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Synthesis, Magneto-Spectral and Thermal Studies of Cobalt(II) and Nickel(II) Complexes of 4-[N-(4-Dimethylaminobenzylidene) amino] Antipyrine

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SYNTHESIS, MAGNETO-SPECTRAL AND THERMAL STUDIES OF COBALT(II) AND NICKEL(II) COMPLEXES OF 4-[N-(4-DIMETHYLAMINOBENZYLIDENE)AMINO]ANTIPYRINE

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ABSTRACT

Reactions of MX_2 (M = Co or Ni, X = Cl^-, Br^-, I^-, NO_3^-, NCS^-, or ClO_4^-) with 4-[N-(4-dimethylaminobenzylidene)-amino]antipyrine (DABAAP) yielded complexes of the type $[M(DABAAP)_2X_2]$ or $[M(DABAAP)_3](ClO_4)_2$. The IR spectra of these complexes indicate that the ligand is a neutral bidentate ligand coordinating through the azomethine nitrogen and carbonyl oxygen. All the complexes are six-coordinated according the data of magnetic and electronic spectral measurements.

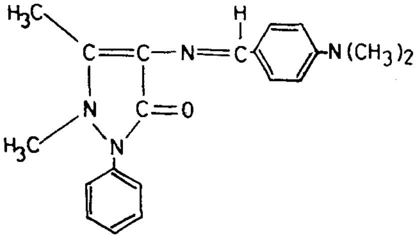
INTRODUCTION

Condensation of a primary amine and a carbonyl group produces the azomethine group, $>C = N-$, which is known to form stable complexes with various metal ions. In the past, a number of workers have used 4-aminoantipyrines as ligands in isolating solid complexes with 3d-metal ions[1-3]. Comparatively, very much less is known about the Schiff base complexes of 4-aminoantipyrine with transition metal ions[4]. In view of this, in this work,we have been concerned with the synthesis, magneto-spectral and thermal properties of Co(II) and Ni(II) with 4/¯N-(4-dimethylaminobenzylidene)-amino_7antipyrine (DABAAP) Schiff base obtained by condensation of 4-dimethylaminobenzaldehyde with 4-aminoantipyrine in alcoholic solution (Fig.1).

EXPERIMENTAL

Materials

All the solvents and reagents used were of AnalR grade. The Schiff base (DABAAP) was synthesized as follows. A solution of p-dimethylaminobenzaldehyde (1 mmol, 0.15 g) in absolute ethanol (20 mL) was mixed with 4-aminoantipyrine (1.1 mmol, 0.22 g) in the same solvent (25 mL) and the mixture was refluxed for 2 h. On cooling, a yellow crystalline product was separated which was filtered off and recrystallized in the same solvent (yield 75%, 0.25 g, yellow, m.p. 203°C, m.f. $C_{20}H_{22}N_4O$. Analysis: Found (Calcd.) %; C, 71.73 (71.85); H, 6.43 (6.58); N, 16.39 (16.76).



4 [N-(4-Dimethylaminobenzylidene)amino]antipyrine
(DABAAP)

Fig. 1. Structure of the Ligand

Synthesis of the Complexes

1. All the cobalt(II) complexes were prepared as follows. The corresponding cobalt salt (1 mmol) dissolved in 10 mL of ethanol was added to an ethanolic solution (20 mL) of the ligand (3 mmol, 1 g). The reaction mixture was refluxed on a water bath for 2-3 h and then concentrated to 1/3 of its volume. On cooling, the crystals of the complexes thus obtained were filtered, washed with ethanol and dried in a vacuum desiccator over P_4O_{10}, yield 60-70%.

2. A general method has been used for the preparation of the nickel(II) complexes. A hot ethanolic solution (15 mL) of the corresponding nickel(II) salt (1 mmol) was mixed with a hot ethanolic solution (20 mL) of the ligand (3 mmol, 1 g). The reaction mixture was refluxed on a water bath for 2-3 h and then concentrated to 1/3 of its volume. On cooling, crystals of the complexes obtained were filtered, washed with ethanol and dried in a vacuum desiccator over P_4O_{10}, yield 60-70%.

Analyses and measurements

The metal content of the complexes was determined complexometrically by an EDTA method and the anions as reported previously[5]. The electrical conductance, molecular weight and infrared measurements were made as reported earlier[6]. The magnetic susceptibility was measured using a Faraday balance (Field 10000 Gauses) using copper sulphate as calibrant at room temperature. Electronic spectra were recorded using a Beckmann spectrophotometer. The infrared spectra of the complexes were recorded on a Perkin Elmer Infrared spectrophotometer model 521 in CsI in the range of 4000-200 cm^{-1}.

RESULTS AND DISCUSSION

The formation of the complexes can be represented by the following two equations.

$$MX_2 + 2\ DABAAP \xrightarrow[Refluxing]{Ethanol} M(DABAAP)_2X_2 \qquad (1)$$

$(M = Co, Ni;\ X = Cl^-, Br^-, I^-, NO_3^-$ or $NCS^-)$

$$M(ClO_4)_2 + 3\ DABAAP \xrightarrow[Refluxing]{Ethanol} M(DABAAP)_3(ClO_4)_2 \qquad (2)$$

$(M = Co$ or $Ni)$

The analytical data (Table I) indicate that the complexes described herein have the general compositions $M(DABAAP)_2X_2$ $(M = Co, Ni;\ X = Cl^-, Br^-, I^-, NO_3^-$, or $NCS^-)$ or $M(DABAAP)_3(ClO_4)_2$ $(M = Co, Ni)$. All the complexes are fairly soluble in acetone, nitrobenzene, DMSO and DMF. TG curves up to 150°C suggest the absence of coordinated or uncoordinated water molecules in the complexes. The values of molar conductance in nitrobenzene for the halo, nitrato and thiocyanato 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 I).

Infrared Spectra

The ligand DABAAP is expected to act as a neutral bidentate species, the possible coordination sites being (a) the carbonyl oxygen and (b) the azomethine nitrogen. The IR spectrum of the free ligand shows very strong bands at 1650 and 1645 cm^{-1} due to the ν(C=O) mode and another strong band at 1590 cm^{-1} due to the ν(C=N) mode. After complexation with Co(II) and Ni(II) ions, these two bands are shifted to lower wave number and appear in the 1620-1590 cm^{-1} and 1575-1530 cm^{-1} regions, respectively. The shifts to lower wave numbers in these complexes suggest that both, the carbonyl and azomethine groups, are coordinated to the metal ions[3,7-9]. In the far IR region an absorption at ca. 660 cm^{-1} has been assigned to C=O in plane bending in the free ligands which shows a shift to higher wave numbers on complexation. Some new medium and weak bands are observed in the frequency range 460-385 cm^{-1} in the complexes and are tentatively assigned to ν(M-O) and ν(M-N) modes[3].

Table I. Analytical, Conductivity, Molecular Weight and Magnetic Moments Data of Co(II) and Ni(II) Complexes of DABAAP

Complex (Formula)	Yield (%)	M.pt. (°C)	Found (Calc.) %			Mol.wt. Found (Calc.)	Λ_M (ohm^{-1} cm^2 mole^{-1})	μ_{eff}^a B.M.
			M	N	Anion			
$CoCl_2$.2 DABAAP ($CoC_{40}H_{44}N_8O_2Cl_2$)	70	240	7.32 (7.39)	13.92 (14.03)	8.67 (8.89)	783 (798)	4.3	4.9
$CoBr_2$.2 DABAAP ($CoC_{40}H_{44}N_8O_2Br_2$)	67	239	6.59 (6.65)	12.50 (12.62)	17.83 (18.03)	874 (887)	4.2	5.1
CoI_2.2 DABAAP ($CoC_{40}H_{44}N_8O_2I_2$)	65	243	5.92 (6.01)	11.32 (11.41)	25.42 (25.89)	968 (981)	4.9	4.6
$Co(NO_3)_2$.2 DABAAP ($CoC_{40}H_{44}N_{10}O_8$)	70	240	6.86 (6.93)	16.36 (16.45)	-	839 (851)	3.2	5.2
$Co(NCS)_2$.2 DABAAP ($CoC_{42}H_{44}N_{10}O_2S_2$)	65	250	6.90 (6.99)	16.52 (16.60)	13.63 (13.76)	829 (843)	2.9	4.8
$Co(ClO_4)_2$.3 DABAAP ($CoC_{60}H_{66}N_{12}O_{11}Cl_2$)	65	219	4.59 (4.68)	13.24 (13.33)	15.66 (15.79)	413 (1260)	52.1	5.0

$NiCl_2$.2 DABAAP ($NiC_{40}H_{44}N_8O_2Cl_2$)	70	240	7.31 (7.39)	13.91 (14.03)	8.66 (8.89)	787 (798)	4.4	3.0
$NiBr_2$.2 DABAAP ($NiC_{40}H_{44}N_8O_2Br_2$)	68	242	6.58 (6.65)	12.51 (12.62)	17.80 (18.03)	873 (887)	5.2	2.9
NiI_2.2 DABAAP ($NiC_{40}H_{44}N_8O_2I_2$)	65	222	5.91 (6.01)	11.33 (11.41)	25.40 (25.89)	969 (981)	5.6	3.2
$Ni(NO_3)_2$.2 DABAAP ($NiC_{40}H_{44}N_{10}O_8$)	68	237	6.86 (6.93)	16.37 (16.45)	-	839 (851)	3.9	2.8
$Ni(NCS)_2$.2 DABAAP ($NiC_{42}H_{44}N_{10}O_2S_2$)	65	245	6.91 (6.99)	16.50 (16.60)	13.53 (13.76)	832 (843)	4.1	2.9
$Ni(ClO_4)_2$.3 DABAAP ($NiC_{60}H_{66}N_{12}O_{11}Cl_2$)	60	212	4.60 (4.68)	13.23 (13.33)	15.55 (15.79)	415 (1260)	52.9	3.1

In the M(DABAAP)$_2$(NO$_3$)$_2$ complexes, the absence of the ν_3 band at ca. 1360 cm^{-1} indicates the absence of ionic nitrate. The coordinated nitrate[10-12] groups which would show absorptions at 1505-1420 (ν_1), 1325-1275 cm^{-1} (ν_5), 1045-1020 cm^{-1} (ν_2) and 810-805 cm^{-1} (ν_6) indicate the covalent nature of nitrate group. The complexes under study show IR bands at 1435 cm^{-1} (ν_1), 1325 cm^{-1} (ν_5), 1020 cm^{-1} (ν_2) and 810 cm^{-1} (ν_6). The separation of 110 cm^{-1} between ν_1 and ν_5 indicates the monodentate[13] nature of the nitrate group. The location and number of the ν(CN), ν(CS) and δ(NCS), IR 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 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. In the M(DABAAP)$_3$(ClO$_4$)$_2$ complexes, the presence of the ν_3 (at ca. 1080 cm^{-1}) and ν_4 (at ca. 625 cm^{-1}) bands indicate that the T_d symmetry of the ClO_4^- is maintained in these complexes[15]. This suggests the presence of ClO$_4$ outside the coordination sphere in the complexes[16].

Magnetic and Electronic Spectral Studies

Cobalt(II) Complexes. Magnetic measurements of the complexes of cobalt(II) (μ_{eff} = 4.6 - 5.1 B.M.) reported herein show that all are paramagnetic and have three unpaired electrons indicating a highspin octahedral configuration[17].

Table II. Electronic Spectral Bands (cm^{-1}) and Ligand Field Parameters for Co(II) Complexes with DABAAP

Complex	ν_2 $^4T_{1g}(F) \longrightarrow {}^4A_{2g}$	ν_3 $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$	Dq (cm^{-1})	B (cm^{-1})	β	Dq/B	ν_1 (cm^{-1})
$[Co(DABAAP)_2Cl_2]$	15400	20500	855	950	0.848	0.90	7830
$[Co(DABAAP)_2Br_2]$	15500	20700	861	956	0.853	0.90	7955
$[Co(DABAAP)_2I_2]$	15450	20670	858	953	0.850	0.90	7806
$[Co(DABAAP)_2(NO_3)_2]$	15400	20500	855	950	0.848	0.90	7830
$[Co(DABAAP)_2(NCS)_2]$	15500	20830	861	956	0.853	0.90	7955

The electronic spectra of all the complexes recorded herein are very similar to each other and consist of two bands - one of the 15400-15500 cm^{-1} and the other and in the 20500-20830 cm^{-1} regions, which clearly indicate the octahedral stereochemistry of the complexes. In Table III 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[18] and the transition energies are given by the equations of Lever[19]. The methods of calculation of ligand field parameters from the ligand field spectra of octahedral Co(II) complexes have been discussed by Reedijk et al.[20] The energy of ν_1 corresponds to 10Dq for weak fields and the value of Dq is obtained from it. With these assignments, B and Dq have also been calculated (Table II). The existence of distortion from a regular octahedral structure is revealed in Co(DABAAP)$_2$X$_2$ by appreciable intensity enhancement. Apart from this, there is no difference in the spectra of regular and pseudo-octahedral complexes of Co(II).

Nickel Complexes. The magnetic moments observed for the present series of Ni(II) complexes ranges from 2.8 to 3.2 B.M., which suggests octahedral stereochemistry.

The absorption spectra of the Ni(DABAAP)$_2$X$_2$ (X = Cl$^-$, Br$^-$ or I$^-$) complexes display four bands at ca. 8000, 11000, 17000 and 27500 cm^{-1}. In all cases, the ν_1 band is more

Table III. Electronic Spectral Bands (cm^{-1}) and Ligand Field Parameters of Ni(II) Complexes of DABAAP

Complex	$^3A_{2g}(F) \xrightarrow{\nu_1} {}^3T_{2g}(F)$ $^3B_{1g}(F) \longrightarrow {}^3E_g, {}^3B_{2g}$	$\xrightarrow{\nu_2} a^3T_{1g}$ $\longrightarrow {}^aA_{2g}, {}^bE_g$	$\xrightarrow{\nu_3} b^3T_{1g}$ $\longrightarrow {}^bA_{2g} \longrightarrow {}^cE_g$
$[Ni(DABAAP)_2Cl_2]$	8270, 10930	17700	27200
$[Ni(DABAAP)_2Br_2]$	8230, 10870	17540	27500
$[Ni(DABAAP)_2I_2]$	8200, 10810	17540	26950
$[Ni(DABAAP)_2(NO_3)_2]$	10990	16950	27400
$[Ni(DABAAP)_2(NCS)_2]$	10930	17700	27000

	Dq(x)	Dq(z)	Dt	Ds	B	β
$[Ni(DABAAP)_2Cl_2]$	1093	561	304	63	794	0.76
$[Ni(DABAAP)_2Br_2]$	1087	559	302	63	829	0.79
$[Ni(DABAAP)_2I_2]$	1081	559	298	62	804	0.77
$[Ni(DABAAP)_2(NO_3)_2]$	1099	-	-	-	750	0.73
$[Ni(DABAAP)_2(NCS)_2]$	1093	-	-	-	794	0.76

intense than ν_2 excluding the possibility of five-coordinate geometry. So pseudo-octahedral geometry may be suggested for these complexes.

Further, ν_2 in all these complexes shows splitting into two components centered at ∼ 8000 and 11000 cm^{-1} which may be assigned as transitions to the $^3B_{2g}$ and ^3E_g levels, obtained from splitting of the $^3T_{2g}$ triplet due to deviations from O_h symmetry caused by non-identical donors. The extent of splitting is suggestive of a trans arrangement of the anions. Whereas the absorption spectra of $Ni(DABAAP)_2X_2(NO_3^-$ or $NCS^-)$ show only three bands at ca. 11000, 17000 and 27000 cm^{-1}. A six-coordinate octahedral geometry may, therefore, be readily suggested for these complexes. A close comparison of the spectra of these complexes with those of the former ($X = Cl^-$, Br^- or I^-) complexes, however, reveals that the ν_1 bands here are symmetrical and unsplit as against unsymmetrical and split in the Cl^-, Br^-, I^- complexes. This observation indicates cis-coordination of the nitrato and thiocyanato group. Different ligand field parameters have been calculated ν_1 directly gives the value of 10Dq in regular octahedral complexes, however, the value of 10Dq in pseudo-octahedral complexes has been calculated by the method reported by Lever[19].

The band at ca. 11000 cm^{-1} in pseudo-octahedral complexes may well be thought to have arisen from the $^3A_{2g}(F) \longrightarrow {}^1T_2(D)$ transition[21,22]. The intensity of this band is comparable with the intensity of the first band, suggesting its origin as due to the departure from D_h symmetry towards D_{4h}. Assuming D_{4h} symmetry, with the ligands coordinated along the Z-axis (Cl^-, Br^- or I^-), the most probable assignment would be ca. 8000 cm^{-1} ($^3B_{1g} \longrightarrow {}^3E_g$) and ca. 11000 cm^{-1} ($^3B_{1g} \longrightarrow {}^3B_{2g}$) in these pseudo-octahedral complexes. The ligand field parameters 10Dq and B in the octahedral complexes have been computed from equations suggested by Lever[23]. These data are in good agreement with those reported for other octahedral complexes.

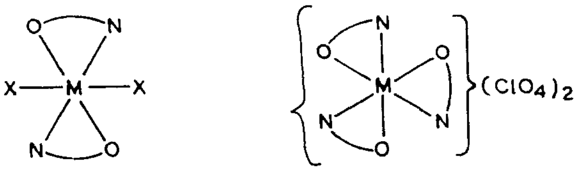
In the pseudo-octahedral complexes, assuming weak ligand fields, the in-plane ligand field strength Dq (X) is obtained as 0.1 ($^3B_{2g}$) while the axial ligand field strength Dq (Z) is 0.1 ($2\nu^{3a}E_g \longrightarrow {}^3B_{2g}$). The ligand field parameters are presented in Table III. The in-plane ligand field strength of DABAAP is practically unchanged in the complexes, 10Dq ranging between 10810 and 10990 cm^{-1}. The axial ligand field strength as given by Dq (Z) is distinctly lower than would be expected by considering the known σ and π antibonding ability of the involved ligands, or of the known spectrochemical, behaviour of the corresponding purely octahedral chromophores. Comparing with previous results, we can say there is a weakening effect of axial ligand strength in the complexes. This weakening effect of the axial ligands is expected because the equatorial ligands exert strong steric hindrance preventing axial ligands from

Table IV. Thermoanalytical Results Obtained for the Co(II) Complexes of DABAAP

Complex	Decomp. Temp. (°C)		Decomp. Products	Weight loss (%)	
	Initial	Final		Found	Calc.
$[Co(DABAAP)_2Cl_2]$	180	270	$Co(DABAAP)Cl_2$	42.32	41.85
	330	390	$CoCl_2$	84.12	83.70
	520	600	Co_2O_3	90.16	89.59
$[Co(DABAAP)_2Br_2]$	170	260	$Co(DABAAP)Br_2$	38.12	37.65
	320	370	$CoBr_2$	78.98	78.49
	510	590	Co_2O_3	91.36	90.64
$[Co(DABAAP)_2(NO_3)_2]$	200	290	$Co(DABAAP)(NO_3)_2$	39.89	39.24
	330	400	$Co(NO_3)_2$	79.32	78.49
	525	605	Co_2O_3	90.86	90.24
$[Co(DABAAP)_2(NCS)_2]$	180	270	$Co(DABAAP)(NCS)_2$	40.12	39.62
	320	380	$Co(NCS)_2$	79.75	79.24
	520	600	Co_2O_3	90.82	90.15

Table V. Thermoanalytical Results Obtained for the Ni(II) Complexes of DABAAP

Complex	Decomp. Temp. (°C)		Decomp. Products	Weight Loss (%)	
	Initial	Final		Found	Calc.
$[Ni(DABAAP)_2Cl_2]$	170	260	$Ni(DABAAP)Cl_2$	42.27	41.85
	320	390	$NiCl_2$	84.17	83.70
	510	590	NiO	91.23	90.60
$[Ni(DABAAP)_2Br_2]$	160	250	$Ni(DABAAP)Br_2$	38.11	37.65
	310	370	$NiBr_2$	78.89	78.49
	505	580	NiO	92.11	91.54
$[Ni(DABAAP)_2(NO_3)_2]$	200	300	Ni(DABAAP)	39.87	39.24
	340	400	$Ni(NO_3)_2$	79.32	78.49
	530	610	NiO	91.89	91.18
$[Ni(DABAAP)_2(NCS)_2]$	170	260	$Ni(DABAAP)(NCS)_2$	40.12	39.62
	310	390	$Ni(NCS)_2$	79.83	79.24
	520	600	NiO	91.89	91.10



(M = Co^{2+} or Ni^{2+}, X = Cl^-, Br^-, I^-, NO_3^- or NCS^-)

Fig. 2. Suggested Structure of the Complexes

approaching the central metal as closely as would be required for optimum covalent bonding[23].

Thermal Studies

The thermal results of some representative Co(II) and Ni(II) complexes of DABAAP are presented in Tables IV and V. The thermogravimetric analysis indicates that except for the perchlorato complex all complexes are stable up to ca. 150°C, which indicates that the complexes are not hygroscopic in nature, after which temperature decomposition and deligation start. More or less similar types of TG curves are obtained in the case of all the metal complexes of DABAAP and the end product is metal oxide in every case. On the basis of the above facts, if the minimum TG decomposition temperature is taken as a rough criterion of the thermal stability then the order of Co(II) and Ni(II) complexes with DABAAP is as follows:

$$NO_3^- > Cl^- > NCS^- > Br^-$$

On the basis of above studies the following structures may be suggested for the complexes (Fig. 2).

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