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Synthesis and Characterization of Co(II) and Ni(II) Complexes of Biologically Active 4[N-(4-dimethylaminobenzalidene)amino] Antipyrine Thiosemicarbazone

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In this paper we report a series of ten complexes of Co(II) and Ni(II) with 4[N-(4-dimethylaminobenzalidene)amino] antipyrine thiosemicarbazone (DABAAPT) having the general composition $MX_2 \cdot (DABAAPT) \cdot H_2O$ ($X = Cl^-$, NO_3^-, NCS^- or CH_3COO^-; $M = Co^{2+}$ or Ni^{2+}) and $M(ClO_4)_2 \cdot 2(DABAAPT)$ ($M = Co^{2+}$ or Ni^{2+}). The complexes were characterized on the basis of elemental analyses, molecular weight, magnetic moment, conductivity measurement, infrared and electronic spectra. In all the complexes DABAAPT behaves as tridentate (N, N, S) ligand. Thermal properties of these complexes were also investigated.

INTRODUCTION

Thiosemicabazones are amongst the most widely studied nitrogen and sulphur donor ligands.[1] They are capable of acting as neutral or charged ligand moieties. Metal complexes of thiosemicarbazones have been known for their pharmacological[2], antitubercular[3], fungicidal[4] and antiviral activities.[4] Recently a number of papers have appeared detailing synthesis and characterization of Co^{2+} and Ni^{2+} complexes of thiosemicarbazones.[5,6] In the present study a series of ten Co^{2+} and Ni^{2+} complexes of 4[N-(4-dimethylaminobenzalidene)amino] antipyrine thiosemicarbazone (DABAAPT) are reported.

EXPERIMENTAL

$MX_2 \cdot nH_2O$ ($M = Co^{2+}$ or Ni^{2+} $X = Cl^-$, NO_3^- or CH_3COO^-) were obtained from B.D.H. and were used as such. $M(SCN)_2$ 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 the filtrate having respective metal thiocyanate was used immediately for complex formation. $M(ClO_4)_2$ were prepared by the addition of an ethanolic solution of sodium perchlorate into respective metal chloride solution. White precipitate of NaCl was filtered off and the filtrate $M(ClO_4)_2$ was used as such for complex formation. The ligand DABAAPT was prepared as reported earlier.[7]

(a) *Co^{2+} complexes*: All the complexes were prepared by mixing ethanolic solutions of metal salt and DABAAPT in either 1 : 1 or 1 : 2 molar ratio. The mxture was refluxed on a water bath for *ca.* 3 h and then concentrated the reaction mixture 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}.

(b) *Ni complexes*: A hot ethanolic solution of the corresponding nickel(II) salt was mixed with a hot ethanolic solution of DABAAPT (ether 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 physico-chemical analyses were performed according to reported method.[8]

RESULTS AND DISCUSSION

The interaction of Co^{2+} and Ni^{2+} salts with DABAAPT resulted in the formation of the complexes of the MX_2(DABAAPT)·H_2O (M = Co^{2+} or Ni^{2+}, X = Cl^-, NO_3^-, NCS^- or CH_3COO^-) and $M(ClO_4)_2$·2(DABAAPT). The analytical data of these complexes are presented 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 and decomposed on heating beyond 270°C. The molar conductance values of the complexes in nitrobenzene (Table-1) indicate that the chloro, nitrato, thiocyanato and acetato complexes are non-electrolytes in nature while the perchlorato complexes dissociate in nitrobenzene and behave as 1 : 2 electrolytes. Magnetic moments on the Co^{2+} complexes show that all the complexes are paramagnetic and have three unpaired electrons indicating a high-spin octahedral configuration.[9] For the present complexes these values lie in the range 4.6–5.4 B.M. The magnetic moment values of Ni^{2+} complexes lie in 2.6–3.2 B.M range which are inconsistent with the octahedral geometry.[9]

A study and comparison of infrared spectra of DABAAPT and its complexes with Co^{2+} and Ni^{2+} imply that the ligand behaves as a neutral tridentate and the metals are coordinated through N and N of two azomethine groups and of S of thioketo group. The strong bands observed at 3440–3270 cm^{-1} region in free ligand have been assigned to ν(NH) vibrations. Practically no effect on these frequencies after complexation preclude the possibility of complexation at this group. The absorption at *ca.* 1600 cm^{-1} in the free ligand is attributed to ν(C═N) of imine nitrogen, which is in agreement with the observations of previous workers.[10,11] On complexation these frequencies were observed to be shifted to lower wavenumbers. In the spectra of present ligand, the bands observed in 1300–1125 cm^{-1} region, 1120–1095 cm^{-1} and 840–730 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) respectively, following the reports of Irving *et al.*[12] Coordination of sulphur with the metal ion would result in the displacement of electrons towards the latter, thus resulting in the weakening of (C═S) bond. Hence, on complexation ν(C=S) stretching vibrations should decrease and that of ν(CN) should increase. In all the present complexes of Co^{2+} and Ni^{2+} with DABAAPT, the frequencies in the range 1300–1125 cm^{-1} get an increase by nearly 50–60 cm^{-1}; similarly bending modes of (N—C—S) and (C=S) also get increased but in lesser amount. On the other hand, on complexation the frequencies in 840–730 cm^{-1} are shifted to lower wavenumbers and intensities of the bands are also reduced. The possibility of thione-thiol tautomerism (H—N—C=S) $\rightleftharpoons$ (C=N—SH) in this ligand has been ruled out for no band around 2700–2500 cm^{-1} characteristics of thiol group displayed in the infrared spectra.[13,14] In far infrared region ν(M—N)/ν(M—S) bands have also been identified (Table-2).

The presence of coordinated water was suggested by the very broad absorption band 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.[15]

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

Complex	%Analysis, found (calcd.)			M.W. Found (calc.)	Λ_m (ohm^{-1} cm^2 mole^{-1})	μ_{eff} (B.M.)
	M	N	S			
$CoCl_2\cdot(H_2O)$(DABAAPT)	10.50 (10.63)	17.40 (17.65)	5.70 (5.76)	550 (555)	3.6	4.8
$Co(NO_3)_2\cdot(H_2O)$(DABAAPT)	9.60 (9.70)	20.53 (20.72)	5.20 (5.26)	602 (608)	2.9	5.1
$Co(NCS)_2\cdot(H_2O)$(DABAAPT)	9.71 (9.83)	20.87 (21.00)	15.59 (16.00)	593 (600)	3.7	5.2
$Co(CH_3COO)_2\cdot(H_2O)$(DABAAPT)	9.70 (9.80)	16.16 (16.27)	5.25 (5.31)	593 (602)	2.8	5.0
$Co(ClO_4)_2$(DABAAPT)	5.42 (5.50)	18.04 (18.28)	5.92 (5.97)	367 (1072)	52.9	4.9
$NiCl_2\cdot(H_2O)$(DABAAPT)	10.51 (10.63)	17.52 (17.65)	5.70 (5.76)	549 (555)	4.1	3.1
$Ni(NO_3)_2(H_2O)$(DABAAPT)	9.61 (9.70)	20.51 (20.72)	5.20 (5.26)	601 (608)	3.9	2.9
$Ni(NCS)_2(H_2O)$(DABAAPT)	9.71 (9.83)	20.84 (21.00)	15.62 (16.00)	594 (600)	5.2	3.2
$Ni(CH_3COO)_2(H_2O)$(DABAAPT)	9.69 (9.80)	16.17 (16.27)	5.23 (5.21)	595 (602)	5.3	2.6
$Ni(ClO_4)_2\cdot2$(DABAAPT)	5.43 (5.50)	18.05 (18.28)	5.92 (5.97)	368 (1072)	52.9	3.2

The presence of the ν_3 (*ca.* 1095 cm^{-1}) and ν_4 (625 cm^{-1}) infrared bands in both perchlorato complexes indicates that the T_d symmetry of ClO_4^- is maintained in both the complexes. This, therefore, suggests the presence of ClO_4^- outside the coordination sphere in these complexes.[8] In both the thiocyanato complexes the three fundamental absorptions (C—N) stretch (ν_1), (C—S) stretch (ν_3) and

TABLE-2

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

Compounds	ν(NH)	ν(C=N)	ν(C=S) + ν(C=N) + ν(C—N)	δ(NCS) and CS-bending	ν(N—N)	ν(C=S)	ν(M—N) and ν(M—S)
DABAAPT	3360 s	1600 vs	1310 m	1115 m	1050 m	830 s	—
	3330 s		1290 m	1095 w		730 m	
$CoCl_2\cdot$(DABAAPT)$\cdot H_2O$	3362 s	1572 m	1365 m	1165 m	1065 m	782 m	440 m
	3320 m		1340 m	1132 m		710 m	325 m
$Co(NO_3)_2$(DABAAPT)$\cdot H_2O$	3360 s	1575 m	1365 m	1160 m	1062 m	770 s	445 s
	3332 m		1342 m	1142 m		705 m	320 w
$Co(NCS)_2$(DABAAPT)$\cdot H_2O$	3362 s	1565 m	1372 m	1165 m	1060 m	775 m	440 m
	3330 m		1345 m	1130 m		722 m	325 w
$Co(CH_3COO)_2\cdot$(DABAAPT)$\cdot H_2O$	3365 s	1565 m	1370 m	1162 m	1065 m	770 m	440 m
	3335 m		1340 m	1135 m		715 m	340 w
$Co(ClO_4)_2\cdot 2$(DABAAPT)	3360 m	1570 m	1370 m	1175 m	1068 m	775 s	435 m
	3335 m		1330 m	1138 m		710 m	340 w
$NiCl_2\cdot$(DABAAPT)$\cdot H_2O$	3370 m	1570 s	1380 s	1155 m	1062 m	780 s	445 m
	3340 m		1330 m	1135 m		722 s	330 w
$Ni(NO_3)$(DABAAPT)$\cdot H_2O$	3362 m	1572 s	1382 s	1162 m	1068 m	785 s	430 m
	3330 m		1335 m	1132 m		725 s	335 w
$Ni(NCS)_2$(DABAAPT)$\cdot H_2O$	3365 m	1560 s	1385 s	1160 m	1065 m	780 s	435 m
	3330 m		1335 m	1135 m		725 s	340 w
$Ni(CH_3COO)_2$(DABAAPT)$\cdot H_2O$	3358 m	1572 s	1380 s	1165 m	1065 m	790 s	440 m
	3332 s		1335 m	1132 m		705 m	342 w
$Ni(ClO_4)_2\cdot 2$(DABAAPT)	3362 s	1570 s	1380 s	1162 m	1058 m	785 s	430 m
	3330 m		1340 s	1132 m		710 s	335 w

(N—C—S) bending (ν_2) are identified, which are associated with the terminal N-bonded isothiocyanate ions.[16] The absence of ν_3 band of ionic nitrate (D_{3h}) at *ca.* 1360 cm^{-1} and the occurrence of two strong bands at *ca.* 1560–1490 cm^{-1} and 1300–1280 cm^{-1} region suggest the covalent nature of NO_3^-. The presence of ν_2, ν_6, ν_3 and ν_5 bands in all these complexes further confirms the covalency of NO_3^- ions in these complexes. By applying Lever separation method, the monodentato nature of nitrate ions in these complexes is suggested. In acetate complexes two bands have been observed at *ca.* 1630 cm^{-1} and 1390 cm^{-1} which may be assigned to antisymmetric and symmetric (COO^-) stretching vibrations[18] respectively.

The electronic spectra of Co^{2+} complexes consist of two bands in the 15,400–18,520 cm^{-1} assigned to $^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$ and the other in the 20,000–20,835 cm^{-1} assigned to the transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3). Ligand field parameters 10 Dq, B and β have been evaluated and ν_1 has been calculated in these complexes. Six-coordinated Ni^{2+} complexes exhibit spectra involving three spin-allowed transitions to $^3T_{2g}(F)(\nu_1)$, $^3T_{2g}(F)(\nu_2)$ and $^3T_{1g}(P)(\nu_3)$ from the ground state $^3A_{2g}(F)$. These occur in 8000–11000 cm^{-1} (ν_1), 15000–17,700 cm^{-1} (ν_2) and 24,400–27,500 cm^{-1} (ν_3) regions respectively. The ligand field parameters 10 Dq, B and β in octahedral complexes have been computed from equations suggested by Lever *et al.* These data are in good agreement with those reported for other octahedral complexes.

Thermal properties of these complexes were studied by thermogravimetric analysis. The t.g. data indicate that the complexes are stable up to 140°C, which indicates that these complexes are non-hygroscopic in nature. At this stage one water mole present in coordination sphere is lost, after which decomposition and deligation process started. The more or less similar type t.g. curves are obtained and the end product is metal oxide in every case. The thermal changes are represented as follows:

$$\mathrm{Co(DABAAPT)\cdot H_2O\cdot Cl_2} \xrightarrow{120\text{–}170^\circ C} \mathrm{Co(DABAAPT)Cl_2} \xrightarrow{220\text{–}280^\circ C}$$

$$\mathrm{Co(DABAAPT)_{0.5}Cl_2} \xrightarrow{380\text{–}440^\circ C} \mathrm{CoCl_2} \xrightarrow{525\text{–}610^\circ C} \mathrm{Co_3O_4}.$$

$$\mathrm{Co(DABAAPT)\cdot H_2O(CH_3COO)_2} \xrightarrow{125\text{–}170^\circ C} \mathrm{Co(DABAAPT)(CH_3COO)_2}$$

$$\xrightarrow{210\text{–}270^\circ C} \mathrm{Co(DABAAPT)_{0.5}(CH_3COO)_2} \xrightarrow{360\text{–}435^\circ C} \mathrm{Co(CH_3COO)_2}$$

$$\xrightarrow{530\text{–}605^\circ C} \mathrm{Co_3O_4}.$$

$$\mathrm{Co(DABAAPT)\cdot H_2O(NO_3)_2} \xrightarrow{130\text{–}175^\circ C} \mathrm{Co(DABAAPT)(NO_3)_2} \xrightarrow{225\text{–}280^\circ C}$$

$$\mathrm{Co(DABAAPT)_{0.5}(NO_3)_2} \xrightarrow{380\text{–}440^\circ C} \mathrm{Co(NO_3)_2} \xrightarrow{520\text{–}610^\circ C} \mathrm{Co_3O_4}.$$

$$\mathrm{Co(DABAAPT)H_2O(NCS)_2} \xrightarrow{125\text{–}170^\circ C} \mathrm{Co(DABAAPT)(NCS)_2} \xrightarrow{230\text{–}275^\circ C}$$

$$\mathrm{Co(DABAAPT)_{0.5}(NCS)_2} \xrightarrow{350\text{–}425^\circ C} \mathrm{Co(NCS)_2} \xrightarrow{525\text{–}605^\circ C} \mathrm{Co_3O_4}.$$

$$\mathrm{Ni(DABAAPT)H_2O{\cdot}Cl_2} \xrightarrow{125\text{–}170^\circ\mathrm{C}} \mathrm{Ni(DABAAPT)Cl_2} \xrightarrow{230\text{–}320^\circ\mathrm{C}}$$

$$\mathrm{Ni(DABAAPT)_{0.5}Cl_2} \xrightarrow{370\text{–}425^\circ\mathrm{C}} \mathrm{NiCl_2} \xrightarrow{540\text{–}605^\circ\mathrm{C}} \mathrm{NiO}.$$

$$\mathrm{Ni(DABAAPT)H_2O{\cdot}(CH_3COO)_2} \xrightarrow{120\text{–}165^\circ\mathrm{C}} \mathrm{Ni(DABAAPT)(CH_3COO)_2}$$

$$\xrightarrow{210\text{–}300^\circ\mathrm{C}} \mathrm{Ni(DABAAPT)_{0.5}(CH_3COO)_2} \xrightarrow{340\text{–}405^\circ\mathrm{C}} \mathrm{Ni(CH_3COO)_2}$$

$$\xrightarrow{530\text{–}595^\circ\mathrm{C}} \mathrm{NiO}.$$

$$\mathrm{Ni(DABAAPT)H_2O(NO_3)_2} \xrightarrow{120\text{–}165^\circ\mathrm{C}} \mathrm{Ni(DABAAPT)(NO_3)_2} \xrightarrow{240\text{–}325^\circ\mathrm{C}}$$

$$\mathrm{Ni(DABAAPT)_{0.5}(NO_3)_2} \xrightarrow{350\text{–}410^\circ\mathrm{C}} \mathrm{Ni(NO_3)_2} \xrightarrow{535\text{–}600^\circ\mathrm{C}} \mathrm{NiO}.$$

In conclusion, the type of complexes isolated during the present study demonstrate that interactions of Co^{2+} and Ni^{2+} salts with DABAAPT may lead to complexes with 1 : 1 and 1 : 2 stoichiometries. The overall experimental evidences show that these metal ions display a coordination number six and presumably have distorted octahedral environment around the central metal ion.

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