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A COMPARTIVE STUDY OF THE INFRARED SPECTRA AND MAGNETIC SUSCEPTIBILITY OF $Zn(3\text{-}C_7H_9N)_2Cl_2$ AND $Zn(4\text{-}C_7H_9N)_2Cl_2$

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ABSTRACT

The infrared spectra of 3-methylaniline and 4-methylaniline complexes of zinc(II) chlorides were investigated over the range of 4000-200 cm^{-1}. The results of chloride analysis, melting points, colors, and magnetic susceptibilities were also reported. The complexes were optained by dissolving equivalent amounts of $Zn(II)Cl_2$ and ligands in ethanol. Analysis of complexes contained two chlors in the structure. The vibrational frequencies were assigned on the infrared spectra recorded at room temperature. The two υZn-N and two υZn-Cl bands as expected from C_{2v} symmetry, can be observed particularly by examining the metal- ligand vibration peaks between 450-200 cm^{-1}. The tetrahedral arrangement of ligants around zinc atom can be concluded from this observation. Magnetic susceptibility studies also support these results.

$Zn(3\text{-}C_7H_9N)_2Cl_2$ İLE $Zn(4\text{-}C_7H_9N)_2Cl_2$ NİN İNFRARED SPEKTRUM VE MAGNETİK DOYGUNLUKLARININ KARŞILAŞTIRMALI OLARAK İNCELENMESİ

ÖZET

3-metilanilin ve 4-metilanilin'in Çinko(II)klörür ile yaptığı komplekslerin infrared spektrumları 4000-200 cm^{-1} aralığında incelendi. Ayrıca, klor analizi, erime noktası ve renk tayini ile magnetik duygunluk sonuçları da rapor edildi. Kompleksler, uygun miktarda $Zn(II)Cl_2$ ve ligandın etanolde karıştırılarak çözündürülmesi ile elde edildi. Komplekslerin analizinden yapıda iki klorun bulunduğu anlaşıldı. Titreşim frekansları, oda sıcaklığında kaydedilen infrared spektrumlarından tayin edildi. C_{2v} simetrisi için beklenilen iki υZn-N ve iki υZn-Cl bandlarının 450-200 cm^{-1} aralığında gözlenmesi çinko atomu çevresinin tetrahedral yapıda olduğunu gösterir. Magnetik duygunluk çalışmaları da bu sonuçları desteklemektedir.

I. INTRODUCTION

Most of metals of the first transition series form complex compounds having the general formula ML_2X_2 where L is 3-methylaniline or 4- methylaniline X is a halogen or pseudo halogen (e.g. - NCS) atom [1.2]. A number of complexes between 3-methylaniline or 4- methylaniline and first row transition metal dihalides have been previously reported in the literature [3–4]. Also, $Zn(4\text{-ma})_2Cl_2$ has been shown by X-ray crystallography to have a tetrahedral structure about the zinc atom [5]. But there have been no complote studies of the spectroscopic and magnetic properties of these compounds.

This paper reports the room temperature magnetic moments of the complex of zinc(II)chlorides with 3-methylaniline and 4- methylaniline together with their infrared spectra, melting points and colors. Infrared spectra and the magnetic susceptibilities have been recorded for the solid complexes at the far infrared spectra are used to determine the probable co-ordination arrangement about the metal atoms in each complex.

II. MATERİALS AND METHODS

In the preparation of complexes 3-methylaniline, 4- methylaniline (Fluka, AG Chemische Fabrik CH-9470 Buchs), and zinc(II) chlorides (E. Merck, Darmstadt) in ethanole were used. For the measurements, we selected the addition product between 3-methylaniline or 4-methylaniline, and zinc(II) chlorides. This product was optained by mixing absulate ethanole solutions of zinc(II) chloride and 3-methylaniline or 4- methylaniline in the stochiometric ratios. The resulting crystalline precipitates were washed with absulate ethanole and were recrystallized from this medium.

The chloride analysis was made at room temperature using Mohr method and showed that two chlors were bound in the molecular structures. The melting points which were determined are given in table 1.

Magnetic susceptibilities were determined by Gouy Method at room temperature. Molecular susceptibilities were corrected for diamagnetism of the ligand atoms by use of pascal constand. The values of gram susceptibility (X_g), molecular susceptibility (X_m) and diamagnetism corrected molar susceptibility ($X_{m'}$) are given also in table 1. The values of magnetic moments (μ) in Bohr magnetons were calculated from.

$$\mu = 2.84\ (X_{m'}\ T)^{1/2} \qquad (1)$$

T is the temperature in Kelvin degrees, while n is the number of unpaired electrons calculated from the

$$\mu = [\ n\ (n+2)]^{1/2} \qquad (2)$$

"spin only" formula. The magnetic data optained in this work are given in table1.

In the infrared spectral studies, the spectra were obtained on the pelletized complex powder- KBr mixture (ratio 1/100). The infrared spectra were recorded in the range of 4000-200 cm^{-1} with Perkin-Elmer model 1330 spectrophotometer and it was possible to eliminate the peaks appearing due to the KBr using its memory substraction facilities. Similar results were optained using Perkin-Elmer 457 Greating Infrared Spectrophotometer using KBr as a reference. The assigments and interprations of infrared spectral data of the free ligands and its complexes with zinc(II)chlorides were made on the basis of previously reported data [1,2,4]. The results of vibrational mode assignments were given with their relative intensities in table 2.

Table 1. The results of chloride analysis and magnetic susceptibilities

		$Zn(3\text{-}ma)_2Cl_2$	$Zn(4\text{-}ma)_2Cl_2$
Chloride	calculated	20.23	20.23
Analysis	found	20.56	20.27
X_g 10^{-6} (cm^3g^{-1})		0.7491	1.843
X_m 10^{-6} (cm^3mol^{-1})		262.64	646.118
$X_{m'}$ 10^{-6} (cm^3mol^{-1})		475.18	858.656
μ(B.M.)		1.063	1.429
n		0	0
melting point (°C)		225	259
color		white	white

III. RESULTS AND DISCUSSIONS

1. Ligants Vibrations associated with the amino group

There are two stretching vibrations known as symmetric and antisymmetric N-H stretching modes that belong to the NH_2 group of 3-methylaniline {4-methylaniline}. { The values of 4-methylaniline are given in parantheses}.These values were optained as 3354 cm^{-1} and 3432 cm^{-1} {3354 cm^{-1} and 3424 cm^{-1}} respectively. These vibrational modes changed on passing from the free ligand spectra to those of complexes reaching up to and 133 cm^{-1} and 164 cm^{-1} {114 cm^{-1} and 143 cm^{-1}} for both two vibrations. The reason for these shifts is attributed to metal-ion coordination [3,9]. A band similer to a N-H...Cl, defined as Cl sensitive N-H bond, was observed at 3221 cm^{-1}{3214 cm^{-1}} for the free ligants and shifted to lower frequencies of about 85 cm^{-1} {79 cm^{-1}} in its metal complexes. The reason for this shift is atributed to the hydrogen bonding or comlex formation. [3,4]. In order to identifiy the band related to NH_2 scissoring vibrations in the 1600 cm^{-1} spectrum range, an earlier ^{15}N isotop labeling study was used [4,7] , and such a band was observed strongly at 1614 cm^{-1} {1622 cm^{-1}} for free ligand. It shifted down to 1582 cm^{-1}{1579 cm^{-1}} in complex molecules. the reason for this behavior was attributed to the change of nitrogen orbitals and its effect on the NH_2 force constand because of the NHN angle change [8,9].

NH_2 twisting vibration is effected and known that is shows change in frequency and intensity from the complex formation methylaniline or similar aniline molecules [9], a band identified as twisting mode upon deuteration, was observed at 1177 cm^{-1} {1077 cm^{-1}} but it changed on passing from the free ligand to those of the complexes (Table2). This shift was attributed to the mass increments due to the transition metal inclusions in the complexes.

NH_2 wagging mode was observed at 721 cm^{-1} {719 cm^{-1}}, and shifted to 727 cm^{-1} {730 cm^{-1}} in its complexes and this was attributed to the increment of the force constant because of the transition metal bonding. The band seen at 548 cm^{-1} {479 cm^{-1}} was assigned to the rocking vibration of 3-methylaniline {for 4-methylaniline}. We can conclude that the NH_2 vibrational values of 3-methylaniline {4-methylaniline} are notable different when they are coordinated compared to being a free ligand. The values of the NH_2 stretching and scissoring modes were found at lower values than the corresponding ones in the free molecule while the NH_2 twisting, wagging and rocking modes were found at higher values. A strong band near 1250 cm^{-1} in the spectra of the ligands and complexes is assigned to C-N stretching vibration, occuring in the region previously reported for this vibration [4,9].

C-H stretching was observed at 3035 cm^{-1} {3019 cm^{-1}}. A very weak band observed at 965 cm^{-1} {812 cm^{-1}} was assigned to C-H (out of plane) bending vibration mode. A medium strenght double band was also observed at 866 cm^{-1} and 855 cm^{-1} for the free ligand 3-methylaniline but it lost its strength in its complexes. Another strong band observed at 773 cm^{-1} due to C-H bending vibration preserved its strenght after complex. A very strong band at 926 cm^{-1} was also assigned to C-H bending, since there are out of plane deformation bands and are expected to be observed at 688, 773 and 855 cm^{-1}.

A strong band related to C-H (in plane) bending vibrations was observed at 1166 cm^{-1} {1178 cm^{-1}} for free ligand 3-methylaniline {for free ligand 4-methylaniline}. This band decreased and nearly lost in strenght in its complexes.

The bands related to aliphatic and aromatic C-H stretching modes were observed 2918 cm^{-1} and 2855 cm^{-1} {2918 cm^{-1} and 2856 cm^{-1}}. In complexes these bands almost disappeared and this was taken as an indication of complex formation.

The bands due to bending vibrations are generally weak because of small dipol moment changes, such a CH_3 bending mode was observed at 1377 cm^{-1} {1375 cm^{-1}} and for its complexes these bands disappeared.

A much more important criterion of stereochemistry is the intensity of the absorption bands, tetrahedral complexes having values about one hundred times those of octahedral. We studied Mn $(ma)_2Cl_2$ complexes which had a polymeric octahedral environment about manganese atom [10].

2. Metal-Ligand Vibrations

Metal-Ligand stretching modes in metal complexes have proved very useful in characteristing the streochemistry of the complexes [6,10]. These modes are expected to be observed of lower than 430 cm^{-1} frequencies for complexes. Also, the assigment of modes has been carried aut from the expanded spectra.

In the range of 430-400 cm^{-1} medium bands, not found in the spectra of the free ligand, were observed two bands 419 and 388 cm^{-1} (412 and 398 cm^{-1}]. It is suggested that these bands are most probably due to υZn-N modes, similar bands have also been observed in this range and assigned to metal-nitrogen modes in the metal(II)halogen-aniline and substituted aniline complexes reported earlier [1-4].

Zinc-chloride stretching bands are expected to be observed in the range of 320-200 cm^{-1}. Referring to Table 2 two bands at 300 and 252 cm^{-1} (298 and 252 cm^{-1}) were obtained. Since the frequency and the number of these bands are in good agreement with similar modes in metal-chloride coplexes having ML_2X_2 stochiometry [1,2,6]. It is suggested that these bands are due to Zn-Cl bands. For the C_{2v} symmetry, tetrahedral streochemistry requires two υZn-N and two υZn-Cl bands [6]. These were observed for the Zn(II) complexes.

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Table 2. The frequencies (cm^{-1}) and assigment of vibrations.

Assigments	3-methylaniline	4-methylaniline	Zn(3-ma)$_2$Cl$_2$	Zn(3-ma)$_2$Cl$_2$
νN-H asym.	3432 s	3424 s	3268 s	3281 s
νN-H sym.	3354 vs	3354 vs	3221 s	3240 s
N-H ... Cl	3221 s	3214 w	3136 s	3135 vw
νC-H aryl	3035 s	3019 m	3035 w	-
CH$_3$ stretch	2918 s	2918 w	2910 vw	2917 w
	2855 s	2856 w	-	-
NH$_2$ scissor	1614 s	1622 s	1582 s	1579 s
νC-C aryl	1599 s	-	1599 m	1609 w
	1493 s	1517 vs	1493 m	1509 vs
	1462 s	1447 w	1466 m	1451 vw
CH$_3$ scissor	1377 w	1375 vw	-	-
νC-N	1290 vs	1270 s	1255 s	1242 s
νC-H aryl i.p.	1166 vs	1178 w	1166 vw	-
NH$_2$ twist.	1177 w	1077 w	1096 vs	1096 vw
	1038 w	1042 vw	1035 vw	1073 vs
δC-H aryl. (bending i.p.)	995 m	-	-	-
δC-H aryl. (bending o.p.)	965 vw	812 vs	965 vw	-
	925 vs	-	917 m	-
	866 m	-	862 w	-
	855 m	-	-	820 m
	773 s	-	785 vs	808 s
	688 m	-	692 s	-
NH$_2$ wagging	721 w	719 vw	727 vw	730 w
NH$_2$ rocking	548 m	497 s	666 m	516 m
	529 s	-	650 w	-
νZn - N	-	-	419 w	412 s
	-	-	388 w	398 s
νZn - Cl	-	-	300 vs	298 s
	-	-	252 vs	252 m

vs: very strong s: strong m: medium w: weak vw: very weak -: not measured

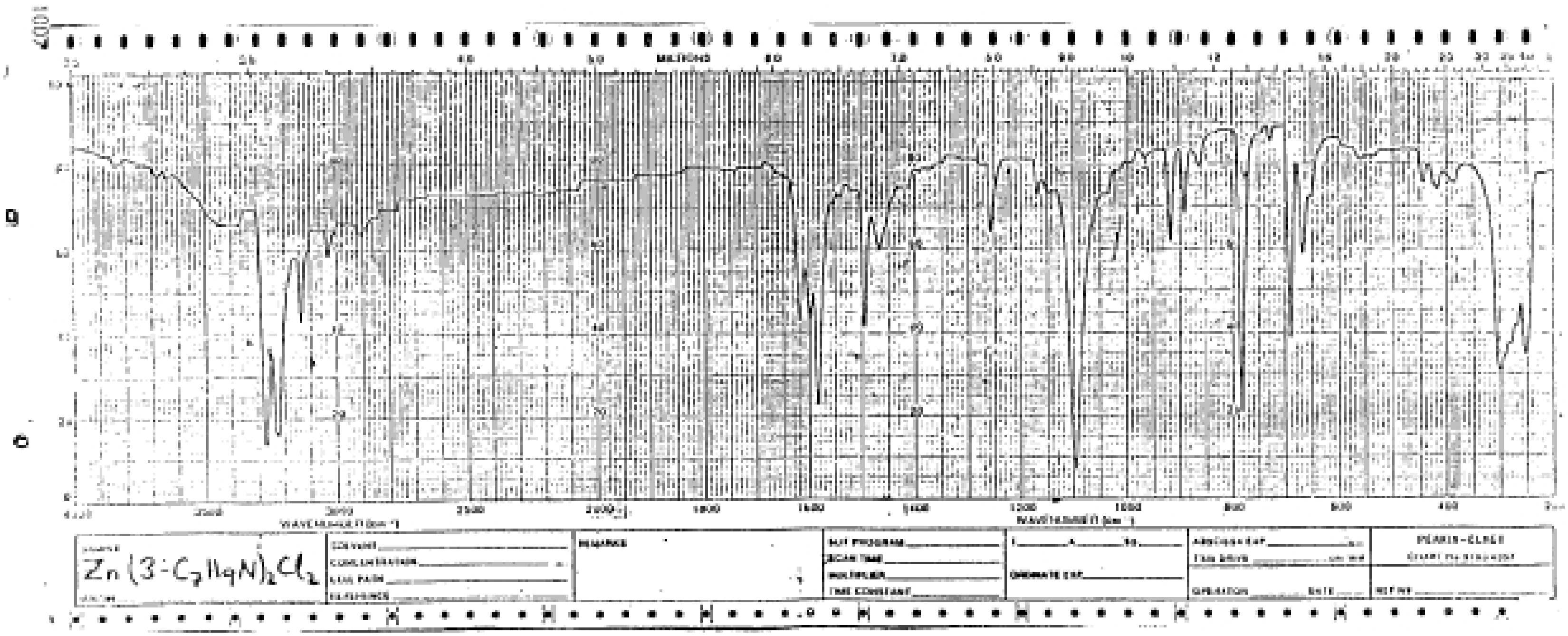

Fig. 1. Infrared Spectrum of $Zn(3\text{-me})_2Cl_2$