

Synthesis of N-chloroacetamide complex with Ni(II) ions

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ABSTRACT

Chloramine can be used as an active ligating species for complexing with Ni (II) and Co (II) metal ions.. The reaction of chloramines with acetates of Ni (II) has been found to result in N- haloacetamide complex. The crystalline complexes so produced were found to have tetrahedral geometry around the metal ion. The metal ion was found to complex in two different ratios with the ligating agent. These transformations were confirmed by several spectral as well as TGA analysis of the complexes.

Key words: N-chloroacetamide, Ni (II) acetate, ligand substitution.

Introduction:

The ligating nature of chloramines is reported in literature.[1,2] For complexing with Ni(II) metal ions chloramine is prepared by the partial oxidation of ammonia by hypochlorite.[3] The chloramine thus formed was treated with anhydrous CuSO₄ to remove excess ammonia present and then estimated iodometrically.

Materials and methods:

Preparation of chloramine ligand:

Chloramine was prepared by the partial oxidation of ammonia by hypochlorite.[4] Sodium hypochlorite prepared by standard procedures[5] was added to aqueous ammonium chloride dropwise in an ice bath with constant stirring. The chloramine formed was extracted with dichloromethane and it was then treated with anhydrous copper sulphate to remove excess ammonia present in it. The chloramine formed was then estimated iodometrically.[6]

Preparation of Ni (II) complex:

Ni (II) acetate tetra hydrate dissolved in water was taken in a round bottom flask and allowed to react with ammonia free chloramine solution in dichloromethane. The solvents were evaporated and green crystals of Ni(II) complex were obtained. The same procedure was adopted for complexing in different ratios.

Estimation and characterization of Nickel complexes:

The metal content of the complex were estimated by standard procedures [7]

The crystalline complexes of Ni (II) with N-chloroacetamide ligand were characterized by magnetic measurement, UV and IR spectroscopy and TGA analysis.

Results and Discussion:

From the electronic spectra, it is evident that the formed complex is different from the original Ni(II) acetate tetra hydrate.[8] The reaction between chloramine and Ni(II) acetate salt involves the insitu formation of N-chloro acetamide. This involves the nucleophilic attack of chloramines on the carbonyl carbon of Ni(II) acetate. N-chloroacetamide is said to be formed from the intermediate. The succeeding step involves the ligand substitution of OH group by N- chloroacetamide.

Ni (II) (1:1) Complex:

The IR spectra of the complex shows peaks at 683 cm^{-1} and 1030.1 cm^{-1} . These may correspond to N-Cl stretching and symmetrical Cl-NHR (R=acyl group) bending frequencies because they are close to the values reported [3] for N-Cl stretch and NH_2Cl symmetrical bending modes of monochloramine.

TGA reports shows 18 % weight loss in the first stage occurring between $31^\circ\text{C} - 175^\circ\text{C}$ and second stage 43% weight loss observed between 300°C and 463°C .

To explain the weight losses observed in TGA, the formula $\text{NiLL}'(\text{H}_2\text{O})_3(\text{OH})$ has been proposed for the Ni(1:1) complex where

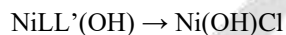
$\text{L} = \text{CH}_3\text{-COO}^-$ and $\text{L}' = \text{CH}_3\text{-CO-NH-Cl}$

The following stages could be ascribed for the formation of the complex which could be a two stage process which was then in agreement with the TGA datas.

I stage:



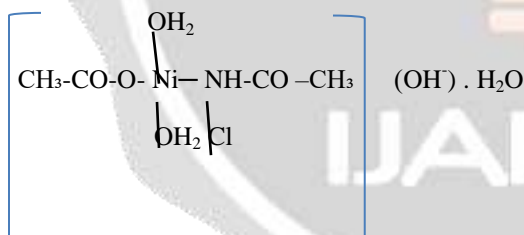
II stage:



The above transformations suggested weight loss observed are in agreement with the TGA and DTA analysis.

The magnetic moment for Ni(II) complex was observed to be 4.14 B.M. This suggests a tetrahedral environment around Ni(II) ion. The electronic spectra also corroborates the Td geometry of Ni(II) ion. The uv spectra of acetatodiaqua (N-chloroacetamide) Ni(II)-hydroxide monohydrate shows bands at $14,684\text{ cm}^{-1}$ and $12,903\text{ cm}^{-1}$. Based on literature [5] these can be assigned to the $\nu_3 (^3\text{T}_1(\text{P}) \leftarrow ^3\text{T}_1(\text{F}))$ transitions and spin forbidden $^1\text{E}_1 \leftarrow ^3\text{T}_1$ transitions respectively.

The suggested structure for the complex is :



Acetatodiaqua (N-chloroacetamide) Ni(II) hydroxide monohydrate.

Ni(II) (1:2) Complex:

For the formation of this complex the chloramine and Ni salts were taken in a mole ratio of $\text{NH}_2\text{Cl} : \text{Ni salt}$ as 2:1. The mechanism of formation of diaqua bis (N-chloro acetamide Nickel (II) hydroxide can be explained similar to the previous one, except that both acetate moiety of Ni(II) acetate salt are attacked by chloramine.

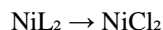
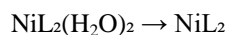
IR spectra of complex has a peak at 1031 cm^{-1} , which can be assigned to symmetric Cl-NHR (R= Acyl) bending. TGA reports 19 % weight loss is occurring between $31^\circ\text{C} - 163^\circ\text{C}$ and second stage 36.4 % weight loss occurs between $350^\circ\text{C} - 494^\circ\text{C}$.

The proposed structure for the complex is

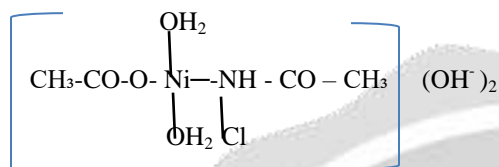
$\text{NiL}_2(\text{H}_2\text{O})_2(\text{OH})_2$ where

$\text{L} = \text{CH}_3\text{-CO-NHCl}$

The various steps suggested in the formation of the complex are ;

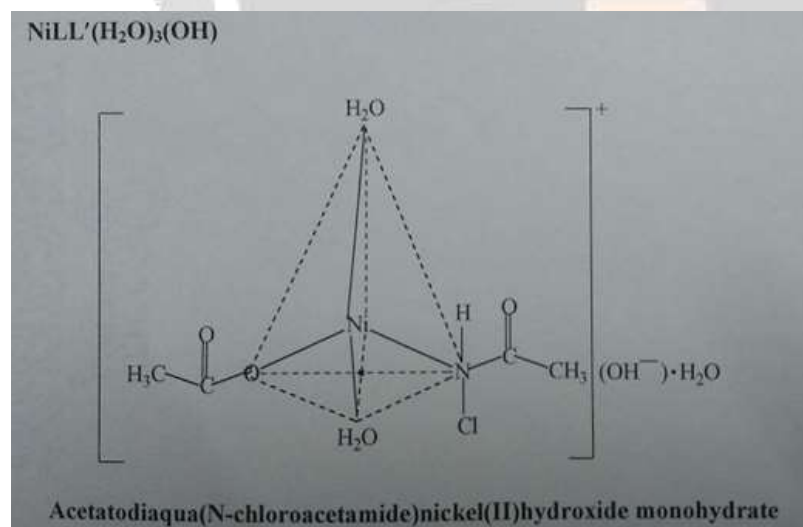


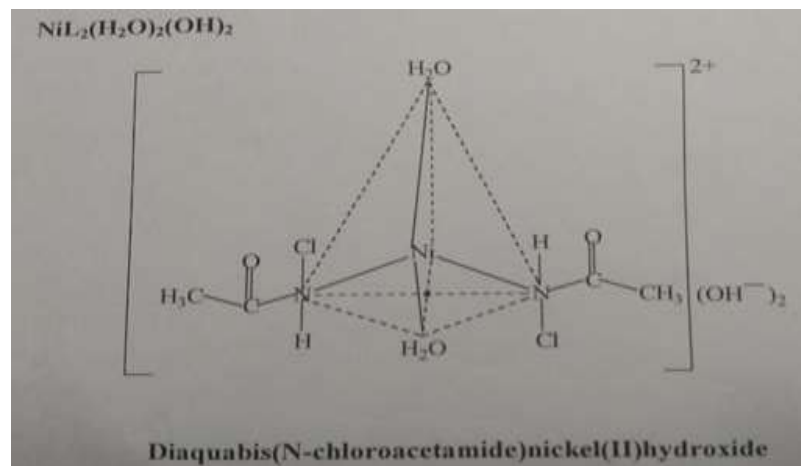
Electronic spectra of diaquabis (N-chloroacetamide) Ni(II)-hydroxide complex shows bands at $14,705\text{cm}^{-1}$ and $13,071\text{cm}^{-1}$. They can be assigned to ν_3 transitions (${}^3\text{T}_1(\text{P}) - {}^3\text{T}_1(\text{F})$) and spin forbidden ${}^1\text{E}_1 - {}^3\text{T}_1$ transitions respectively. The magnetic moment studies also shows Td structure around Ni(II) ions.



Diaquabis (N-chloroacetamide) Ni(II) hydroxide.

From the magnetic moment studies it is inferred that the geometry around the Ni(II) atom is tetrahedral in both the complexes under study. Therefore the structures of the complexes can be represented as follows:



**Table- 1** Magnetic moment and IR Spectral data

S.No	Complex	γ N-Cl & γ NHR-Cl	μ eff (B.M)
1.	Ni (II) (1:2)	1036.1	4.07
2.	Ni (II) (1:1)	683 1030.1	4.14

Table- 2 Electronic absorption spectral data

S.No	Complex	Wave Number (cm^{-1})
1.	Ni (II) (1:2)	$\gamma_3 \rightarrow 14,705$
2.	Ni (II) (1:1)	$\gamma_3 \rightarrow 14,684$

Table-3 TGA Report

S.No	Complex	% wt loss in 1 st stage	% wt loss in 2nd stage	% wt of residue
1.	Ni (II) (1:2)	19	36.4	44.6
2.	Ni (II) (1:1)	18	43	39

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