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Determination of the Protonation Constants of 2-[4-Dimethylaminocinnamalamino] Benzoic Acid (DACAB) in Dioxane - Water Medium and Preparation of Some of its Transition Metal Complexes

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In this study, the Schiff base 2-[4-Dimethylaminocinnamalamino]- benzoic acid [$(CH_3)_2N.C_6H_4.CH$: $CH.N.C_6H_4.COOH$] (DACAB) was prepared by the reaction of 2-Aminobenzoic acid with p-Dimethylaminocinnamaldehyde. The protonation constants of the ligand were determined in a 50% (v/v) dioxane - water medium using the Irving-Rossotti and PKAS-BEST computer methods.

The complexes of Fe(III), Co(II), Ni(II), Cu(II) with DACAB were synthesized and the structures of these complexes were elucidated by means of data obtained from elemental analysis, using IR, ^{1}H-NMR methods. The magnetic properties of the solid complexes were measured.

Introduction

Schiff bases prepared by the reaction between aldehydes and substituted amines are used in analytical chemistry for the selective extraction and determination of some metal ions^{1,2}. Additionally, these compounds have become of enormous importance in recent years with respect to biological activities. They can be used in dyestuff production, liquid crystal industries and also in pharmacology. They are synthetic oxygen carriers. They have been produced from intermediate products in enzymatic reactions and used as antitumors$^{3-5}$. Therefore, it is very important to determine the protonation constants of DACAB and prepare its transition metal complexes.

The ligand (DACAB) has been synthesized from the reaction between ligands and some transition metals at suitable pH values in ethanol media. The structures of these complexes have been elucidated by means of the data obtained from their melting points. Infrared, ^{1}H-NMR spectra, and elemental analysis.

The ligand forms complexes by giving electrons to metal cations through donor atoms, nitrogen and oxygen. It seems that the ligand behaves as a bidentate ligand. It does not coordinate through the nitrogen atom on the dimethylammine group. The ligand forms stable and colored complexes with metal ions such as Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}.

These complexes have found application in the production of dyestuff. The complexes can be used in the selective extraction and spectrophotometric determination of some metal ions.

Experimental

Material and methods: All chemicals used in the study were purchased from Merck and Fluka. For IR spectra and for potentiometric titration a Mattson 1000 FTIR spectrophotometer and a Metrohm 654 pH-Meter were used. Elemental analysis and ^{1}H-NMR measurements were carried out by the TUBITAK Research Institute, Gebze. A Sherwood Scientific magnetic susceptibility balance was used for magnetic measurements.

The Synthesis of Ligand: An equimolar solution of 4-Dimethylaminocinnamaldehyde and antranilic acid was mixed in absolute ethanol. This solution was warmed on a water bath for 30 minutes and kept overnight at room temperature. Bright violet-colored crystals formed. These crystals were isolated by filtration and recrystallised in CCl_4, dried in vacuo over P_2O_5 in a dessicator (yield 71.31 %), m.p. 125-126 °C. Elemental Analysis (%): $C_{18}H_{18}N_2O_2$. Expected: C:73.47, H:6.12, N:9.52. Found: C:73.35, H:6.41, N:9.07. IR (KBr): $v_{\max}(\text{cm}^{-1})$: 3412, 1676, 1575, 1498, 1389, 1337, 1275, 1172, 1059, 946, 832, 770, 698, 678.

Calculation of the Protonation Constants of the Ligand: The ligand (DACAB) was acidified with $HClO_4$ in a 50% (v/v) dioxane-water medium and the ionic strength was kept constant by means of $NaClO_4$. The ligand was titrated with 0.1 N Tetrabutylammoniumhydroxide (TBAH) using Calvin-Wilson and Calvin-Bjerrum pH titration techniques. The curves of pH versus mL-base were plotted[6–12] (Figure 1). Protonation constants were calculated from the pH values obtained from the titration using the Irving-Rossotti method[6–12] and PKAS-BEST computer program[13] based on the weighted least squares algorithm (Table 1).

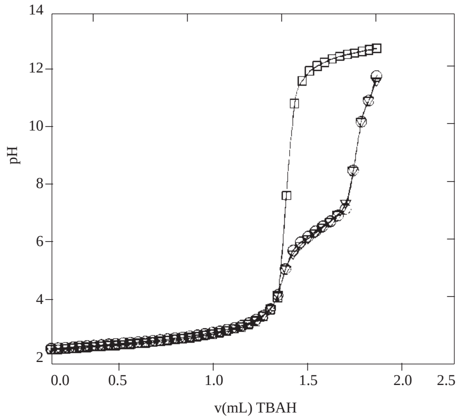


Figure 1. Determination of ionization constants of $DACABH^+$ in dioxane-water 50% (v/v). Initial concentrations of $HClO_4$ (3×10^{-3} M), Ligand (1×10^{-3} M) and $NaClO_4$ (0.1M) are in 50 ml total volume. ((expn): $HClO_4$; ∇(expn), O(calc by PKAS): $HClO_4$ + DACAB values).

Synthesis of Complexes: The absolute alcoholic solution of 0.02 mole ligand and 0.01 mole metal salt ($FeCl_3 . 6H_2O$, $CoCl_2 . 6H_2O$, $CuCl_2 . 2H_2O$, $NiCl_2 . 6H_2O$) was transferred into a boiling flask and refluxed for 1-1.5 hours. This was kept at room temperature for one night. Crystals formed, which were collected and dried. The melting points, elemental analysis and colors of the complexes are shown in Table 2. Characteristic IR bands of the complexes are shown in Table 3.

Table 1. The protonation constants of ligand (DACAB) and deprotonation of $DACABH_2^{++}$

	Direct Method	Irving-Rossotti	PKAS-BEST
pK_1	-	-	1.96 ± 0.01
pK_2	-	2.75	2.69 ± 0.03
pK_3	6.65 ± 0.07	6.62 ± 0.17	6.60 ± 0.07

Table 2. Elemental analysis data of metal-ligand complexes.

Compound Empirical Formula	Colour	Yield (%)	M.p. (°C)	Elemental C	Analysis H	Found % Calcd % N
$[CuL_2]Cl_2H_2O$	mustard			58.43	4.84	7.96
$[C_{36}H_{34}N_4O_4Cu].Cl_2.H_2O$	colour	84	214-215	58.49	4.92	7.58
[NiL Cl]Cl				59.37	4.24	4.76
$[C_{18}H_{17}\text{-}N_2O_2NiCl]Cl$	brown	62	>300	60.35	4.79	4.82
$[CoLCl_2]$				52.40	4.74	6.81
$[C_{18}H_{17}\text{-}N_2O_2Co\ Cl_2]$	black	78	215-216	51.07	4.02	6.62
$[FeLCl_2]$				49.87	4.27	7.11
$[C_{18}H_{17}\text{-}N_2O_2FeCl_2]$	red-brown	81	209-210	51.42	4.05	6.67

Table 3. Characteristic IR bands of complexes as KBr pellets (cm^{-1}).

Compound	$v[(CH_3)_2N\text{-}Ar]$	$v(OH)$	$v(C{=}O)$	$v(C{=}N)$	$v(C{=}C)$ Aromatic	$v(C{=}C)$ Aliphatic
$C_{18}H_{18}N_2O_2(L)$	770	3412	1575	1498	1389-1250	1172-823
$[CuL_2]Cl_2H_2O$	760	3285	1667	1460	1604-1460	1171-1090
[NiL Cl]Cl	760	3310	1605	1415	1594-1545	1065-873
$[CoLCl_2]$	770	3310	1605	1389	1491-1337	1265-1162
$[FeLCl_2]$	790	3464	1625	1399	1553-1491	1327-1162

Measurements of the Magnetic Susceptibilities of Complexes: For measurement of the magnetic susceptibilities of the complexes a Gouy balance was used. Powdered complexes were put in standard tubes. The weight of the tube was measured first in normal conditions and then in a magnetic field[14]. By considering the differences in the weight, temperature and the height of the substance in the tube, the momentum and numbers of unpaired electrons were calculated (Table 4).

Table 4. Magnetic momentums of the compounds

Compound	Magnetic momentum χ_g (cgs)	Numbers of unpaired electrons (n)
CuL_2 complex	2.510×10^{-6}	1
NiL complex	17.850×10^{-6}	2
CoL complex	14.004×10^{-6}	3
FeL complex	23.527×10^{-6}	5

Results and Discussions

The ligand (DACAB), which is composed of bright dark purple crystals, has low solubility in water. However, it has high solubility in both acidic and basic media. The hydrolysis rate in acidic media is quite high. Color variations were observed according to the pH of the medium. It is easily soluble in solvents such as CCl_4. $CHCl_3$, DMSO, CH_2Cl_2, CH_3COCH_3 and dioxane.

IR bands v(OH)(3412m), v(C=O)(1675m), v(C=N)(1645m), v(C=C)(1575, 1564, 1498, 1460) were determined using a KBr disc. Comparing these bands with the bands obtained from other Schiff bases, it can be seen that they are compatible[5,14–17]. However, because of the existence of double conjugated bands in the structure (-CH=CH-CH=N-), it is hard to differentiate the peak of the (-C=N-) group by means of IR spectra.

The protonation constants of the ligand, determined in 50% (v/v) dioxane-water mixture with different potentiometric titration methods, are shown in Table 1. One constant was calculated using the direct method, two constants with the Irving-Rossotti method and three constants with the PKAS-BEST computer method[17]. The protonation constant data can be explained by the following equations (Figure 2):

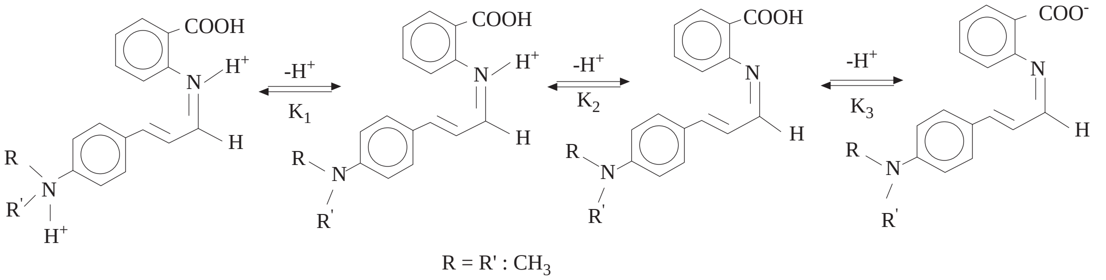


Figure 2. The ionization of the ligand (DACAB)

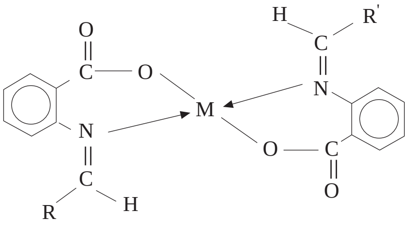
The values calculated by the three different methods are similar to each other and consistent with the protonation constant values given for Schiff bases which have a similar structure.

The ligand forms stable rigid complexes with transition metals. Although the ligand seems tridentate since the electron donor nitrogen atom in the p-location (N-) in the extremity of the molecule does not play a role in the formation of the complex because of the magnitude and steric effects of the ligand molecule, the ligand (DACAB) acts as a bidentate ligand.

The data concerning complex formation; namely, color, yield, melting points, IR and elemental analyses of the solid complexes formed by the ligand with Cu(II), Ni(II), Co(II) and Fe(III) cations, are shown in Table 2 and Table 3. Evaluation of the IR data shows that the wavelength absorptions (-C= and -C=N) of the ligand in the stretched frequencies shifted to the lower frequencies. The -C=O peak of the carboxyl group becomes clearer with the formation of the complex. Metal-N and metal-O peaks appear in the lower frequencies.

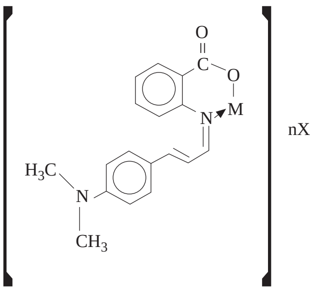
The ligand forms complexes with the Cu(II) ion in a metal/ligand ratio of 1/2 and with the Ni(II), Co(II) and Fe(III) ions in a metal/ligand ratio of 1/1 (Formula: 1 and 2). The ligand forms complexes of the metalocyclic structure, consisting of six rings with metal cations. These complexes are dark-colored, with low solubility and high melting points. Depending on the pH of the medium, the ligand forms complexes such as ML_2, ML and MLH_n with metal cations.

The magnetic properties of the complexes show that they were paramagnetic (Table 4) and they had unpaired electrons in their structure.



$R=R'=(CH_3)_2N.C_6H_4.CH{:}CH$, $M=Cu^{2+}$

Formula 1. Structure of the complex of ML_2 type



M	X
Cu(II)	$2Cl^-$ or CH_3COO^-
Ni(II)	$2Cl^-$ or CH_3COO^-
Co(II)	$2Cl^-$
Fe(III)	$2Cl^-$

Formula 2. Structure of the complex of ML type.

The determination of the protonation constants of the ligand and the properties of its metal complexes are useful for metal extraction in analytical chemistry. This should facilitate accurate determination of some metal cations and research into the utilization of these colored complexes in analytical chemistry.

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