Effect of Concentration of $AgNO_3$ on the Rate of Formation of a Complex Salt, $[Co(H_3)_6](NO_3)_3$ and Estimation of Molar Concentration of the Complex

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Abstract

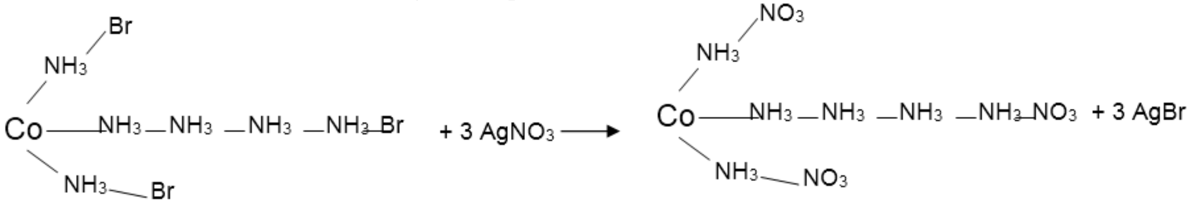
Different molar concentrations of $AgNO_3$ (0.10 M, 0.15 M, 0.20 M, 0.25 M and 0.30 M) were prepared and 50.00cm^3 of 0.20 M of $[CO(NH_3)_6]Cl_3$ A new complex was formed and , the time taken as well as the rate at which the complex was formed were determined for each reaction. The insoluble component (AgCl) and soluble component (new complex) formed were separated from the reaction mixture by filtration. The residue (AgCl) was dried between filter papers in fume cupboard while the filtrate, which contained the new complex was first evaporated and finally crystallized by cooling under tap. The weights and molar concentrations of AgCl and new complex formed were determined. Confirmatory tests of the substituted anions (NO^-_3 and Cl^-) were conducted. The work showed that the times taken for the formation of the new complex and AgCl were 32 sec, 27 sec, 21 sec, 16 sec and 12 sec. for 0.10 M, 0.15 M, 0.20 M, 0.25 M and 0.30 M of $AgNO_3$ respectively; the corresponding rates (cm^3/sec) were 1.56, 1.85, 2.38, 3.22 and 4.20, respectively; the weights of the AgCl and new complex formed were 27.27g and 58.99g, respectively; the molar concentrations of AgCl and new complex obtained were 0.19 mol/dm^3 and 0.17 mol/dm^3 and; the qualitative analyses of the swapped anions confirmed the presence of NO^-_3 in the new complex and Cl^- in AgCl.

Keywords: Complex salts; substitution reactions; rate of reaction; crystallization; precipitation.

1. Introduction

In everyday language, the word salt refers to common table salt or sodium chloride (NaCl). In scientific language however, the word salt means more than sodium chloride. In fact, sodium chloride is just one of numerous salts. In a scientific sense, the term salt refers to a chemical compound which results from the replacement of one or more hydrogen ions (H^+) of a corresponding acid by an equivalent number of metallic ions (Ababio, 1985). There are five (5) types of salts namely: normal salts, acid salts, basic salts, double salts and complex salts (Ababio, 1985).

In this work, the focus is on the complex salts, which are ionic compounds that dissolve in water to give complex ions (Ojokuku, 1998). Complex compounds (complex salts inclusive) are the ones that contained a central metal ion linked to other atoms, ions or molecules called ligands. The ligands can be monodentate (unidentate) bidentate or ploydentate/multidentate (Harrison and de Mora, 1996). If the ligands are easily removed from the complex, the complex is said to be unstable and; if the ligands are not easily removed from the complex, the complex is regarded as stable (Yaro, 2011). Complex salts undergo reactions such as redox reaction, combustion reaction, thermal reaction and substitution reaction. These reactions serve as the ways of converting the complexes into the required compounds (Zuru, 1992). For the preparation of labile complexes (i.e complexes that have the tendency to release their ligands or exchange their ligands with other compounds), substitution reaction is always employed. The rate of the reation varies with the nature of the ligands, if the ligands is labile, the rate of the reaction will be very fast and; if the ligand is inert the rate of the reaction will be low (Zuru, 1992). Based on chain theory of complexes, substitution reaction occurs as follows:

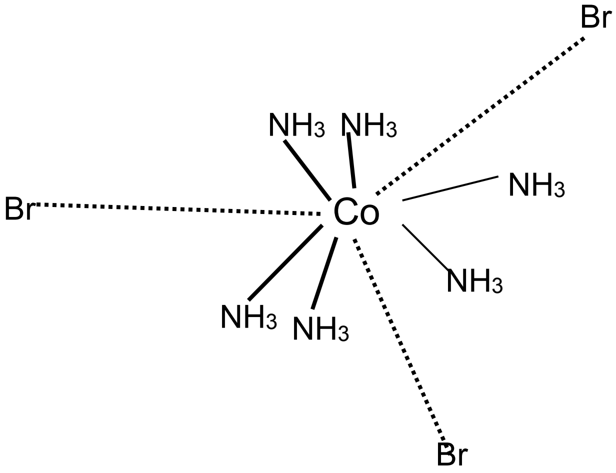


In the above reaction, it is indicated that when $AgNO_3$ is added to $[Co(NH_3)_6]Br_3$, there will be a white precipitate of AgBr, showing that Br^- was displaced from the complex by NO^-_3, which indicated that Br–atoms were not directly bonded to Co in the complex, rather bonded to NH_3 molecules, which were directly bonded to Co, hence NH_3 molecules served as bridging (Zuru, 2000). In the reaction, there will be two different precipitations. The first precipitation will be due to Br–atom bonded to 4 molecules of NH_3 as Co – NH_3 –NH_3 – NH_3 – NH_3 – Br, being the longest chain while the second precipitation will be due the Br–atoms bonded to 1 molecule of NH_3 each as Co – NH_3 – Br, which is relatively shorter and more stable, but only one precipitate will be formed in this case because the two (2) Co-NH_3-Br bonds are of the same chemical environment (Zuru, 2000).

In addition to chain theory of complexes, Alfred Werner's theory of complexes explained the nature of the bonds exist within complexes using primary and secondary valences (Yaro, 2011). The theory is based on the following postulates as reported by Zuru (2000):

-Each atom in a complex has two (2) valences (i.e. primary, 1^o and secondary, 2^o valences)
-Both the 1^o and 2^o valences must be satisfied when a complex compound combined with the other molecule(s).
-In coordination system, molecules that are within the coordination sphere, possessed 2^o valences while those that are outside the sphere possessed 1^o valences.

For instance, consider a complex compound, $[Co(NH_3)_6]Br_3$ whose structure is drawn as follows:



In this structure, the NH_3 molecules are directly bonded to Co using 2^o valences while Br-atoms are not directly bonded to Co and, they are due 1^o valences. This makes Br-atoms in the complex to be easily replaced when combined with other molecules (Zuru, 2000).

During precipitation, the first step is the formation of a very tiny particles of the precipitate called nuclei by a process called nucleation, after which another process called "particle growth" take place in 3 dimensions, where the tiny nuclei become relatively large particles (Makarfi, 1992). When reactants are mixed with solutions (solution of complex salt inclusive), there will be an induction period before nucleation occur. The induction period varies with different precipitates, through, in most reactions nucleation occurs concurrently almost as soon as the precipitating agents are added (Makarfi, 1992).

Development of liquid state synthetic method of producing complexes of desired qualities such as solubility, reactivity and so on, through substitution reaction could serve as a means of generating complexes using low technological skill at low cost.

This paper reports studies on the possibility of generating a relatively more soluble and very reactive complex compound, $[Co(NH_3)_6](NO_3)_3$ from another complex compound, $[Co(NH_3)6]Cl_3$ through substitution reaction. The paper also reports the rates at which the reaction occurred and, the amounts and molar concentrations of $[Co(NH_3)_6](NO_3)_3$ and AgCl generated.

2. Materials and Methods

2.1 Chemicals / Reagents

The Chemicals / Reagents used for the research were obtained from British Drugs House (BDH). The Chemicals/Reagents were of analytical grade and of good purity, hence no further purifications were carried out on them.

2.2 Preparation of Reagents and Solutions

All the reagents and solutions used for the work were prepared according to the known standard methods of preparation using appropriate solvents.

2.3 Preparation of 0.10M, 0.15M, 0.20M, 0.25M and 0.30M $AgNo_3$, 17.00g of $AgNO_3$ Solutions

In order to prepare 0.10M, $AgNO_3$, 17.00 g of $AgNO_3$ was accurately weighed and diluted to $1dm^3$ using distilled water in a $1dm^3$ volumetric flask. The same procedure was followed for the preparation of 0.15M, 0.20M, 0.25M and 0.30M solutions using 25.50 g, 34.00 g, 42.00 g and 51.00 g of $AgNO_3$, respectively.

2.4 Preparation of 0.20M $[Co(NH_3)_6]Cl_3$ Solution

A quantity measure of 53.50 g of $[Co(NH_3)_6]Cl_3$ was accurately weighed and diluted to $1dm^3$ using distilled water in a 1dm^3 volumetric flask.

2.5 Formation of New Complex

For the formation of the new complex, $[Co(NH_3)_6](NO_3)_3$. The method described by Ababio (1985) was adopted in which 50.0cm^3 of 0.10M $AgNO_3$ solution was mixed with 50.0cm^3 of 0.20M $[Co(NH_3)_6]Cl_3$ in a 250cm^3 beaker and gently stirred using a glass rod. A stop clock was started at the time of addition of 0.10M $AgNO_3$ solution to 0.2M solution of the reacting complex, $[Co(NH_3)_6]Cl_3$ and, the time taken for complete formation of white precipitate of AgCl was noted (Omwirhiren, 2005). The same procedure was followed for the formation of the complex, $[Co(NH_3)_6](NO_3)_3$ using 50.00cm^3 each of 0.15M, 0.2M, 0.25M and 0.30M of $AgNO_3$ solutions. The equation for the reaction is illustrated below:

$$\underset{\text{(soluble)}}{[Co(NH_3)_6]Cl_3} + \underset{\text{(soluble)}}{3\,AgNO_3} \longrightarrow \underset{\text{(soluble)}}{[Co(NH_3)_6](NO_3)_3} + \underset{\text{(insoluble)}}{3\,AgCl}$$

2.6 Isolation of $[Co(NH_3)_6](NO_3)_3$ from AgCl in the Solution Mixture

The isolation of the complex, $[Co(NH_3)_6](NO_3)_3$ from AgCl was achieved through the following steps:

2.6.1 Step 1: Precipitation of AgCl in the Solution Mixture

In order to precipitate the insoluble component of the solution mixture, the resulting solution obtained from the reaction of 0.20M $[Co(NH_3)_6]Cl_3$ and 0.20M $AgNO_3$ was used because the reactant that formed the products (i.e soluble complex component and insoluble AgCl) were of equal molar concentrations. The solution mixture was kept in a refrigerator for 24hrs in order to facilitate homogeneity of the solution, which results in proper accumulation of the soluble component of the solution within the matrix of the solvent (distilled water) used in preparing the reactants and, maximum coagulation of the insoluble component of the solution mixture (Ekwenchi *etal,* 2013). The complex compound in the solution being the soluble component remained in the matrix of the solvent while the insoluble AgCl settled at the bottom of the solution mixture as white sludge.

2.6.2 Step 2: Separation of Components by Filtration

The overnight refrigerated solution mixture was filtered off using Whatman filter proper (18.5cm diameter), where the residue (AgCl) was separated from the complex, $[Co(NH_3)_6](NO_3)_3$ .The residue was then put in an evaporating dish and heated slowly to dryness in a fume cupboard, where the white crystals of AgCl were formed. The weight of the crystals was weighed and recorded.

2.7 Recovery of the Complex from the Filterate

The recovery of the complex from the filterate was achieved through the following two (2) steps:

2.7.1 Step 1: Evaporation of Excess Solvent from the Filtrate

The filterate was first boiled in a boiling tube, where excess water (solvent) was eliminated from the filterate and become concentrated (Ababio, 1985).

2.7.2 Step 2: Crystallization of the Concentrated Filterate

Since the complex formed is labile (i.e the complex has the tendency to release its ligand, NO^-_3 on heating to dryness), the concentrated filterate obtained was (after evaporation) subsequently cooled under a tap, whereupon crystals of the salt formed (Ababio, 1985). The crystals were dried between filter papers in fume cupboard and weighed (Igwe and Olayiwola, 1999).

2.8 Estimation of Molar Concentrations of the Complex, $[Co(NH_3)_6](NO_3)_3$ and AgCl produced

Since the molar concentration of any pure substance is equal to its number of moles, therefore, the molar concentrations of the complex and AgCl obtained were evaluated as follows:

Molar concentration of a substance = no. of moles of the substance

$$\text{But, no. of moles of a substance} = \frac{\text{mass of the substance}}{\text{molar mass of the substance}}$$

Therefore, the molar concentration of the product obtained = MPO/MMO,
where MPO = mass of the product obtained
MMO = molar mass of the product obtained.

2.9 Qualitative Analysis of the Exchanged Anions (NO_3^- and Cl^-)

In order to confirmed the presence of NO^-_3 in the complex compound and the Cl^- in the residue (AgCl), the following confirmatory tests were conducted:

2.10 Confirmatory Test of NO^-_3 in the Complex

A quantity of 0.50g of the crystatlized complex was accurately weighted and dissolved in a test-tube using distilled water and, a few drops of freshly prepared saturated solution of $FeSO_4$ were added. The mixture was kept in slanting position and a few drops of concentrated H_2SO_4 were gently added down the side of the test-tube (Adelakun and Falope, 1972). The formation of a brown ring at the junction of the acid and aqueous layer indicated and confirmed the presence of NO_3^- in the complex.

2.11 Confirmatory Test of Cl^- in the Residue (AgCl)

A quantity measure of 0.50g of the dried residue was accurately weighed and subsequently dissolved in a test-tube using distilled water. The resulting solution of the residue was acidified with excess dil. HNO_3 (to prevent the precipitation of other salt if any) and, a few drops of $AgNO_3$ solution were added (Omwirhiren, 2005). The formation of white precipitate of AgCl indicated and confirmed the presence of Cl^- in the residue.

3. Results and Discussions

3.1 Results

The results of all the analyses and estimations carried out in this work are presented in Tables 1 and 2. Table 1 shows the rate of formation of $[Co(NH_3)_6](NO_3)_3$ from 0.20M of $[Co(NH_3)_6]Cl_3$ and different molar concentrations of $AgNO_3$ solution. Table 2 gives the amount (g) of $[Co(NH_3)_6](NO_3)_3$ and AgCl produced, as well as their molar concentrations.

3.2 Discussions

In all the reactions carried out, there was formation of white precipitate when 0.10M, 0.15M, 0.20M, 0.25M and 0.30M of $AgNO_3$ solutions were separately added to 0.20M of $[Co(NH_3)_6]Cl_3$ solution. This indicated that the chloride ions (Cl^-) were displaced from the reacting complex by the nitrate ions (NO^-_3) from $AgNO_3$ and, formed AgCl. The displacement of Cl- from the reacting complex by the NO^-_3 is attributed to the fact that NO^-_3 is more electronegative than Cl^- (Ababia,1985).

From the qualitative analyses of the anions (NO_3 and AgCl) carried out, the formation of brown ring observed at the junction the acid and aqueous layer indicated and confirmed the presence of NO^-_3 in the complex (Ojokuku,1992) while the formation of white precipitate when a few drops of $AgNO_3$ were added to acidified residue confirmed the presence of Cl^- in the residue (Omwirhiren,2005).

From Table 1, it could be seen that though, equal volumes of $AgNO_3$ and $[Co(NH_3)_6]Cl_3$ were reacted, but the rates at which the reactions occurred were influenced by the concentration of $AgNO_3$. The results (Table 1) showed that the rate of the reaction was directly proportional to the concentration of $AgNO_3$ used. This may be attributed to the fact that reacting particles react more often if they are overcrowded in a small space, which results in a corresponding increase in effective collisions of the reactants and hence in the reaction rate (Dagari, 2006). For labile complexes, where there are many atoms in their molecules, the collisions will be more because the electric field of the electron clouds of the atoms in the molecule of the complex are high, which causes frequent mutual interaction between the atoms of the complex and any incoming reactants, i.e. atoms, ions or molecules (Matthews, 1996). Additionally, when the number of reacting particles is large, the separation (distance) between the particles will be very small and, the mutual interaction of the particles within the reacting vessel will be very high in a very short time. This proximity of the particles within the reacting vessel will also lead to series of collisions between the reacting particles among which some are effective (i.e. at particular angle and with a minimum energy value equals to activation energy). This is in accordance with the collision theory of reactions as reported by Matthews (1996); Dagari (2006).

Table 2 gives the masses and molar concentrations of the new complex, $[Co(NH_3)_6](NO_3)_3$ and AgCl produced. The difference in the molar concentration of the new complex (0.17 mole/dm^3) and that of $AgNO_3$ (0.19 mole/dm^3) noted may be connected to relative low molar concentration of the new complex (0.17mol/g) may be connected to operational or personal error as (Birnin-Yauri , 2000). This is because during the process of separating the new complex from AgCl, a very minute quantity of the new complex may trapped within the matrix of the little water content of the residue, which could possibly make the residue (AgCl) to have a gain in mass while the new complex to have a relative decrease in its mass. This is based on the statement of Makarfi (1992)

Conclusion

The production and isolation of a very reactive soluble complex, $[Co(NH_3)_6](NO_3)_3$ was achieved using simple technological skills and, during the reaction, the rate of formation of the complex was found to be directly proportional to the concentration of the reactant ($AgNO_3$).

A Short Biography of the Author

Dr. M. N. Yaro was born at Dawakin-Tofa town, Dawakin-Tofa L.G.A., Kano State-Nigeria on the 26th December, 1971. He attended Central Primary School D/Tofa from 1976 – 1981; G.S.S. D/Tofa from 1981 to 1986; Advanced Teachers' College, Gumel, where he Obtained NCE (Chemistry / Physics) in 1989; Usmanu

Danfodiyo University, Sokoto-Nigeria, where he obtained BSc. and MSc Degrees in Applied Chemistry in 1994 and 2004, respectively and; University of Jos-Nigeria from 2004 to 2010, where he obtained Ph.D in Applied Physical Chemistry in February, 2011. Dr. Yaro also attended a computer training course at Kano State College of Education from June 2004 – September 2004, where he obtained a Certificate in Computer Application and Data Processing. The area of research interest of Dr. Yaro is Renewable Energy and Environmental Chemistry. Dr. Yaro is a registered members of the:Institute of Chartered Chemistry of Nigeria (ICON), Chemical Society of Nigeria (CSN) and Teachers' Registration Council of Nigeria (TRCN). Dr. Yaro worked with Kano State Ministry of Education (As a teacher) from 1989 – 2001 and Federal College of Education (Technical), Bichi from 2002 – 2012 (as Chemistry Lecturer). Dr. Yaro is Currently a senior lecturer in the Department of Chemistry of the Federal University, Dutse, Jigawa-Nigeria.

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Table 1: Rate of Complex Formation Using Different Molar Concentrations of $AgNO_3$ solution

Molar Conc. of $AgNO_3$ (Mol/dm$_3$)	Vol of AgNO (cm^3)	$[Co(NH_3)_6]Cl_3$ (cm^3)	Time (second)	Rate of formation of the new complex and AgCl
0.10	50.00	50.00	32.00	1.56
0.15	50.00	50.00	27.00	1.85
0.20	50.00	50.00	21.00	2.38
0.25	50.00	50.00	16.00	3.22
0.30	50.00	50.00	12.00	4.20

Table 2: Evaluated Masses and Molar Concentrations of the $[Co(NH_3)_6](NO_3)_3$ and AgCl Formed

Product obtained	Mass of crystals(g)	Molar concentration (mol/dm^3)
$[Co(NH_3)_6]\ (NO_3)_3$	58.99	0.17
AgCl	27.27	0.19