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Synthesis and Characterization of Nickel(II) Coordination Compounds of 4-[N-(2′-Hydroxy-1′-Naphthalidene)amino] antipyrine thiosemicarbazone and 4-[N-(Cinnamalidene) amino]antipyrine thiosemicarbazone

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A new series of ten complexes of nickel(II) of 4-[N-(2′-hydroxy-1′-naphthalidene)amino]antipyrine thiosemicarbazone (HNAAPTS) and 4-[N-(cinnamalidene)amino]antipyrine thiosemicarbazone (CAAPTS) were prepared. The complexes were characterized on the basis of elemental analysis, molecular weight, conductivity, magnetic moment, infrared and electronic spectral data. In all the complexes both the thiosemicarbazones act as neutral tridentate (N, N, S) ligands. The coordination number of Ni^{2+} in these complexes is presumed to be six and have an octahedral geometry.

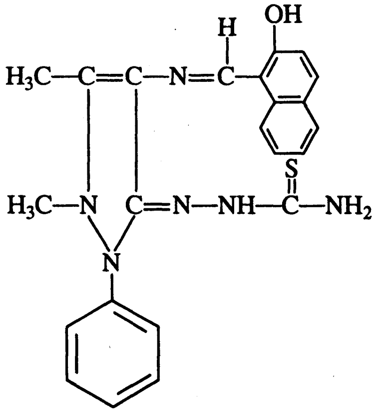
Key Words: Nickel(II) chelates, Thiosemicarbazones.

INTRODUCTION

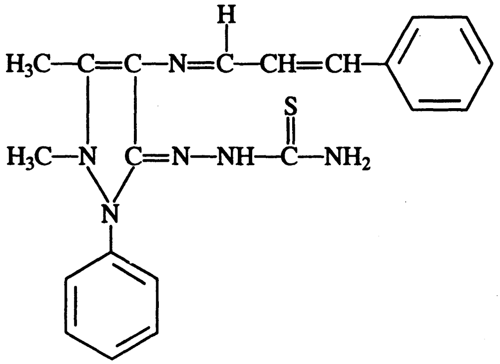
Thiosemicarbazones which comprise a well known group of NS donors have been extensively used for complex formation in the recent past[1–3]. Many of the complexes of thiosemicarbazones and other NS donor ligands are widely employed in medicinal science[4]. Since the discovery of the antitubercular activity of thiosemicarbazones by Domagk,[5] studies on their pharmacology have required a great deal of interest[6–10]. A few of these derivatives have been systematically investigated and the possibilities of their chelation with metal ions in relation to their antitumour and microbiological activity have been suggested. In continuation of the author's work on metal chelates of thiosemicarbazones, he intends to describe a novel series of Ni^{2+} chelates of 4-[N-(2′-hydroxy-1′-naphthalidene) amino]antipyrine thiosemicarbazone (HNAAPTS) and 4-[N-(cinnamalidene) amino]antipyrine thiosemicarbazone (CAAPTS) (Fig. 1).

EXPERIMENTAL

$NiX_2 \cdot nH_2O$ ($X = Cl$, NO_3 or CH_3COO) were obtained from BDH and were used as such. $Ni(SCN)_2$ was prepared by mixing nickel(II) chloride in ethanol and ethanolic solution of potassium thiocyanate in 1 : 2 molar ratio. Precipitated KCl was filtered off and the filtrate having $Ni(SCN)_2$ was used immediately for complex formation. $Ni(ClO_4)_2$ was prepared by the addition of an ethanolic solution of sodium perchlorate into nickel(II) chloride solution. White precipitate of NaCl was filtered off and the filtrate $Ni(ClO_4)_2$ was used as such for complex formation. Both the ligands HNAAPTS and CAAPTS were prepared by reported method[11].



4-[N-(2′-Hydroxy-1-naphthalidene) amino] antipyrine thiosemicarbazone (HNAAPTS)



4-[N-(cinnamalidene)amino]antipyrine thiosemicarbazone (CAAPTS)

Fig. 1

Synthesis of the complexes

A hot ethanolic solution of the corresponding nickel(II) salt was mixed with a hot ethanolic solution of thiosemicarbazone (in 1 : 1 or 1 : 2 molar ratio). The reaction mixture was refluxed on a water bath for *ca.* 2 h. On cooling at room temperature, the coloured complexes precipitated out in each case. They were filtered, washed with ethanol and dried over P_4O_{10} under vacuum.

All the analyses and physico-chemical studies of the complexes were performed by reported method[12].

RESULTS AND DISCUSSION

The reaction of Ni^{2+} salts with HNAAPTS and CAAPTS gave complexes of the general composition $NiX_2 \cdot L \cdot H_2O$ (X = Cl, NO_3, NCS or CH_3COO) or $Ni(ClO_4)_2 \cdot 2L$ (L = HNAAPTS or CAAPTS). The analytical data of these complexes are given in Table-1. All the complexes are quite stable and could be stored for months without any appreciable change. The complexes do not have sharp melting points but decomposed on heating beyond 250°C. The electrical conductivity data (Table-1) of these complexes in $PhNO_2$ indicate that the chloro, nitrato, thiocyanato and acetato complexes are essentially non-electrolytes, while the perchlorato complexes dissociate in nitrobenzene and behave as 1 : 2 electrolytes. The molecular weight determined cryoscopically in $PhNO_2$ are in broad agreement with the conductance data. The magnetic moment values (Table-1) for the present Ni^{2+} complexes range from 2.8–3.2 B.M., which is in consistent with the octahedral stereochemistry of the complexes[12, 13].

TABLE-1
ANALYTICAL, CONDUCTIVITY, MOLECULAR WEIGHT AND MAGNETIC MOMENT DATA OF Ni^{2+} COMPLEXS OF HNAAPTS AND CAAPTS

Complex	Analysis %: Found (Calcd.)				m.w. Found (Calcd.)	Ω_m (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
	Ni	N	S	Anion			
$NiCl_2 \cdot (HNAAPTS) \cdot H_2O$	10.11 (10.20)	14.46 (14.54)	5.49 (5.54)	12.16 (22.28)	572 (578)	2.1	3.1
$Ni(NO_3)_2 \cdot (HNAAPTS) \cdot H_2O$	9.29 (9.35)	17.65 (17.75)	5.02 (5.07)	—	624 (631)	3.0	3.0
$Ni(NCS)_2 \cdot (HNAAPTS) \cdot H_2O$	9.40 (9.47)	17.84 (17.98)	5.30 (15.41)	18.47 (18.62)	617 (623)	2.3	2.8
$Ni(CH_3COO)_2 \cdot (HNAAPTS) \cdot H_2O$	9.37 (9.44)	13.32 (13.44)	5.07 (5.12)	—	618 (625)	2.7	2.9
$Ni(ClO_4)_2 \cdot (HNAAPTS)$	5.20 (5.27)	14.90 (15.03)	5.64 (5.72)	17.68 (17.80)	371 (1118)	54.3	3.2
$NiCl_2 \cdot (CAAPTS) \cdot H_2O$	10.88 (10.96)	15.47 (15.61)	5.87 (5.94)	13.03 (13.19)	531 (538)	2.9	2.9
$Ni(NO_3)_2 \cdot (CAAPTS) \cdot H_2O$	9.91 (9.98)	18.61 (18.95)	5.33 (5.41)	—	583 (591)	2.7	3.1
$Ni(NCS)_2 \cdot (CAAPTS) \cdot H_2O$	10.04 (10.12)	19.07 (19.21)	16.32 (16.46)	19.70 (19.89)	577 (583)	3.1	3.2
$Ni(CH_3COO)_2 \cdot (CAAPTS) \cdot H_2O$	10.02 (10.08)	14.26 (14.35)	5.39 (5.57)	—	578 (585)	2.6	2.8
$Ni(ClO_4)_2 \cdot 2(CAAPTS)$	5.63 (5.68)	16.07 (16.18)	6.09 (6.16)	19.01 (19.17)	341 (1038)	53.9	2.7

Infrared spectra

The strong bands observed at 3315–3200 cm^{-1} region in both thiosemicarbazones have been assigned to ν(NH) vibrations. Practically no effect on these frequencies after complexation precludes the possibility of complexation at this group. The absorption in 1620–1605 cm^{-1} in the free ligands can be attributed to (C=N) stretching vibrations of imine groups[14, 15]. On complexation these frequencies were observed to be shifted to lower wave number (Table-2). These observations suggest involvement of unsaturated nitrogen atoms of the two azomethine groups in bonding with the Ni^{2+} ion. In the spectra of present ligands the bands observed in 1330–1260 cm^{-1}, 1125–1080 cm^{-1} and 840–760 cm^{-1} region are assigned to [ν(C=S) + ν(C=N) + ν(C—N)], [δ(N—C—S) + δ(C=S)] and ν(C=S) stretchings respectively[16]. Coordination of sulphur with the metal ion would result in the displacement of electrons toward the latter, thus resulting in the weakening of (C=S) bond. Hence, on complexation, (C=S) stretching vibrations should decrease and that of (CN) should increase[17, 18]. In all the present complexes, the frequencies in the range 1330–1260 cm^{-1} get an increase by 30–45 cm^{-1}. Similarly bending modes of (N—C—S) and (C=S) also get an increase but in lesser amount. On the other hand, on complexation, the frequencies in 840–765 cm^{-1} are shifted to lower wave numbers and intensity of the bands is also reduced. These observations clearly indicate sulphur bonding with metal ion. The possibility of thione-thiol tautomerism (H—N—C=S) $\rightleftharpoons$ (C=N—SH) in these ligands has been ruled out for no bands around 2700–2500 cm^{-1}; characteristics of thiol group are displayed in the infrared absorption[19]. In all the complexes of HNAAPTS, the stretching frequency in 3400 cm^{-1} region is attributed to ν(OH). In all the complexes, the hydroxyl frequency appears at the same region as in the free ligand clearly indicating that the —OH group is not taking part in the coordination. In far infrared ν(Ni—N) and ν(Ni—S) have also been identified[20]. In conclusion, the infrared spectral studies suggest the tridentate (N,N,S) nature, by pointing out the sites of possible donor atoms.

The presence of coordinated water was suggested by the very broad absorption centred around 3450 cm^{-1} in the infrared spectra. Bands at *ca.* 930 and 770 cm^{-1} may be attributed to rocking and wagging modes of the coordinated water[21].

In perchlorato complexes, the presence of the ν_3 (*ca.* 1100 cm^{-1}) and ν_4 (*ca.* 625 cm^{-1}) bands indicate that the T_d symmetry of ClO_4^- is maintained in both the complexes which suggests the presence of ClO_4^- outside the coordination sphere in the complexes[22]. In thiocyanato complexes, the three fundamental absorption C—N stretch (ν_1), C—S stretch (ν_3) and N—C—S bending (ν_2) are identified. These frequencies are associated with the terminal N-bonded isothiocyanate ions[23]. In both nitrato complexes, the occurrence of two strong absorption bonds at *ca.* 1520 and 1300 cm^{-1} is attributed to ν_4 and ν_1 modes of vibrations respectively of the covalently bonded nitrate groups[24]. Other absorptions associated with covalently bonded nitrate groups are also observed in the spectra of these complexes (*viz.*, ν_2, ν_6, ν_3/ν_5) at *ca.* 1030, 820 and 740 respectively. In case of all the nitrato complexes, a separation of 15–20 cm^{-1} in the combination bonds ($\nu_1 + \nu_4$) in the 1800–1700 cm^{-1} region conclude the monodentate nitrate coordination[25]. In acetato complexes, two bands have been observed at *ca.* 1630 and 1390 cm^{-1}, which may be assigned to asymmetric and symmetric (COO^-) stretching vibrations respectively[26].

TABLE-2: KEY INFRARED BANDS (cm^{-1}) OF Ni^{2+} COMPLEXES OF HNAAPTS AND CAAPTS

Assignments / Complexes	ν(NH)	ν(C═N)	ν(C═S) + ν(C═N) + ν(C—N)	δ(NCS) +CS bending	ν(N—N)	ν(C—S)	ν(NC—N) + ν(NC—S)
HNAAPTS	3310 s	1620 s	1295 s	1130 s	1045 m	846 m	—
	3200 s		1265 us	1085 m		765 m	
$NiCl_2 \cdot HNAAPTS \cdot H_2O$	3305 m	1570 s	1340 m	1150 m	1055 m	790 m	440 m
	3202 m		1280 m	1115 m		725 m	320 w
$Ni(NO_3)_2 \cdot HNAAPTS \cdot H_2O$	3300 m	1560 s	1340 m	1165 m	1060 m	792 s	442 m
	3205 m		1282 m	1110 m		720 m	322 w
$Ni(NCS)_2 \cdot HNAAPTS \cdot H_2O$	3302 m	1555 s	1350 m	1160 m	1055 m	790 s	440 m
	3205 m		1280 m	1112 m		730 m	325 w
$Ni(CH_3COO)_2 \cdot HNAAPTS \cdot H_2O$	3300 m	1560 s	1352 m	1162 m	1060 m	792 s	445 m
	3262 m		1285 m	1110 m		720 m	320 w
$Ni(ClO_4)_2 \cdot 2(HNAAPTS)$	3305 m	1565 s	1345 m	1160 m	1053 m	795 s	440 m
	3200 m		1280 m	1105 m		715 m	325 w
CAAPTS	3315 s	1605 s	1305 s	1125 s	1060 m	840 m	—
	3200 s		1280 m	1085 m		770 s	
$NiCl_2 \cdot CAAPTS \cdot H_2O$	3320 m	1550 s	1330 s	1152 m	1070 m	810 m	445 m
	3200 m		1303 m	1120 m		755 m	325 w
$Ni(NO_3)_2 \cdot CAAPTS \cdot H_2O$	3315 m	1552 s	1335 s	1145 m	1072 m	815 m	430 m
	3205 m		1315 m	1122 m		750 m	320 w
$Ni(NCS)_2 \cdot CAAPTS \cdot H_2O$	3312 m	1570 s	1342 s	1150 m	1080 m	810 m	435 m
	3202 m		1310 m	1125 m		740 m	325 w
$Ni(CH_3COO)_2 \cdot CAAPTS \cdot H_2O$	3315 m	1572 s	1340 s	1140 m	1078 m	807 m	440 m
	3205 m		1315 m	1120 m		735 m	320 w
$Ni(ClO_4)_2 \cdot 2(CAAPTS)$	3320 m	1575 s	1360 s	1145 m	1075 m	815 m	435 m
	3299 m		1310 m	1125 m		730 m	325w

Electronic spectra

The absorption spectra of the Ni^{2+} complexes studied herein display four bands at *ca.* 8000, 11000, 17500 and 27500 cm^{-1}, whereas rest of the complexes show only three bands. In may be assumed that the former type of complexes are pseudo octahedral while the latter type may be regular octabedral. The bands at *ca.* 17000 (ν_2) and 27000 cm^{-1} (ν_3) are characteristic of an octabedral complex whereas the first band (ν_1) in the latter type of complexes appears at *ca.* 11000 cm^{-1} and is split into two at *ca.* 8000 and 11000 cm^{-1} in the former type of complexes. The ν_1 band in regular octahedral complexes directly yields the 10 Dq value. The ligand field parameters 10 Dq and B in octahedral complexes have been computed from equations suggested by Lever *et al.*[27] These data (Table-3) are in good agreement with those reported for other octahedral complexes.

TABLE-3

ELECTRONIC SPECTRAL DATA (cm^{-1}) AND LIGAND FIELD PARAMETERS OF Ni^{2+} COMPLEXES OF HNAAPTS AND CAAPTS

Complex	ν_1	ν_2	ν_3	Dq (cm^{-1})	B (cm^{-1})	β
$NiCl_2\cdot(HNAAPTS)\cdot H_2O$	8270 10930	17700	27200	1093	794	0.76
$Ni(NO_3)_2\cdot(HNAAPTS)\cdot H_2O$	8230 10870	17540	27500	1087	829	0.79
$Ni(NCS)_2\cdot(HNAAPTS)\cdot H_2O$	8200 10810	17540	26950	1081	804	0.77
$Ni(CH_3COO)_2\cdot(HNAAPTS)\cdot H_2O$	10990	16950	27400	1099	750	0.73
$Ni(ClO_4)_2\cdot 2(HNAAPTS)$	10930	17700	27000	1093	794	0.76
$NiCl_2\cdot(CAAPTS)\cdot H_2O$	9090	15150	25000	909	988	0.91
$Ni(NO_3)_2\cdot(CAAPTS)\cdot H_2O$	9600	15385	25640	960	1043	0.96
$Ni(NCS)_2\cdot(CAAPTS)\cdot H_2O$	9800	16700	24500	980	1065	0.98
$Ni(CH_3COO)_2\cdot(CAAPTS)\cdot H_2O$	9900	16660	24390	990	1076	0.99
$Ni(ClO_4)_2\cdot 2(CAAPTS)$	9600	16200	24400	960	1043	0.96

Thermal studies: Thermogravimetric data of $[Ni(HNAAPT)H_2O\cdot Cl_2]$ indicate that the complex is stable up to *ca.* 140°C, which indicate the complex is not hygroscopic in nature. At this stage one water molecule is lost, after which decomposition and deligation processes start. NiO is obtained as end product. The thermal decomposition can be shown as:

$$\mathrm{Ni(HNAAPT)H_2O\cdot Cl_2} \xrightarrow{120\text{–}180^\circ\mathrm{C}} \mathrm{Ni(HNAAPT)Cl_2} \xrightarrow{220\text{–}280^\circ\mathrm{C}}$$

$$\mathrm{Ni(HNAAPT)_{0.5}Cl_2} \xrightarrow{480\text{–}560^\circ\mathrm{C}} \mathrm{NiCl_2} \xrightarrow{640\text{–}700^\circ\mathrm{C}} \mathrm{NiO}$$

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