

Synthesis and Magneto-spectral Studies of Cobalt(II) and Nickel(II) Complexes of 4[N-(*p*-Dimethylaminobenzalidene) Amino] Antipyrine Semicarbazone

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A series of Co(II) and Ni(II) complexes of 4[N-(*p*-dimethylaminobenzalidene) amino] antipyrine semicarbazone (DABAAPS) of the general composition $\text{MX}_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Co}^{2+}$ or Ni^{2+} , $\text{X} = \text{Cl}^-$, NO_3^- , NCS^- or CH_3COO^-) or $\text{M}(\text{ClO}_4)_2 \cdot 2(\text{DABAAPS})$ ($\text{N} = \text{Co}^{2+}$ or Ni^{2+}). These complexes were characterized through elemental analysis, electrical conductance, magnetic studies, infrared and electronic spectra. In all the complexes DABAAPS behaves as tridentate (N,N,O) ligand and has octahedral geometry. Thermal properties of these complexes were also investigated.

Key words: Cobalt, nickel, complexes, semicarbazones, characterization.

INTRODUCTION

In the last three decades, a number of workers were interested in isolating solid complexes of transition metal ions with biologically active ligands^{1,2}. In the present work we report the synthesis and characterization of Co^{2+} and Ni^{2+} complexes of 4[N-(*p*-dimethylaminobenzalidene) amino] antipyrine semicarbazone (DABAAPS).

EXPERIMENTAL

All the solvents and reagents used were of AnalaR grade. the ligand DABAAPS was synthesized in the laboratory by reported method^{3,4}.

Synthesis of the complexes

1. All the cobalt(II) complexes were prepared as follows. Hot ethanolic solution of the corresponding cobalt salt (1 mmol) and hot ethanolic solution of DABAAPS were mixed in molar ratio 1 : 2. The mixture was refluxed on a water bath for *ca.* 1 h. On cooling, the contents, pink to red coloured complex separated out. It was filtered, washed with ethanol and dried in an electric oven at *ca.* 60°C. Yield 60–70%.
2. In case of synthesis of nickel(II) complexes, a hot ethanol solution of corresponding nickel(II) salt (1 mmol) was mixed with a hot ethanolic solution of DABAAPS (2 mmol). The mixture was heated to reflux on a water bath for 3–4 h. On cooling, a coloured complex separated out. This was filtered, washed with ethanol and dried over P_4O_{10} . Yield 60–70%.

All the physico-chemical studies of the complexes were performed as reported earlier⁵.

RESULTS AND DISCUSSION

The analytical data (Table-1) show that all the complexes have the general compositions $\text{MX}_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Co}^{2+}$ or Ni^{2+} , $\text{X} = \text{Cl}^-$, NO_3^- , NCS^- or CH_3COO^-) or $\text{M}(\text{ClO}_4)_2 \cdot 2(\text{DABAAPS})$ ($\text{M} = \text{Co}^{2+}$ or Ni^{2+}). All the complexes are fairly soluble in common organic solvents. The molar conductance values of the complexes in PhNO_2 (Table-1) indicate that the chloro-, nitro-, thiocyanato- and acetato- complexes are essentially non-electrolytes, while the perchlorato-complexes behave as 1 : 2 electrolytes. The molecular weights in freezing PhNO_2 are in broad agreement with the conductance data (Table-1). Magnetic measurements on the Co^{2+} complexes (Table-1) show that all the complexes are paramagnetic and have three unpaired electrons indicating a high-spin octahedral configuration⁶. For these complexes the magnetic values lie in the range 4.6–5.2 B.M. The magnetic moments observed for the present Ni^{2+} complexes of DABAAPS range from 2.8–3.3 B.M. which suggests octahedral stereochemistry⁵.

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

Complex	% Analysis, found (calcd.)			m.w., found (calcd.)	Λ_m ($\text{ohm}^{-1} \text{cm}^2$ mole^{-1})	μ_{eff} (B.M.)
	M	N	Anion			
$\text{CoCl}_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$	10.85 (10.94)	18.09 (18.18)	13.08 (13.17)	532 (539)	2.3	4.9
$\text{Co}(\text{NO}_3)_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$	9.89 (9.96)	21.19 (21.28)	—	585 (592)	2.7	5.1
$\text{Co}(\text{NCS})_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$	9.97 (10.10)	21.48 (21.57)	19.63 (19.86)	578 (584)	2.1	4.6
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$	9.93 (10.06)	16.60 (16.72)	—	579 (586)	2.0	5.2
$\text{Co}(\text{ClO}_4)_2 \cdot 2\text{DABAAPS}$	5.59 (5.67)	18.73 (18.84)	19.03 (19.13)	339 (1040)	52.3	4.8
$\text{NiCl}_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$	10.86 (10.94)	18.09 (18.18)	13.09 (13.17)	533 (539)	2.4	3.0
$\text{Ni}(\text{NO}_3)_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$	9.87 (9.96)	21.19 (21.28)	—	587 (592)	2.9	2.9
$\text{Ni}(\text{NCS})_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$	9.99 (10.10)	21.44 (21.57)	19.65 (19.86)	578 (584)	2.3	3.3
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$	9.95 (10.06)	16.60 (16.72)	—	580 (586)	2.1	2.8
$\text{Ni}(\text{ClO}_4)_2 \cdot 2\text{DABAAPS}$	5.60 (5.67)	18.73 (18.84)	19.04 (19.13)	341 (1040)	51.9	2.9

Infrared spectra: The key infrared spectral bands of DABAAPS and its Co^{2+} and Ni^{2+} complexes are presented in Table-2. As expected, the $\nu(\text{NH}_2)$ band of the hydrazinic nitrogen of semicarbazide (1622 cm^{-1}) is absent in the infrared spectra of the semicarbazone⁷. It has also been observed that the amide-II band is shifted towards the lower energy side compares to that of the semicarbazone. The effect is due to the electron density drift from the hydrazinic nitrogen⁸.

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

Compounds	Assignments	$\nu(\text{C}=\text{N})$ (azo- methinic)	$\nu(\text{C}=\text{N})$ (hydra- zinic)	$\nu(\text{C}=\text{O})$			$\nu(\text{M}-\text{N})$ $\nu(\text{M}-\text{O})$
				I	II	III	
DABAAPS		1620 s	1605 s	1705 s	1570 s	1350 m	—
$\text{CoCl}_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$		1582 s	1632 m	1650 s	1530 m	1332 m	460 m 390 w
$\text{Co}(\text{NO}_3)_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$		1590 s	1635 m	1645 s	1537 m	1340 m	455 m 385 w
$\text{Co}(\text{NCS})_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$		1595 s	1630 s	1650 s	1540 m	1337 m	445 m 375 w
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$		1590 s	1635 s	1645 s	1535 m	1335 m	450 m 380 w
$\text{Co}(\text{ClO}_4)_2 \cdot 2\text{DABAAPS}$		1593 s	1625 s	1642 s	1532 m	1330 m	455 m 375 w
$\text{NiCl}_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$		1585 s	1630 s	1648 s	1535 m	1325 m	460 m 385 w
$\text{Ni}(\text{NO}_3)_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$		1590 s	1632 s	1645 s	1530 m	1328 m	465 m 380 w
$\text{Ni}(\text{NCS})_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$		1582 s	1630 s	1650 s	1535 m	1325 m	470 m 395 w
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$		1585 s	1632 s	1652 s	1532 m	1328 m	465 m 390 w
$\text{Ni}(\text{ClO}_4)_2 \cdot 2\text{DABAAPS}$		1582 s	1635 s	1650 s	1535 m	1325 m	465 m 392 w

The characteristic absorption of the carbonyl group in DABAAPS is observed at 1705 cm^{-1} . In these complexes, this band is shifted towards lower energy in the $1650\text{--}1642 \text{ cm}^{-1}$ region. The amide-II band in the free ligand has been observed at 1570 cm^{-1} . In all the present complexes, this band is also shifted towards lower wave numbers. This observation suggests coordination through the carbonyl-oxygen atom⁹. The strong band at 1605 cm^{-1} in free DABAAPS apparently has a large contribution from the $\nu(\text{C}=\text{N})$ mode of semicarbazone moiety¹⁰. This has been observed as a blue shift in the position of the $(\text{C}=\text{N})$

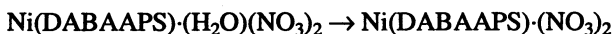
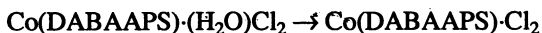
band in all complexes as compared to the free ligand. Another strong band was observed at 1620 cm^{-1} due to azomethinic ($\text{C}=\text{N}$) absorption. On complexation this band is shifted towards the lower frequency region, clearly indicating the coordination through the azomethine N-atom^{11, 12}. In $470\text{--}375\text{ cm}^{-1}$ region the bands due to $\nu(\text{M}-\text{N})/\nu(\text{M}-\text{O})$ also appeared^{1, 5}. 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 water¹³.

In the $\text{M}(\text{NO}_3)_2 \cdot \text{DABAAPS} \cdot \text{H}_2\text{O}$ complexes, the absence of the ν_3 band at *ca.* 1360 cm^{-1} indicates the absence of ionic nitrate. The coordinated nitrate groups^{14, 15} which would show absorptions at $1505\text{--}1420\text{ cm}^{-1}$ (ν_1), $1325\text{--}1275\text{ cm}^{-1}$ (ν_5), $1045\text{--}1025\text{ cm}^{-1}$ (ν_2), and $810\text{--}805\text{ cm}^{-1}$ (ν_6), indicate the covalent nature of nitrate group. The complexes under study show IR-bands at *ca.* 1435 cm^{-1} (ν_1), 1330 cm^{-1} (ν_5), 1025 cm^{-1} (ν_2), and 810 cm^{-1} (ν_6). The separation of 105 cm^{-1} between ν_1 and ν_5 indicates the monodentate nature of the nitrate group¹⁶. The location and number of the $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$, infrared bands for the thiocyanato complexes are generally diagnostic of the mode of coordination of the NCS group. The bands at *ca.* 2050 cm^{-1} , 820 cm^{-1} and 475 cm^{-1} are due to $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$, respectively. These frequencies are attributable to the N-bonded thiocyanate group in these complexes¹⁷. In the $\text{M}(\text{DABAAPS})_2 \cdot (\text{ClO}_4)_2$ 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 complexes¹⁸. This suggests the presence of ClO_4^- outside the coordination sphere in the complexes¹⁹.

The electronic spectra of all the cobalt(II) complexes recorded herein are very similar to each other and consist of two bands—one in the $17200\text{--}16700\text{ cm}^{-1}$ and the other in the $22000\text{--}20400\text{ cm}^{-1}$ region which clearly indicates the octahedral stereochemistry of the complexes²⁰.

The present six-coordinated nickel(II) complexes exhibit a spectrum involving three spin-allowed transitions to ${}^3\text{T}_{2g}(\text{F})(\nu_1)$, ${}^3\text{T}_{1g}(\text{F})(\nu_2)$ and ${}^3\text{T}_{1g}(\text{P})(\nu_3)$ from the ground state ${}^3\text{A}_{2g}(\text{F})$. These occur in the $11000\text{--}7000\text{ cm}^{-1}$ (ν_1), $19000\text{--}15000\text{ cm}^{-1}$ (ν_2), and $29000\text{--}25000\text{ cm}^{-1}$ (ν_3) regions respectively²⁰.

Thermal studies: The thermal properties of two representative Co(II) and Ni(II) complexes of DABAAPS have been studied. A careful analysis of t.g. curves suggests that these complexes contain one molecule of coordinated water, which is evident by loss in weight at *ca.* 160°C . There is no change up to *ca.* 250°C . After that there is a break in the curves due to evaporation of 0.5 molecule of DABAAPS. The remaining ligand is removed from the coordination sphere at *ca.* 320°C . Finally at *ca.* 600°C oxide formation takes place. In brief, the thermal equations are shown as:



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