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SYNTHESIS AND CHARACTERIZATION OF *p*-DIMETHYLAMINOBENZALDEHYDE COMPLEXES OF Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) AND Zn(II)

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ABSTRACT

The complexes of *p*-dimethylaminobenzaldehyde with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have been prepared and characterized by elemental analysis, magnetic susceptibility, spectral and thermal analysis techniques. It is concluded that the ligand is coordinated to the metal ions as a monodentate ligand through the oxygen of the carbonyl group. The chloride ion and, in some cases, water molecules are coordinated to the metal ions to complete the geometry around the metal ions.

INTRODUCTION

p-Dimethylaminobenzaldehyde (DMABA) was used to react with various molecular and ionic species due to its ability of forming complexes. Especially, chromophoric complexes of this molecule were utilized in the colorimetric determination of indole[1], hydrazine[2,3], amino acids[4], urea[5], nitrite[6] and as well as a number of other species[7]. Its use as a coloring agent was reported by Rathore et al[8]. DMABA also shows biological activity. For example, it plays an important role in differentiating between serum eruptions and true scarlet fever. As a model for the enzymatic interactions, a complex between this compound and Zn(II) was prepared and the nature of binding of DMABA to the catalytic zinc of equine liver alcohol dehydrogenase was studied by infra-red (IR) and Raman spectroscopy[9,10]. However, any characterization, other than UV, IR and Raman spectra were not performed for the Zn(II) complex. The crystal structures of the dichlorodiphenyltin(IV) complex[11] and hydrobromide salt[12] of DMABA were also reported.

Our interest in coordination chemistry led us to study the ligating properties of DMABA with transition metal ions since its coordination chemistry is not yet reported in the literature. In the present paper, we report the preparation, spectroscopic examination and molecular structure of DMABA complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II).

EXPERIMENTAL

Materials and Instrumentation

All reagents used in this work were analytical reagent products (Merck). DMABA ($C_9H_{11}NO$) was also purchased from Merck and recrystallised from water to remove any impurity present. Metal chlorides were used without further purification.

UV-VIS spectra were obtained with a UNICAM UV2 spectrometer in 10^{-2} and 10^{-5} M alcohol solutions. IR spectra were recorded with a MATTSON 1000 FTIR spectrometer using KBr pellets. ^1H NMR spectra were obtained with a 200 MHz BRUKER AC spectrometer using acetone-d_6 as solvent and TMS as the internal reference. Magnetic susceptibilities of the complexes were measured using a SHERWOOD SCIENTIFIC MX I model Gouy magnetic balance. Melting points and decomposition temperatures were determined using a RIGAKU TG 8110 thermal analysis instrument.

Preparation of Complexes

Hydrated metal chlorides (3 mmol) were dissolved in absolute ethanol (15 mL) in a beaker. A solution of DMABA (6 or 9 mmol) in absolute ethanol (10 mL) was added portionwise to this solution. The change in color and the subsequent precipitation of complexes occurs during this process. The solutions were then kept at 40 ±2° C to allow the completion of the crystallization. The crude products were washed with benzene to remove any excess DMABA and then washed with acetone, and dried in air. The analytical results were listed in Table I.

RESULTS AND DISCUSSION

Synthesis and Thermogravimetric Analysis

The results in Table I show that the complexes were prepared in high yields and two or three molecules of the ligand DMABA are attached to the metal ions. Cl ions and H_2O molecules are also bonded to the metal ions to complete the coordination geometry around the metal ions. The elemental analyses agreed with their proposed formulas.

The presence of coordination and crystallization water is revealed from the endothermic effects in the differential thermal analysis curves. Thermoanalytical data for the dehydration of the complexes were presented in Table II. A definite weight loss occurs between approx. 50 and 125° C corresponding to the presence of the coordinated water molecules in the Cr(III), Mn(II) and Co(II) complexes. The crystallization water present in the Ni(II) complex gave a weight loss at 55 - 115° C. Thermogravimetric analyses of the complexes clearly indicated that the Fe(III), Cu(II), and Zn(II) did not contain crystallization or coordination water, these anhydrous complexes do not show any weight loss up to approx. 150° C. The melting point of the parent ligand DMABA is 74° C. As given in Table I, the complexes have much higher melting points than DMABA.

Magnetic Susceptibility of the Complexes

Magnetic susceptibility measurements provide sufficient information to characterize the structure of the complexes. The magnetic moments indicate that the metal complexes are of the high-spin type and the experimental data in Table III are in accord with the calculated data of the high-spin electronic arrangement. Thus, the Cr(III), Mn(II), and Co(II) complexes have octahedral geometry while the Fe(III), Ni(II), Cu(II) and Zn(II) show tetrahedral geometry. All complexes, except for the Zn(II) complex, were found to be paramagnetic. The Zn(II) complex was diamagnetic as expected.

Table I. Analytical Data for the Metal Complexes of DMABA

Complex	Color	F.W.	Found (Calc.) %			M.P.	Yield
			C	H	N	(°C)	(%)
$[CrCl_3(OH_2)(DMABA)_2].2H_2O$ $C_{18}H_{28}N_2O_5Cl_3Cr$	brown	510.61	42.65 (42.34)	5.30 (5.53)	5.00 (5.49)	140	60.4
$[MnCl_2(OH_2)_2(DMABA)_2]$ $C_{18}H_{26}N_2O_4Cl_2Mn$	yellow-orange	460.26	47.09 (46.99)	5.81 (5.70)	6.08 (6.09)	125	65.8
$[FeCl_2(DMABA)_2]\ Cl$ $C_{18}H_{22}N_2O_2Cl_3Fe$	dark-green	460.41	47.29 (46.96)	5.01 (4.82)	6.10 (6.08)	125	87.5
$[CoCl_2(OH_2)_2(DMABA)_2]$ $C_{18}H_{26}N_2O_4Cl_2Co$	pale brown	464.07	46.65 (46.59)	6.03 (5.65)	6.02 (6.04)	124	83.3
$[NiCl_2(DMABA)_2].3H_2O$ $C_{18}H_{28}N_2O_5Cl_2Ni$	pale green	481.87	43.81 (44.87)	5.89 (5.86)	5.38 (5.81)	135	84.4
$[CuCl(DMABA)_3]\ Cl$ $C_{27}H_{33}N_3O_3Cl_2Cu$	brown	581.76	55.13 (55.74)	5.90 (5.72)	7.16 (7.22)	141	68.7
$[ZnCl_2(DMABA)_2]$ $C_{18}H_{22}N_2O_2Cl_2Zn$	pale yellow	434.49	49.20 (49.76)	5.09 (5.10)	6.07 (6.45)	157	85.7

Table II. Thermoanalytical Data for the Dehydration Stages of the Metal Complexes of DMABA

Complex	Stage	Temperature range (°C)	Weight loss(%)		Residue
			Found	Calc.	
$[CrCl_3(OH_2)(DMABA)_2].2H_2$	1	50-92 (endo)	7.34	7.05	$[CrCl_3(OH_2)(DMABA)_2]$
	2	92-125 (endo)	3.32	3.52	$[CrCl_3(DMABA)_2]$
$[MnCl_2(OH_2)_2(DMABA)_2]$	1	58-125 (endo)	8.05	7.82	$[MnCl_2(DMABA)_2]$
$[CoCl_2(OH_2)_2(DMABA)_2]$	1	50-120 (endo)	7.80	7.76	$[CoCl_2(DMABA)_2]$
$[NiCl_2(DMABA)_2].3H_2O$	1	55-115 (endo)	11.75	11.21	$[NiCl_2(DMABA)_2]$

endo: Endothermic

Electronic Absorption Spectra of the Complexes

The UV-VIS spectral data are given in Table III. The ligand DMABA gives an absorption peak with maxima at 202, 242 and 351 nm. All complexes show distinct bands at 202, 242 and 341 nm being due to intraligand transitions. The shift in absorbtion maxima of the complexes from 351 to 340 nm is due to complexation with metal ions. The Cr(III), Co(II), Ni(II) and Cu(II) complexes exhibit characteristic d-d bands. The complexes containing metal ions such as Mn(II) and Fe(III) with d^5 electronic structures do not show any d-d transition because of the high-spin electronic arrangement in octahedral and tetrahedral ligand fields, respectively. The Zn(II) complex does not give any d-d band and its spectra are dominated only by the ligand bands. Some of the d-d bands overlap with the absorption bands of the ligand. The d-d transitions observed in the visible region of the spectra were assigned as given in Table III.

These transitions are characteristic of the relevant geometry around the metal ions[13]. In contrast to the absence of d-d transitions, the Mn(II), Fe(III) and Zn(II) complexes as well as the others exhibit intense colours which are attributed to the presence of charge transfer from the ligand to the metal ions. The charge transfer bands of the complexes occur in the visible region of the spectra between 390 and 490 nm depending on the type of complex. A weak charge transfer of DMABA in pure water with a maximum at about 400 nm was reported by Kundu and Chattopadhyay[14].

IR Spectra of the Complexes

The most significant frequencies in the IR spectra of DMABA and its metal complexes were summarized in Table IV. Detailed vibrational assignments of DMABA have been reported by Rosencrance and Jagodzinski[10]. The free ligand comprised strong bands at 1661 and 591 cm^{-1} which are attributed to the C=O stretching vibration and the in-plane C=O bonding motion, respectively. The characteristic vibrations of the ring CH stretching and dimethylamino group are readily resolved in the spectra[10]. Upon complexation with the transition metal ions, the signal at about 1660 cm^{-1}, which is due to the carbonyl stretching vibration, completely disappeared in the spectra of the complexes. This dramatic change clearly indicates that complexation occurs through the carbonyl oxygen

Table III. Electronic Spectra and Magnetic Moments of DMABA and the Metal Complexes

Compound	λmax(nm)					$\mu_{eff.}$(BM)[b]	Assignment of d-d transitions
	L			CT[a]	d-d		
DMABA	202	242	351	-	-	-	-
$[CrCl_3(OH_2)(DMABA)_2].2H_2O$	202	242	341	454	671	3.28 (3.87)	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
$[MnCl_2(OH_2)_2(DMABA)_2]$	202	242	341	390	-	5.34 (5.92)	-
$[FeCl_2(DMABA)_2]$ Cl	202	242	341	487	-	5.40 (5.92)	-
$[CoCl_2(OH_2)_2(DMABA)_2]$	202	242	342	395	600 656	4.58 (3.87)	$T_{1g}(F) \rightarrow {}^4A_{2g}$ $T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$[NiCl_2(DMABA)_2].3H_2O$	202	242	342	398	731	3.02 (2.83)	$^3T_1(F) \rightarrow {}^3T_2$
$[CuCl(DMABA)_3]$ Cl	202	242	342	432	855	1.50 (1.73)	$^2E_{2g} \leftarrow {}^2T_{2g}$
$[ZnCl_2(DMABA)_2]$	202	242	341	392	-	Diamagnetic	-

[a]Charge transfer
[b]Calculated values in parentheses

Table IV. IR Spectra of DMABA and the Metal Complexes

Compound	Assignment (cm^{-1})					
	ν (OH_2)	ν (C=O)	ν (C–H)	ν (C–C)	ν (C–O)	ν (M–O)
DMABA	-	1661s	1374s	1313m	937m	-
$[CrCl_3(OH_2)(DMABA)_2].2H_2O$	3137m	-	1364s	1320m	936m	410w
$[MnCl_2(OH_2)_2(DMABA)_2]$	3345s	-	1381s	1312m	942m	374w
$[FeCl_2(DMABA)_2]$ Cl	-	-	1370s	1328m	942m	383w
$[CoCl_2(OH_2)_2(DMABA)_2]$	3342s	-	1384s	1312m	940m	356w
$[NiCl_2(DMABA)_2].3H_2O$	3323s	-	1378s	1317m	938m	385w
$[CuCl(DMABA)_3]$ Cl	-	-	1374s	1320m	945m	390w
$[ZnCl_2(DMABA)_2]$	-	-	1380s	1322m	938m	376w

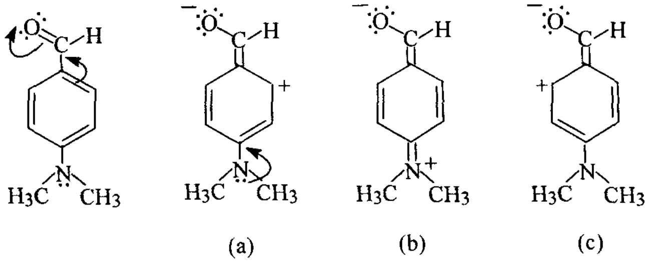
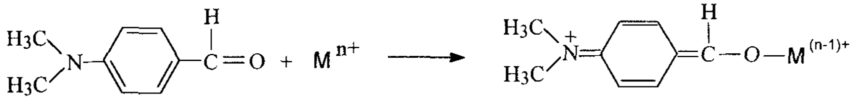


Fig. 1. Resonance Structures of DMABA

and not through the amino nitrogen. Thus, DMABA exhibits a quinonoid-like arrangement in the complexes. The complexation may be represented as shown below.



DMABA DMABA - Metal complex

The ligand exhibits a number of resonance structures as illustrated in Fig. 1. However, on the basis of the IR spectra, it may be suggested that the resonance form b does indeed contribute to the structure of the complexes to a considerable extent.

The absence of double bond character after complexation led to formation of a band at about 1265 cm^{-1} which is tentatively ascribed to the C–O bond stretching motion. The coordination and the bonding of the ligand to the metal ions was illustrated by single crystal X-ray studies on the Mn(II) complex and will be discussed elsewhere[15]. The presence of coordinated and crystallization water molecules in the metal complexes has been confirmed by new bands appearing at 3250 - 3420 cm^{-1} in the IR spectra of the complexes. Also, the rocking mode of coordinated water molecules appeared as a weak vibrational band[16] at 840 cm^{-1}. In the other cases, the band observed at about 605 - 660 cm^{-1} indicates the presence of crystallization water molecules[17]. The metal-ligand vibrations are expected below 600 cm^{-1} and the presence of bands between 350 and 410 cm^{-1}

Table V. ^{1}H NMR Spectra of DMABA and the Metal Complexes, δ (ppm)

Compound	–COH	–OC–$(CH)_2$–(ring)	–$(CH)_{2(ring)}$–CN–	$N(CH_3)_2$
DMABA	9.73 (s)	7.69-7.74 (d)	6.78-6.82 (d)	3.10 (s)
$[CrCl_3(OH_2)(DMABA)_2].2H_2O$	9.70 (s)	7.65-7.80 (d)	6.75-6.85 (d)	2.80 (s)
$[MnCl_2(OH_2)_2(DMABA)_2]$	9.75 (s)	7.75 (s)	6.85 (s)	3.10 (s)
$[FeCl_2(DMABA)_2]$ Cl	10.50 (s)	7.88 (s)	7.25 (s)	3.40 (s)
$[CoCl_2(OH_2)_2(DMABA)_2]$	13.80 (s)	7.63-7.68 (d)	6.81-6.85 (d)	3.14 (s)
$[NiCl_2(DMABA)_2].3H_2O$	9.75 (s)	7.65-7.75 (d)	6.75-6.85 (d)	3.09 (s)
$[CuCl(DMABA)_3]$ Cl	10.30 (s)	7.68-7.73 (d)	6.80-6.90 (d)	3.11 (s)
$[ZnCl_2(DMABA)_2]$	9.71(s)	7.70-7.74 (d)	6.76-6.82 (d)	3.10 (s)

s:singlet, d:doublet

were suggested to be due to bonding to metal through the oxygen atom of the ligand[17].

^{1}H NMR Spectra of the Complexes

The ^{1}H NMR spectra of free DMABA give distinct resonances at 9.73 (s), 7.69-7.74 (d), 6.78-6.82 (d) and 3.10 (s) for -COH, OC–$(CH)_2$(ring), $(CH)_2$–CN(ring) and –$(CH_3)_2$, respectively (Table V). After complexation, significant shifts were observed in the signal of the aldehyde proton. This effect is more pronounced for the Fe(III), Co(II) and Cu(II) complexes. The signals of the other groups present in the complexes remained almost unchanged. These observations also confirm that the ligand reacts with metal ions through the carbonyl oxygen.

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