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Synthesis, Magneto-Spectral and Thermal Studies of Cobalt(II) Complexes of 4-[N-(Benzalidene)amino] antipyrine thiosemicarbazone and 4-[N-(2′-Hydroxybenzalidene)amino] antipyrine thiosemicarbazone

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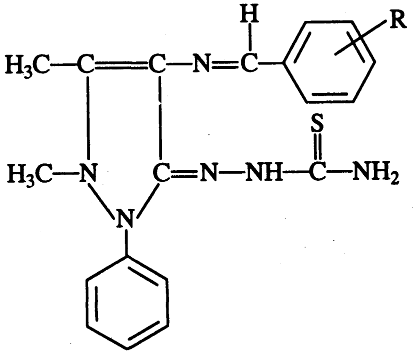
Reactions of CoX_2 (X = Cl, NO_3, NCS, CH_3COO or ClO_4) with 4-[N-(benzalidene)amino]antipyrine thiosemicarbazone (BAAPTS) or 4-[N-(2′-hydroxybenzalidene)amino]antipyrine thiosemicarbazone (HBAAPTS) yielded complexes of the type $CoX_2\cdot(L)\cdot H_2O$ or $Co(ClO_4)_2\cdot 2L$ (L = BAAPTS or HBAAPTS). The infrared spectra of these complexes indicate that the thiosemicarbazones behave as neutral tridentate (N,N,S) ligands. All the complexes are six-coordinated according to the data of magnetic and electronic spectral measurements.

Key Words: Cobalt(II), Chelates, Thiosemicarbazone.

INTRODUCTION

A number of thiosemicarbazone ligands have been derived by simply condensing aliphatic, aromatic or heterocyclic aldehydes or ketones with thiosemicarbazide compounds. Many of these compounds possessed wide spectrum of medicinal properties, including activity against influenza[1], protozoa[2], small pox[3], certain kinds of tumour[4], tuberculosis[5], leprosy[6], bacterial[7] and viral infections[8], psoriasis[9], rheumatism[10], tripanosomiasis[11], coccidiosis[12], malaria[13] and have been suggested as possible pesticides[14] and fungicides[15]. Their activity has frequently been thought to be due to their ability to chelate trace metals. Liebermeister[16] showed that copper ions enhance the antitubercular activity of *p*-acetamidobenzaldehyde thiosemicarbazone. Similarly Petering *et al.*[17] showed that the active intermediate in the anti-tumour activity of 3-ethoxy-2-oxo-butyraldehyde bis-(thio-semicarbazone) (H_2KTS) was the chelate Cu(KTS). These findings have led recently to an increased interest in the chemistry of transition metal chelates of thiosemicarbazones. Thus, in view of the above the author reports in the present work ten Co^{2+} chelates of 4[N-(benzalidene)amino] antipyrine thiosemicarbazone (BAAPTS) and 4-[N-(2′-hydroxybenzalidene)amino]antipyrine thiosemicarbazone (HBAAPTS) (Fig. 1).



(i) R = H; 4-[N-(Benzalidene)amino]antipyrine thiosemicarbazone (BAAPTS)
(ii) R = 2′-OH; 4-[N-(2′-Hydroxybenzalidene)amino]antipyrine thiosemicarbazone (HBAAPTS)

Fig. 1.

EXPERIMENTAL

$CoX_2 \cdot nH_2O$ (X = Cl, NO_3 or CH_3COO) were obtained from BDH and were used as such. $Co(SCN)_2$ was prepared by mixing cobalt(II) chloride in ethanol and ethanolic solution of potassium thiocyanate in 1 : 2 molar ratio. Precipitated KCl was filtered off and the filtrate having $Co(SCN)_2$ was used immediately for complex formation. $Co(ClO_4)_2$ was prepared by the addition of an ethanolic solution of sodium perchlorate into cobalt(II) chloride solution. White precipitate of NaCl was filtered off and the filtrate $Co(ClO_4)_2$ was used as such for complex formation. Both the ligands BAAPT and HBAAPTS were prepared by reported method[18].

Synthesis of the complexes

All the cobalt(II) complexes were prepared by mixing ethanolic solution of BAAPTS or HBAAPTS and metal salt in 1 : 1 or 1 : 2 molar ratio. The reaction mixture was refluxed on a water bath for 2–3 h and then concentrated to a small volume on a hot plate at *ca.* 40°C. On cooling, crystals of complexes obtained were filtered, washed with ethanol and dried in vacuum over P_4O_{10}.

All the analyses and physico-chemical studies of the complexes were performed by reported method[19].

RESULTS AND DISCUSSION

The formation of the Co^{2+} complexes can be represented by the following two equations:

$$CoX_2 \cdot nH_2O + L \xrightarrow[\text{Refluxing}]{\text{Ethanol}} [CoL \cdot H_2O \cdot X_2]$$

(X = Cl, NO_3, NCS or CH_3COO; L = BAAPTS or HBAAPTS).

$$Co(ClO_4)_2 + 2L \xrightarrow[\text{Refluxing}]{\text{Ethanol}} [Co(L)_2](ClO_4)_2$$

The analytical data (Table-1) indicates that the complexes described herein have the general compositions $CoX_2{\cdot}L{\cdot}H_2O$ (X = Cl, NO_3, NCS or CH_3COO) or $Co(ClO_4)_2{\cdot}2L$ (L = BAAPTS or HBAAPTS). 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 values of molar conductance in nitrobenzene for chloro, nitrato, thiocyanato and acetato complexes are too low to account for any dissociation. Therefore, these complexes seem to be non-electrolytes. However, the perchlorato complexes are 1 : 2 electrolytes. The molecular weights determined by the cryoscopic method in nitrobenzene are in broad agreement with the conductance data (Table-1). Magnetic measurements of the complexes of cobalt(II) (μ_{eff} = 4.7–5.4 B.M.) reported herein show that all are paramagnetic and have three unpaired electrons indicating a high spin octahedral configuration[20].

TABLE-1
ANALYTICAL, CONDUCTIVITY, MOLECULAR WEIGHT AND MAGNETIC MOMENT DATA OF Co^{2+} COMPLEXES OF BAAPTS AND HBAAPTS

Complex	Analysis: Found (calcd.) %				m.w. Found (calcd.)	Ω_m (ohm^{-1} cm^2 $mole^{-1}$)	μ_{eff} (B.M.)
	Co	N	S	Anion			
$CoCl_2(H_2O)(BAAPTS)$	11.45 (11.52)	16.31 (16.40)	6.20 (6.25)	13.73 (13.86)	506 (512)	3.3	4.9
$Co(NO_3)_2(H_2O)(BAAPTS)$	10.37 (10.44)	19.72 (19.82)	5.61 (5.66)	—	561 (565)	2.7	5.1
$Co(NCS)_2(H_2O)(BAAPTS)$	10.52 (10.59)	20.00 (20.10)	17.18 (17.23)	20.69 (20.82)	552 (557)	3.1	5.2
$Co(CH_3COO)_2(H_2O)(BAAPTS)$	10.49 (10.55)	14.91 (15.02)	5.67 (5.72)	—	553 (559)	3.7	4.8
$Co(ClO_4)_2{\cdot}2(BAAPTS)$	5.93 (5.98)	16.91 (17.03)	6.43 (6.49)	19.98 (20.18)	324 (986)	52.7	5.0
$CoCl_2(H_2O)(HBAAPTS)$	11.09 (11.17)	15.81 (15.90)	6.00 (6.06)	13.34 (13.44)	521 (528)	3.7	5.2
$Co(NO_3)_2(H_2O)(HBAAPTS)$	10.09 (10.15)	19.21 (19.27)	5.44 (5.50)	—	573 (581)	3.1	4.9
$Co(NCS)_2(H_2O)(HBAAPTS)$	10.21 (10.29)	19.46 (19.54)	16.68 (16.75)	20.13 (20.24)	567 (573)	2.9	5.1
$Co(CH_3COO)_2(H_2O)(HBAAPTS)$	10.19 (10.26)	14.53 (14.60)	5.50 (5.56)	—	566 (575)	2.8	4.7
$Co(ClO_4)_2{\cdot}2(HBAAPTS)$	5.71 (5.79)	16.22 (16.30)	6.22 (6.28)	19.45 (19.54)	334 (1018)	54.9	5.4

Infrared spectra

A study and comparison of infrared spectra of free ligands (BAAPTS or HBAAPTS) and their Co^{2+} complexes (Table-2) imply that both thiosemicarbazones behave as neutral tridentate and Co^{2+} ion is coordinated through N & N of two azomethine groups and of S of thioketo group. The strong bands observed at 3440–3270 cm^{-1} in both thiosemicarbazones have been assigned to ν(NH) vibrations. Practically no effects on these frequencies after complexation preclude the possibility of complexation at this group, the absorption at 1605 ± 5 cm^{-1} in free ligands can be attributed to (C═N) stretching vibrations of imine groups[21, 22]. On complexation these frequencies were observed to be shifted to lower wavenumber (Table-2). These observations suggest involvement of unsaturated nitrogen atoms of the two azomethine groups in bonding with the Co^{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[23]. 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[24, 25]. In all the present complexes, the frequencies in the region 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 840–760 cm^{-1} are shifted to lower wave numbers and intensities of the bands are also reduced. These observations clearly indicte sulphur bonding with Co^{2+} 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[26]. In all the complexes of HBAAPTS, 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(Co—N) and ν(Co—S) have also been identified.

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 coordinated water[28].

In the $Co(NO_3)_2 \cdot L \cdot H_2O$ complexes, the absence of the ν_3 band at *ca.* 1360 cm^{-1} indicates the absence of ionic nitrate. The coordinated nitrate groups[29, 30] which would show absorptions at 1505–1420 (ν_1), 1325–1275 (ν_5), 1045–1020 (ν_2) and 810–805 cm^{-1} (ν_6) indicate the covalent nature of nitrate group. The complexes under study show infrared bonds at 1440 (ν_1), 1325 (ν_5), 1020 (ν_2) and 815 cm^{-1} (ν_6). The separation of 115 cm^{-1} between ν_1 and ν_5 indicates the monodentate nature of the nitrate groups[31]. The location and number of the ν(CN), ν(CS) and δ(NCS) infrared bands for the thiocyanato complexes are generally diagnostic of the mode of coordination of the NCS group. The bands at *ca.* 2050, 820 and 470 cm^{-1} are due to ν(CN), ν(CS) and δ(NCS) respectively. These frequencies are attributable to the N-bonded thiocyanate group in these complexes[32]. In both perchlorato complexes, the presence of the ν_3 (at *ca.* 1080 cm^{-1}) and ν_4 (at *ca.* 625 cm^{-1}) bands indicates that the T_d symmetry of the ClO_4^- is maintained in these complexes.[33] This suggests the presence of ClO_4^- outside the coordination sphere in the complexes[34]. In acetato complexes two bands have been observed at *ca.* 1630 and 1390 cm^{-1} due to asymmetric and symmetric (COO^-) stretching vibrations.

TABLE-2

KEY INFRARED BANDS (cm^{-1}) OF Co^{2+} COMPLEXES OF BAAPTS AND HBAAPTS

Assignments	ν(NH)	ν(C=N)	ν(C=S) + ν(C=N) + ν(C—N)	δ(NCS) + (C—S) bending	ν(N—N)	ν(C=S)	ν(Co—N)/ ν(Co—S)
BAAPTS	3440 s	1600 us	1330 s	1120 m	1050m	820 s	—
	3270 s		1305 s	1095 m		760 us	
$CoCl_2 \cdot BAAPTS \cdot H_2O$	3437 s	1572 s	1380 s	1160 m	1062m	790 s	455 m
	3265 m		1330 m	1130 m		710 m	350 m
$Co(NO_3)_2 \cdot BAAPTS \cdot H_2O$	3442 s	1570 s	1382 s	1155 m	1065m	780 m	460 m
	3270 m		1335 m	1130 m		715 m	340 m
$Co(NcS)_2 \cdot BAAPTS \cdot H_2O$	3430 s	1560 s	1375 s	1160 m	1060m	782 m	440 m
	3270 s		1330 m	1135 m		720 m	330 w
$Co(CH_3COO)_2 \cdot BAAPTS \cdot H_2O$	3442 s	1570 m	1375 m	1155 m	1062m	780 m	445 m
	3279 m		1335 m	1130 m		725 m	325 w
$Co(ClO_4)_2 \cdot 2(BAAPTS)$	3430 s	1572 m	1370 m	1162 m	1065m	780 m	450 m
	3270 m		1325 m	1140 m		722 m	335 m
HBAAPTS	3440 s	1610 us	1290 s	1125 s	1050m	840 s	—
	3270 s		1260 us	1080 m		760 us	
$CoCl_2 \cdot HBAAPTS \cdot H_2O$	3445 s	1578 s	1340 s	1170 m	1060m	890 m	450 m
	3272 s		1282 m	1110 m		700 m	350 m
$Co(NO_3)_2 \cdot HBAAPTS \cdot H_2O$	3442 s	1580 s	1355 s	1180 m	1065m	890 m	445 m
	3275 s		1285 m	1130 m		730 m	348 m
$Co(NCS)_2 \cdot HBAAPTS \cdot H_2O$	3440 s	1575 s	1350 s	1175 m	1060m	885 m	450 m
	3270 s		1280 m	1125 m		725 m	325 w
$Co(CH_3COO)_2 \cdot HBAAPTS \cdot H_2O$	3435 s	1550 s	1340 m	1170 m	1062 m	885 m	435 m
	3275 s		1282 m	1130 m		732 m	345 w
$CO(ClO_4)_2 \cdot 2(HBAAPTS)$	3440 s	1570 s	1345 m	1190 m	1065 m	870 m	440 m
	3272 s		1280 m	1150 m		720 m	340 w

Electronic spectra

The electronic spectra of all the complexes recorded herein are very similar to each other and consist of two bands—one in the 18500–15400 and the other in 20850—20000 cm^{-1} regions, which clearly indicate the octahedral stereochemistry of the complexes. In Table-3, the band maxima and their assignments and the calculated ligand field parameters are listed. When all the bands ν_1, ν_2 and ν_3 are observed to be free of shoulders, the ligand field parameters Dq and B are, in principle, calculated using first order perturbation theory[35] and the transition energies are given by the equations of Lever[36]. The methods of calculation of ligand field parameters from the ligand field spectra of octahedral Co^{2+} complexes have been discussed by Reedijk *et al.*[37] The energy of ν_1 corresponds to 10 Dq for weak fields and the value of Dq is obtained from it. With these assignments, B and Dq have also been calculated (Table-3). The existence of distortion from a regular octahedral structure is revealed in the present Co^{2+} complexes by appreciable intensity enhancement.

TABLE-3

ELECTRONIC SPECTRAL DATA (cm^{-1}) AND LIGAND FIELD PARAMETERS OF Co^{2+} COMPLEXES OF BAAPTS AND HBAAPTS

Complex	ν_2 $^4T_{1g}(F) \rightarrow {}^4A_{2g}$	ν_3 $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Dq (cm^{-1})	B (cm^{-1})	β	Dq/B	ν_1 (cm^{-1})
$CoCl_2\cdot(BAAPTS)\cdot H_2O$	18520	20000	1115	1070	0.960	1.04	8772
$Co(NO_3)_2\cdot(BAAPTS)\cdot H_2O$	18100	20835	1105	1061	0.950	1.04	8700
$Co(NCS)_2\cdot(BAAPTS)\cdot H_2O$	18000	20835	1104	1060	0.950	1.04	8690
$Co(CH_3COO)_2\cdot(BAAPTS)\cdot H_2O$	18180	20000	1104	1060	0.950	1.04	8700
$Co(ClO_4)_2\cdot 2(BAAPTS)$	18520	20000	1115	1070	0.960	1.04	8770
$CoCl_2\cdot(HBAAPTS)\cdot H_2O$	15500	20830	861	956	0.853	0.90	7955
$Co(NO_3)_2\cdot(HBAAPTS)\cdot H_2O$	15400	20500	855	950	0.848	0.90	7830
$Co(NCS)_2\cdot(HBAPTS)\cdot H_2O$	15450	20670	858	953	0.850	0.90	7806
$Co(CH_3COO)_2\cdot(HBAAPTS)\cdot H_2O$	15500	20720	861	956	0.853	0.90	7955
$Co(ClO_4)_2\cdot 2(HBAAPTS)$	15400	20500	855	950	0.848	0.90	7830

Thermogravimetric analyses

Two representative cobalt(II) complexes of BAAPTS and HBAAPTS, *viz.*, $[Co(BAAPTS)H_2O\cdot Cl_2]$ and $[Co(HBAAPTS)H_2O\cdot(CH_3COO)_2]$ have been undertaken for thermal studies. In all cases Co_3O_4 is the end product. Details of the thermal data are presented in Table-4.

TABLE-4
THERMAL DECOMPOSITION DATA FOR COBALT(II) COMPLEXES OF BAAPTS AND HBAAPTS

Complex	Stage of decomposition	Thermal reaction	Peak temp in d.t.g. (°C)	Temp. range in d.t.g. (°C)	Peak temp in d.t.a. (°C)
$[Co(BAAPTS)\cdot H_2O\cdot Cl_2]$	I	$[Co(BAAPTS)\cdot H_2O\cdot Cl_2] \rightarrow Co(BAAPTS)\cdot Cl_2$	150	105–175	160 (endo)
	II	$Co(BAAPTS)\cdot Cl_2 \rightarrow Co(BAAPTS)_{0.35}\cdot Cl_2$	460	420–510	465 (exo)
	III	$Co(BAAPTS)_{0.35}Cl_2 \rightarrow CoCl_2$	610	570–650	595 (exo)
	IV	$CoCl_2 \rightarrow Co_3O_4$	750	710–790	765 (exo)
$[Co(HBAAPTS)\cdot H_2O\cdot(OAc)_2]$	I	$[Co(HBAAPTS)\cdot H_2O\cdot(OAc)_2] \rightarrow Co(HBAAPTS)(OAc)_2$	150	110–150	155 (endo)
	II	$Co(HBAAPTS)(OAc)_2 \rightarrow Co(HBAAPTS)_{0.3}(OAc)_2$	440	400–480	425 (exo)
	III	$Co(HBAAPTS)_{0.3}(OAc)_2 \rightarrow Co(OAc)_2$	630	590–670	640 (exo)
	IV	$Co(OAc)_2 \rightarrow Co_3O_4$	760	700–780	770 (exo)

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