
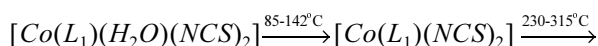
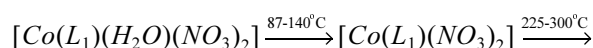
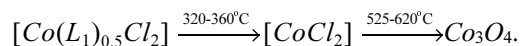
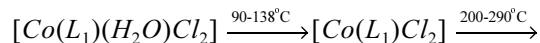
the corresponding octahedral [MX₂(L)(H₂O)] (M=Ni²⁺, X=Cl⁻, Br⁻ or NCS⁻) confirmed the distortion from a regular octahedral structure.² This due to the fact that the equatorial ligand's steric hindrance prevents axial ligands to form optimum covalent bonding with the Ni(II) and Co(II) central metal ions.

Thermogravimetric studies

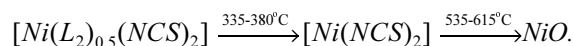
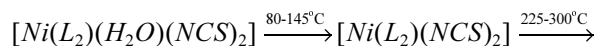
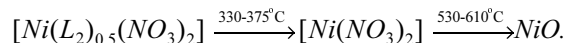
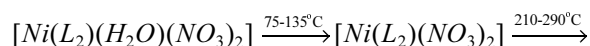
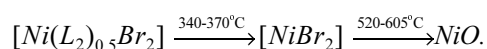
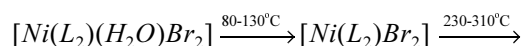
The thermogravimetric results of few representative cobalt(II) complexes of EBAAPTS (L₁) are presented in Table 6. The thermogravimetric data indicated that the complexes were stable up to 85-90 °C and non-hygroscopic in nature. In the temperature range of 80-142 °C, one coordinated water molecule is lost, after which decomposition and deligation processes started. Finally, at ~600 °C, Co₃O₄ was obtained as final residue. The thermal decomposition may be represented by the following equations:

Table 6. Thermoanalytical results obtained for the Co(II) and Ni(II) complexes of EBAAPTS

Complex	Decomp. temp. (°C)		Decomp. products	Weight loss (%)	
	Initial	Final		Found	Calcd.
[CoCl ₂ (EBAAPTS)H ₂ O]	90	138	CoCl ₂ (EBAAPTS)	3.60	3.53
	200	290	CoCl ₂ (EBAAPTS) _{0.5}	40.13	39.26
	320	360	CoCl ₂	77.29	75.36
	525	620	Co ₃ O ₄	85.29	83.76
[Co(NO ₃) ₂ (EBAAPTS)H ₂ O]	87	140	Co(NO ₃) ₂ (EBAAPTS)	3.48	3.39
	225	300	Co(NO ₃) ₂ (EBAAPTS) _{0.5}	39.87	38.69
	320	365	Co(NO ₃) ₂	74.69	73.86
	530	625	Co ₃ O ₄	83.39	82.69
[Co(NCS) ₂ (EBAAPTS)H ₂ O]	85	142	Co(NCS) ₂ (EBAAPTS)	3.20	3.15
	230	315	Co(NCS) ₂ (EBAAPTS) _{0.5}	37.60	38.10
	330	380	Co(NCS) ₂	73.89	72.96
	532	640	Co ₃ O ₄	84.39	83.62
[NiCl ₂ (DMBAAPTS)H ₂ O]	80	130	NiBr ₂ (DMBAAPTS)	3.59	3.47
	230	310	NiBr ₂ (DMBAAPTS) _{0.5}	38.62	37.98
	340	370	NiBr ₂	72.32	70.86
	520	605	NiO	87.39	86.89
[Ni(NO ₃) ₂ (DMBAAPTS)H ₂ O]	75	135	Ni(NO ₃) ₂ (DMBAAPTS)	3.40	3.27
	210	290	Ni(NO ₃) ₂ (DMBAAPTS) _{0.5}	35.39	34.86
	330	375	Ni(NO ₃) ₂	69.88	68.36
	530	610	NiO	86.49	86.03
[Ni(NCS) ₂ (DMBAAPTS)H ₂ O]	80	142	Ni(NCS) ₂ (DMBAAPTS)	3.10	2.99
	225	300	Ni(NCS) ₂ (DMBAAPTS) _{0.5}	36.36	35.89
	335	380	Ni(NCS) ₂	70.81	69.77
	535	615	NiO	87.52	86.93



The thermal results of few representative Ni(II) complexes of DMBAAPTS (L₂) are also presented in Table 6. Ni(II) DMBAAPTS complexes are also stable upto the temp range 75-80 °C. The careful analysis of thermogravimetric curves showed the following thermal equations:



Biological properties

The agar-cup method in DMF solvent at a concentration of 50 µg/mL was used to study the antibacterial activities of some representative cobalt(II) complexes and standard drugs. The antibacterial activities of EBAAPTS, DMBAAPTS, their cobalt(II) complexes, and standard: ampicillin and tetracycline were screened under identical conditions against gram positive bacteria *Bacillus subtilis* (*B.s.*) and *Staphylococcus aureus* (*S.a.*) and gram negative bacteria *Escherichia coli* (*E.c.*) and *Salmonella typhi* (*S.t.*). The results are presented in Table 7 in form of the diameters of zone of inhibition (mm). The data presented in Table 7 shows that the cobalt(II) and EBAAPTS or DMBAAPTS complexes have moderate antibacterial activities against these bacteria. It is important to note that these complexes exhibit greater activity than the parent ligand and the same was found during our previous studies.¹

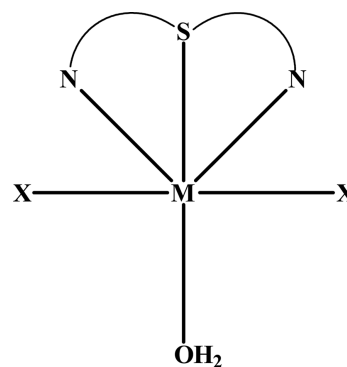
The thiosemicarbazones EBAAPTS, DMBAAPTS and

Table 7. Antifungal and antibacterial activities of cobalt(II) complexes of EBAAPTS and DMBAAPTS

Complex	Antibacterial activity				Antifungal action	
	Zone of inhibition (mm)				<i>A. niger</i>	<i>C. albicans</i>
	<i>B. s</i>	<i>S. a</i>	<i>E. c.</i>	<i>S. t.</i>		
Ampicillin	24	22	17	16	-	-
Tetracycline	18	17	20	21	-	-
Salicylic acid	-	-	-	-	++++	++++
DMBAAPTS	9	8	10	9		
[CoCl ₂ (EBAAPTS)H ₂ O]	15	16	14	14	++	++
[CoBr ₂ (EBAAPTS)H ₂ O]	13	11	11	11	++	++
[Co(NO ₃) ₂ (EBAAPTS)H ₂ O]	12	11	10	12	++	++
[Co(NCS) ₂ (EBAAPTS)H ₂ O]	16	16	15	15	+++	++
[Co(CH ₃ COO) ₂ (EBAAPTS)H ₂ O]	11	12	11	11	++	++
DMBAAPTS	8	7	8	7		
[CoCl ₂ (DMBAAPTS)H ₂ O]	12	10	10	12	+	+
[CoBr ₂ (DMBAAPTS)H ₂ O]	12	11	11	10	+	+
[Co(NO ₃) ₂ (DMBAAPTS)H ₂ O]	11	10	12	11	+	+
[Co(NCS) ₂ (DMBAAPTS)H ₂ O]	14	12	11	10	+	+
[Co(CH ₃ COO) ₂ (DMBAAPTS)H ₂ O]	11	10	11	11	+	+

their cobalt(II) complexes were also studied for their antifungal activities against two fungi: *Aspergillus niger* and *Candida albicans* (*A. niger* and *C. albicans*) and salicylic acid as standard. On the basis of the results presented in Table 7 it was found that almost all complexes showed nearly the same extent of activity, but they were found less active compared to salicylic acid. However, EBAAPTS complexes showed increased antifungal activity than that of DMBAAPTS complexes. It may be due to presence of furan ring and comparatively faster diffusion of EBAAPTS complexes. These compounds were found to be efficient antifungal agents.

Few researchers have investigated the biological and medicinal properties of transition metal complexes of thiosemicarbazones³⁶⁻⁴¹ where the antitumour activities of Mn(II), Co(II), Ni(II) and Cu(II) chelates of anthracene-9-carboxaldehyde thiosemicarbazone have been studied.³⁷ The cytotoxic activity of phenylglyoxal bis(thiosemicarbazone) against *Ehrlich ascites* carcinoma cells have also been studied.³⁸ These compounds were also screened for antimicrobial activity on *B. subtilis* and *E. coli*. They inhibited the bacterial growth considerably.³⁸ The antibacterial and antifungal activities of the present complexes were also compared with the activity results of some other cobalt(II) and nickel(II) complexes having different ligands.⁴²⁻⁴⁵ It was found that the present complexes are less potent bactericides with respect to reported cobalt(II) and nickel(II) complexes^{42,43} while some other complexes have almost comparable^{44,45} or less⁴⁵ antibacterial and antifungal activities. However their experimental conditions are different.^{42,45}

**Fig. 3.** Proposed structure of [MX₂(L)H₂O] M=Co(II) or Ni(II); X=Cl⁻, Br⁻, NO₃⁻, NCS⁻ or CH₃COO⁻; L=EBAAPTS or DMBAAPTS.

CONCLUSION

The compounds [MX₂(L)H₂O] (M=Co²⁺ or Ni²⁺; X= Cl⁻, Br⁻, NO₃⁻, NCS⁻ or CH₃COO⁻; L=EBAAPTS or DMBAAPTS) represent the first example of Co(II) and Ni(II) complexes involving N, N and S donor chelating agents EBAAPTS and DMBAAPTS and X forming six coordinated compounds and are stable in solid and solution states. The isolated complexes demonstrate that interactions of Co(II) and Ni(II) salts separately with EBAAPTS or DMBAAPTS i.e. thiosemicarbazones lead to 1:1 stoichiometries. Co(II) complexes of EBAAPTS or DMBAAPTS showed moderate antibacterial activities against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Salmonella typhi*. The present compounds have antifungal activity against *A. niger* and *C. albicans*. DMBAAPTS complexes showed lesser antifungal activity than that of EBAAPTS

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 *Fig. 3*.

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