

Production and Estimation of the Rate of Formation of a Complex, $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ from a Labile Complex, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ at Varying Concentrations Of AgNO_3

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Abstract—A Complex, $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ was prepared by reacting 100.00cm³ of 2.00M of a labile complex, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ with 100.00cm³ of five (5) different molar concentrations of AgNO_3 . The concentrations of AgNO_3 used were 0.50 M, 1.00 M, 1.50 M, 2.00 M and 2.50 M. The reactions were carried out in five (5) different reactors, which were labeled A, B, C, D and E and, the time taken for complete reaction in each reactor was recorded. The reaction products were separated by precipitation and, the new complex formed was concentrated by evaporation and subsequently crystallized by crystallization under tap. The crystals formed were dried between filter papers in fume cupboard and weighed. The rate at which the complex formed in each reactor was evaluated. The work showed that the weights of the complexes formed in the reactors (A, B, C, D and E), were 2.24 g, 2.40 g, 2.52 g, 2.61 g and 2.63 g, respectively; the respective times (sec) for complete formation of the complexes in the reactors were 23, 18, 14, 10 and 5 and; the corresponding rates(g/sec.) of reactions in the reactors were 0.10, 0.13, 0.18, 0.26 and 0.53, respectively.

Keywords—Complex compounds; rate of reaction; labile complex; concentration; complex formation

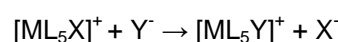
I. INTRODUCTION

Complex salts are those ionic compounds that dissolve in water to give complex ions. A complex ion contains a central metal atom surrounded by neutral molecules or ions called ligands. A ligand is an electron-rich particles such as NH_3 , H_2O or NO or an anion such as Cl^- , Br^- , I^- , OH^- , CN^- or H^- [1]. The ligands can be monodentate (unidentate) bidentate or polydentate/multidentate [2]. 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 [3]. 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 [4].

In general, complex compounds (complex salts) are the ones in which the number of bonds formed by one of the atoms is greater than the expected from the usual valence considerations. Thus, trivalent Co forms six (6) bonds with NH_3 molecules in the complex cation, $[\text{Co}(\text{NH}_3)_6]^{3+}$ while a divalent Ni forms four (4) bonds with Cl in the complex anion, $[\text{NiCl}_4]^{2-}$. Though, there are complexes such as $[\text{C}(\text{diars})_2]\text{Br}_4$ in which the number of covalent or coordinate bonds is the same as the group valency, which are instinctively thought as complexes [3]. Complex compounds undergo the following reactions: substitution reaction, redox reaction, combustion reaction and thermal reaction.

Substitution reaction of complexes is mostly exhibited by labile complexes (i.e complexes that have the tendency of releasing their ligands). Substitution reaction of complexes is generally represented by the following general equation [3]



Where [] = Coordination sphere

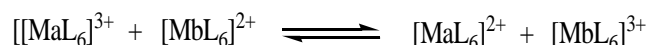
M = Central metal atom

L = Ligand

X and Y = exchangeable Ligands.

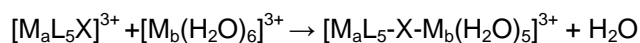
Redox reaction of complexes occurs in either of the following concepts: Outer-sphere concept and inner-sphere concept. In outer-sphere concept, the oxidation states of the central metal atoms in the reacting complexes are

exchanged, which indicates that oxidation and reduction occurred at the same time without affecting the contents [3]. The general equation below illustrates the process.



In the inner-sphere concept, one of the ligands from one of the reacting complexes serves as bridging ligand, which connects the two (2) reacting complexes

with elimination of a ligand from the other reacting complex. The process occur between the two (2) different complexes involving different central metal atoms of equal oxidation states [5]. The process is generally represented by the following general equation:

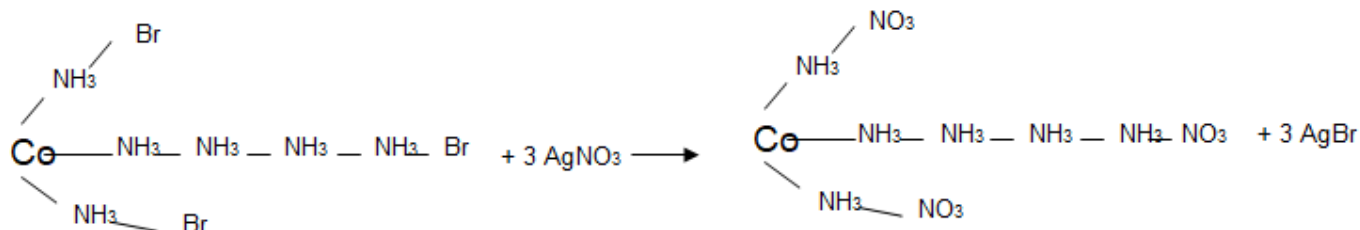


Combustion reaction of complexes: This involves burning of a complex compound in air (oxygen) to form the oxide of the central metal atom.

Thermal reaction of complexes: This occurs when a complex compound is heated at a temperature that can cause structural disorder of the

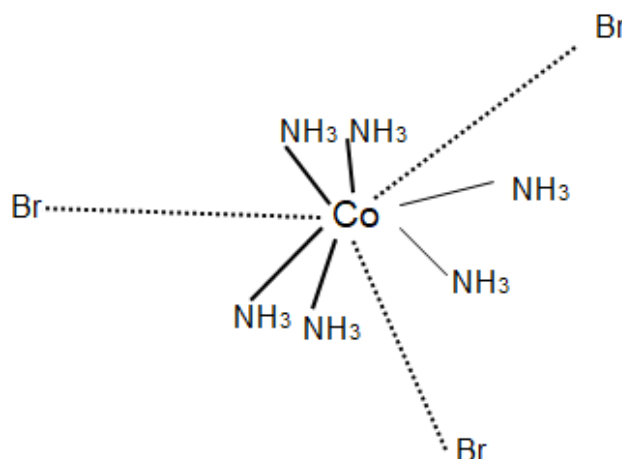
complex, which may result in the formation of a new complex through elimination or addition of ligands.

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 reaction varies with the nature of the ligands, if the ligands are labile, the rate of the reaction will be very fast and; if the ligand is inert the rate of the reaction will be low [4]. 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 ligands [5]. 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 [5].

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



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 [3]. The theory is based on the following postulates [5]. Each atom in a complex has two (2) valences (i.e. primary, 1° and secondary, 2° valences); both the 1° and 2° valences must be satisfied when a complex compound combined with the other molecule(s) and; in coordination system, molecules that are within the coordination sphere, possessed 2° valences while those that are outside the sphere possessed 1° valences.

In this structure, the NH_3 molecules are directly bonded to Co using 2° valences while Br^- atoms are not directly bonded to Co and, they are due 1° valences. This makes Br^- atoms in the complex to be easily replaced when combined with other molecules [5].

During precipitation, the first step is the formation of 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 [6]. 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 [6].

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, $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ from another complex compound, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, which is labile in nature through substitution reaction. The paper also reports the rates at which the reaction occurred and, the amounts of $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ generated in each reactor at room temperature.

II. MATERIALS AND METHODS

A. 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.

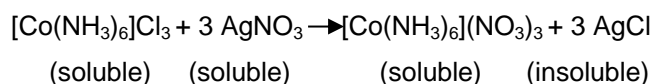
B. Preparation of Reagents and Solutions

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

C. Production of $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$

The new complex was prepared according to the method described by Omwirhiren (2005) with few adjustments [7].

The equation for the reaction is illustrated below:



D. Isolation of $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ by precipitation

In order to precipitate the insoluble component of the solution mixture, the resulting solution obtained was used. The solution mixture was kept in a refrigerator for 24hrs in order to facilitate homogeneity of the solution, and maximum coagulation of the insoluble component of the solution mixture [8]. 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. The refrigerated solution mixture was filtered off using Whatman filter paper (18.5cm diameter), where the residue (AgCl) was separated complex, $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ and discarded.

E. Recovery of the Complex from the filtrate

The filtrate was concentrated by evaporation according to the method described by Yaro (2016) with few adjustments. The concentrated filtrate obtained was crystallized under tap, whereupon crystals of the salt (complex) formed [9]. The crystals were dried between filter papers in fume cupboard and weighed [10].

F. Estimation of Molar Concentrations of the Complex, $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$

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

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

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 = $\frac{\text{MPO}}{\text{MMO}}$,

Where MPO = mass of the complex obtained
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III. 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 $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ from 0.20M of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and different molar concentrations of AgNO_3 solution. Table 2 gives the amount (g) of $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ obtained and its molar concentration.

Table 1: Rate of Complex Formation Using Different Molar Concentrations of NaNO_3 solution

Molar Conc. of NaNO_3 (Mol/dm ³)	Vol of NaNO_3 (cm ³)	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (cm ³)	Time (second)	Rate of formation of the new complex
A 0.50	100.00	100.00	23.00	0.10
B 1.00	100.00	100.00	18.00	0.13
C 1.50	100.00	100.00	14.00	0.18
D 2.00	100.00	100.00	10.00	0.26
E 2.50	100.00	100.00	05.00	0.53

Table 2: Evaluated Weights and Molar Concentrations of $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ Formed

Reactors	A	B	C	D	E
Mass (g)	2.24	2.40	2.52	2.61	2.63
Molar Conc. (mol/dm ³) x10 ⁻³	6.5	6.91	7.30	7.52	7.60

Discussions

Formation of white precipitate was observed in all the reactors (A, B, C, D and E) when five (5) different molar concentrations of AgNO_3 (0.50 M, 1.00 M, 1.50 M, 2.00 M and 2.50 M) were separately added to 0.2 M $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

Cl_3 . This is a clear indication that the chloride ions (Cl^-) in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

were displaced from the complex and replaced by the NO_3^- ions from AgNO_3 . The displacement of Cl^- from the complex and its subsequent replacement by the NO_3^- is attributed to the fact that NO_3^- is more electronegative than Cl^- [9].

Table 1 shows the times and rate at which the complex formed. From the result (Table 1), it could be seen that despite the fact that the volumes of AgNO_3 and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ used were equal so also the concentrations of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ used in all the reactors, but the rates at which the reactions occurred were affected by the concentrations of the AgNO_3 solutions used. The results showed that the rate of the reactions were directly proportional to the concentration of AgNO_3 . This may be connected to the fact that reacting particles react more often if they are overcrowded in a small place, which results in a corresponding increase in the effective collisions of the reacting species and hence in the reaction rate [11]. 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 [12]. 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 respective molar concentrations of the new complexes formed. The results showed that the masses and molar concentrations are directly proportional to one another. This is not surprising because molar concentration of a substance depends solely on the mass of the substance and its molecular weight as reported by [6].

Conclusion

Formation of a new complex from a labile complex through substitution reaction was achieved using very cheap and simple technology at laboratory scale. This could serve as a way forward for a large scale

(industrial) production of complexes for specific needs.

References

- [1] Ojokuku, G. O. (1992): Practical Chemistry for Senior Secondary Schools, PTF Low Price Education. Published by Glabeks Publishers Limited, SW8/1948A, Ring Road, NEPA Bus-Stop Challenge, Ibadan – Nigeria. Pp. 20.
- [2] Harrison, R. M. and de Mora, S. J. (1996): Introductory Chemistry for the Environmental Science, Second Edition, Published by the Press Syndicate of the University of Cambridge. Pp. 109.
- [3] Yaro, M. N. (2011): CHE 315 (Transition Elements); a course undertook by Chemistry Students in the Department of Chemistry, Federal College of Education (Technical), Bichi, Kano – Nigeria.
- [4] Zuru, A. A. (1992): CHE 4322 (Inorganic Chemistry IV); a course undertook by 300 level students in the Department of Pure and Applied Chemistry, Usmanu Danfodiyo University, Sokoto-Nigeria.
- [5] Zuru, A. A. (2000): CHE 706 (Transition Metals Chemistry); a course undertook by Postgraduate students in the Department of pure and Applied Chemistry, Usmanu Danfodiyo University, Sokoto-Nigeria.
- [6] Makarfi, S. M. (1992): CHE 4323 (Quantitative Analysis); a course undertook by 300 level students in the Department of pure and Applied Chemistry, Usmanu Danfodiyo University, Sokoto-Nigeria.
- [7] Omwirhiren, E. M. (2005): Systematic Practical Chemistry for Schools and Colleges. Published by Mouson and Moses Nigeria Limited, Egbele Street, Orerokpe-Delta State, Nigeria Pp. 175-176.
- [8] Ekwenchi, M. M., Gumel, S. M. and Yaro, M. N. (2013): Production of Biogas by Microbial Digestion of Banana leaves and Adduction of Paraffins from Saturates using Urea and Thiourea Solutions. *Techno Science Africana Journal* 8 (1). Pp 85-90.
- [9] Ababio, O. Y. (1985): New School Chemistry, Certificate, Science Series, Revised Edition. Africana – FEB Publishers Limited, Sabon-Gari Zaria Pp. 124-130.
- [10] Egwe, I. O. and Olayiwola, M. A. (1999): Concise practical Chemistry Textbook. First Edition, Published by Adedayo Printing (Nigeria) Limited, 35, Iworoko Road, Ado – Ikiti, Ikiti State – Nigeria Pp. 37.
- [11] Dagari, M. S. (2006): Basic Physical Chemistry (with over 200 solved problems) for level 1 University Science and Science – based students. Second Edition Gidan Dabino Publishers, No. 570, Sabon Titi- Dangado, Kano – Nigeria. Pp. 66-67.
- [12] Matthews, P. (1996): Advanced Chemistry (Low Price Edition). Published by the press syndicate of the University of Cambridge Pp. 465.