

Cobalt Complexes: Introduction and Spectra Analysis

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Abstract:

Little abundant on the Earth's surface, cobalt is obtained from the extraction of ores and the most common oxidation states for this element are +2 and +3. The objective of this work was to obtain the hexamincobalt (III) chloride complex from binder substitution reactions and oxidation of the metal center. The complex was characterized by UV-Vis spectroscopy and FTIR. The characteristic bands of strain and stretching of the NH₃ molecule present in the compound were identified by FTIR. In the UV-Vis, two bands referring to the electronic transitions $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ were identified, in addition to the TCML load transfer band. This work aims to contribute to the practical classes of inorganic chemistry.

Keywords: coordination chemistry; complexes; Tanabe-Sugano; transition metal

1. Introduction

Cobalt is a potentially toxic and chemically active metal, so it is not naturally found in metallic form [1]. Although not very abundant, it is distributed in rocks, mineral waters and in the sea. It is found in nature and extracted from other ores, among them, the most important are cobaltite (CoAsS), esmaltite (CoAs₂), erythrite (Co₃(AsO₄)₂·8H₂O) and linneite (Co₃S₄). It presents applications in the metallurgical industry for steel production, in the chemical industry as a catalyst, and in the ceramics industry [2-4].

It is a transition metal belonging to group 8B of the periodic table, showing atomic number 27 and molecular mass of 58.93 u [5]. In the metallic form it has silver blue color, besides having great hardness and being resistant to high temperatures, so it is used in the component of metallic alloys (iron, nickel, aluminum), surface coatings and electroplating. It has a wide range of spectroscopic properties, semiconductors and high light stability [6].

Transition metals have as their main characteristic the variation of the oxidation numbers of the formed compounds [2]. In the case of cobalt, oxidation states are mainly +2 and +3. The Co²⁺ ion, of pink color, exerts the role of reductive agent, whereas the cobaltous hydroxide (Co(OH)₂), in acidic medium, presents blue coloration [3,7].

The transition metals have the outermost *d* incomplete layer and are rarely in the isolated form, but may be covalently bound to other molecules or ions, forming coordination compounds, which are also called complexes [8].

Coordination compounds were considered a true mystery and a major challenge for chemists. These compounds, for being very unusual and difficult to understand and explain, ended up receiving from Alfred Werner (1866-1919) the suggestive name of "complexes" [9].

Werner was one of the precursors of the coordination chemistry, defining that a central metallic atom is a Lewis acid (receives

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electrons), whereas the binders that are Lewis bases (donate electrons to the metal) [7]. From the studies of Werner, it was possible to predict the geometries of the complexes, the structures of the electrons, the coloration of transition metals (absorption of light in the visible in the sublayers *d* or *f* by filling), resonance and their valence. Since the metal had two valences, the primary valency one responsible for the ion charge number, better known as oxidation state; and the secondary valency which is the amount of binders bound to the metal, called the coordination number. These findings contributed greatly to the concepts of ionic bonding and covalent bonding [2].

The stereochemistry of the complexes demonstrates coordination numbers from two to nine, influencing the geometry (planar square, tetrahedral, octahedral), as for example, coordination numbers with six binders have octahedral geometry. The amount of binders close to the central atom shows whether the binder is monodentate or bidentate and, thus, the coordination compounds present different types of isomerism: optical, geometric, bonding, ionization, among others [10].

The interaction between a metal ion and a binder allows the obtaining of compounds with various coordination numbers, oxidation states and, consequently, different geometries. In addition, the characteristics of the metal ion associated to the kinetic and thermodynamic aspects of the obtained compound allow obtaining structures with a wide variety of applications and broad spectrum of reactivity [11].

In coordination compounds, the binders exert different field intensities. This polarization is due to the effect of the atom or molecule that is binding with the metal center [12].

The influence of the binders on the interaction with the metal center depends on the strength of the binder field and is stronger on complexes that have strong field binders, according to the spectrochemical series, and consequently a higher crystalline field stabilization energy. On the other hand, the complexes that present weak field binders present the lower EECC and stability. The substitution of these binders can be determined by the color change [12, 13].

Among the most commonly used techniques for the characterization of complexes are visible ultraviolet (UV-Vis) and Fourier transform infrared (FTIR) spectroscopies.

Spectroscopy studies the interaction of electromagnetic radiation with matter, one of the main objectives being the determination of the energy levels of atoms or molecules. In the case of molecules, the spectral region where the transitions are observed depends on the type of levels involved, which may be vibrational or electronic. The vibrational transitions are located in the infrared region and the electronics in the ultraviolet or visible region [14].

Fourier Transform Infrared spectroscopy (FTIR) is a widely used technique to study a wide range of substances ranging from simple molecules to complex systems, and it is possible to analyze samples in amorphous or crystalline solid state, aqueous solutions, solvents films, potassium bromide tablets (KBr), and membranes [15, 16].

Infrared radiation is invisible to the human eye and in the electromagnetic spectrum, it occurs in the range between the visible and the microwave. It is characterized by wavelengths between 730 and 1.000.000 nm, the most common unit being the wave number and the range of most interest is in the region of 4000 to 400 cm^{-1} . Infrared spectroscopy is based on the effects of radiation absorption and is due to interaction with matter, with the coupling of the oscillating electric field of the molecular vibration and that of the incident radiation [15-18].

One molecule absorbs only selected frequencies of infrared radiation and encompasses molecular vibrational frequencies, which can be classified as axial deformations or angular stretches and strains. The stretches are changes in the distance between the atoms involved in the bonding and the angular deformations involve change in the bonding angle. However, not all bonds in a molecule are capable of absorbing energy in the infrared, it being necessary that the molecular vibrations have a change in the dipole moment. The oscillating electric dipole of the connection may then couple with the electromagnetic field of the incident radiation, which varies in sinusoid form. Thus, a symmetric connection having identical or substantially identical groups at each end will not

absorb in the infrared [7, 15].

On the other hand, ultraviolet and visible spectroscopy is one of the analytical methods most used in the various areas due to robustness, relatively low cost and large number of applications. It can be applied both for determination of inorganic compounds and organic compounds, involving the characterization of chemical and biochemical reactions, research of new pharmacological agents, thin films, besides the determination of physicochemical parameters, such as equilibrium constants, mechanisms and reaction velocities [19-21].

The ultraviolet region of the spectrum is generally considered in the range of 200 to 400 nm, with energies of 150 to 72 kcal.mol⁻¹, and the visible region covers 400 to 800 nm and energies of 72 to 36 kcal.mol⁻¹ [20, 22].

When radiation through the sample, some of that radiation can be absorbed and the atoms or molecules passes from a lower energy state (ground state) to a higher energy state (excited state). In general, by absorbing energy, the electron transition occurs from the highest energy occupied orbital (HOMO) to the low energy idle orbital (LUMO). The absorption of the radiation depends on the number and arrangement of the electrons in the molecules or ions and, consequently, the absorption band can be correlated with the type of binding that exists in the analyzed species [7, 20, 23].

In the case of an atom, the absorption spectrum can be composed of sharp lines. For compounds, absorption usually occurs over a

wide range of wavelengths, since the molecules can have many possible electronic transitions with small differences between them. Each of the transitions involves several lines so close together that the spectrophotometer cannot define and encompass all of them, leading to a wide band of absorption centered on the wavelength of the main transition [7].

For the interpretation of the UV-Vis spectra the electronic transitions of the diagrams elaborated by Yukito Tanabe and Satoru Sugano in 1954 are used. The pair known as Tanabe-Sugano performed the calculations of the binder field levels for all dⁿ configurations. Based on these calculations, quantitative energy diagrams, known as Tanabe-Sugano diagrams, have been developed and can serve as a basis for binder field transitions. They are correlation diagrams that describe the energies of the electronic states of the complexes as a function of the force of the binder field, where the ground state acts as the baseline and the other states present in relation to this fundamental state [7, 24-26].

The allowed transitions are those that happen between the ground state and the excited state, in addition to having the same spin multiplicity [5, 24]. To the left of the Tanabe-Sugano diagram is observed the transitions of the weak field complexes, and the right side, the strong field transitions. By the diagram of the Co²⁺ complex, with electronic configuration d⁷, the fundamental state ⁴T_{1g} is observed in the weak field, and ²E_g in the strong field. For the Co³⁺ complexes, with electronic configuration d⁶, we observe the fundamental state ⁵T_{2g} in the weak field and ¹A_{1g} in the strong field (Figure 1).

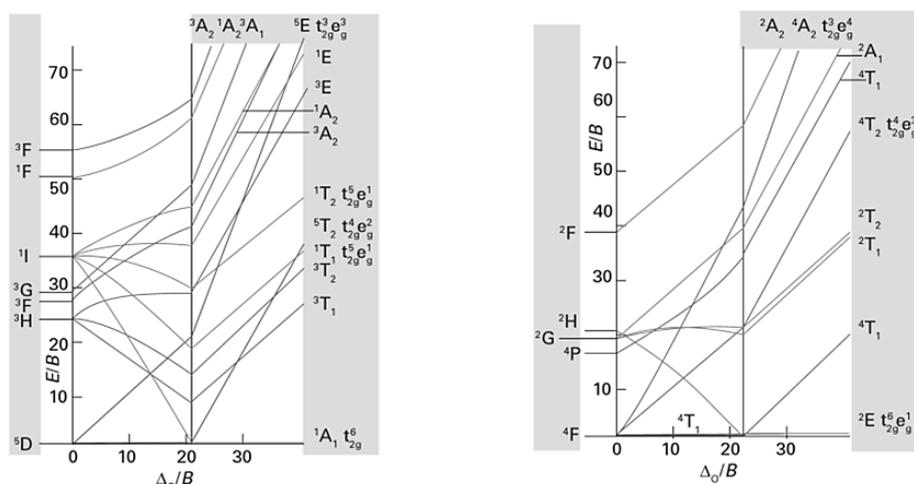


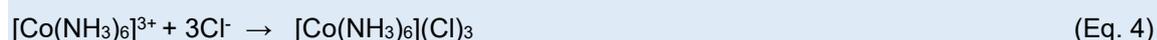
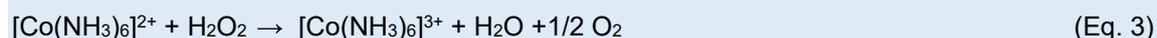
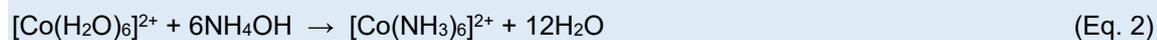
Figure 1. Tanabe-Sugano diagrams for d⁶ (left) and d⁷ (right) [24].

In this sense, the objective of this work was to obtain a cobalt complex and to analyze the UV-Vis spectra for identification of the electronic transition and load transfer bands, as well as the identification of the characteristic bands of the FTIR spectrum, in order to aid in the classes inorganic chemistry.

2. Results and Discussion

2.1 Synthesis

According to the methodology used, the following scheme of reactions was proposed for the synthesis:



Equation 1 represents the dissolution of cobalt chloride (Fig. 2-A) in the presence of ammonium chloride and the formation of a blue color compound which is cobalt complex bound to six molecules of water (Fig. 2-B). Reaction 2

describes the exchange of water by NH_3 binder from the addition of ammonium hydroxide, forming the cobalt (II) complex bound to six molecules of ammonia $[\text{Co}(\text{NH}_3)_6]^{2+}$, with a brown color, as shown in Figure 2-C.

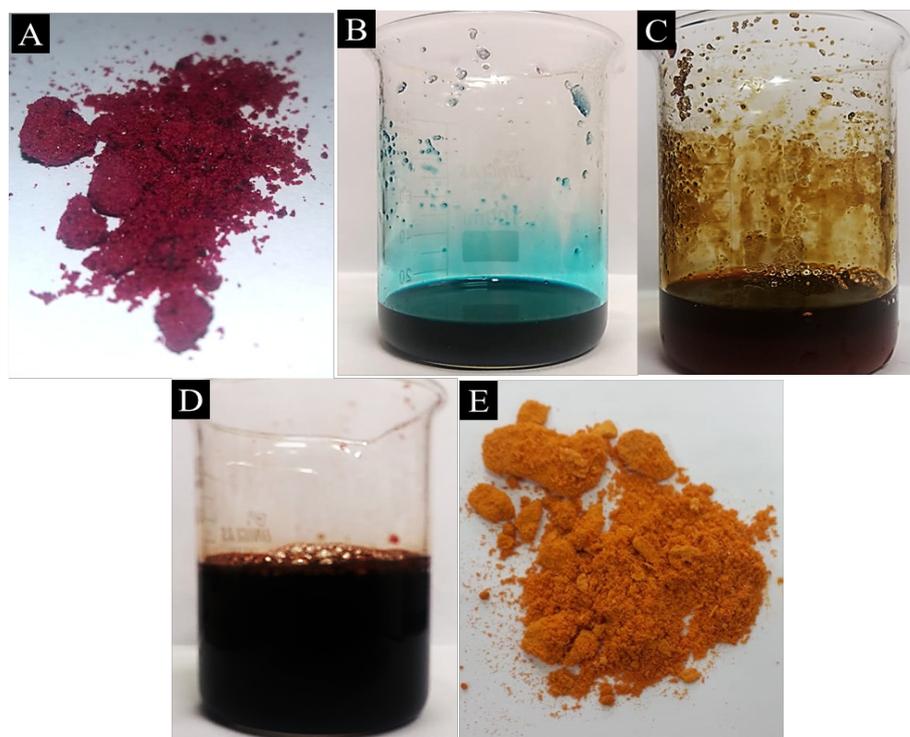


Figure 2. Stages of the synthesis of hexamincobalt(III) chloride.

In reaction 3 the action of hydrogen peroxide is described, in which the oxidation number (NOX) of the metal center of Co^{+2} is changed to Co^{+3} , since H_2O_2 is a strong oxidizing agent. At

this stage the complex changes color again, resulting in a dark purple coloration (Figure 2-D).

The reaction in the equation 4 is the last one,

in which the addition of chlorine as a counter ion occurs in the presence of the activated carbon, which acts as a catalyst, forming the complex of interest: hexamincobalt (III) chloride (Figure 2-E). The presence of the catalyst is of extreme importance for the reaction to occur quickly and in a single step. Without the catalyst, the $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ complex could be obtained, and with the addition of HCl, besides the presence of chlorine as a counter ion, the H_2O ligand could also be replaced by Cl, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ complex.

2.2 Spectroscopic Analysis

The UV-Vis spectra of the complex obtained (Figure 3) show the presence of transitions at 341 nm and 475 nm. Based on the Tanabe-Sugano diagram (Figure 1) for the d^6 configuration, the band at 341 nm is assigned to the transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$, while the band at 475 nm refers to the transition ${}^1A_{1g} \rightarrow {}^1T_{2g}$.

Due to the fact that it is a complex with predominance of strong field binders and, consequently, low spin, it is possible to observe a TCML type transfer band at approximately 250 nm.

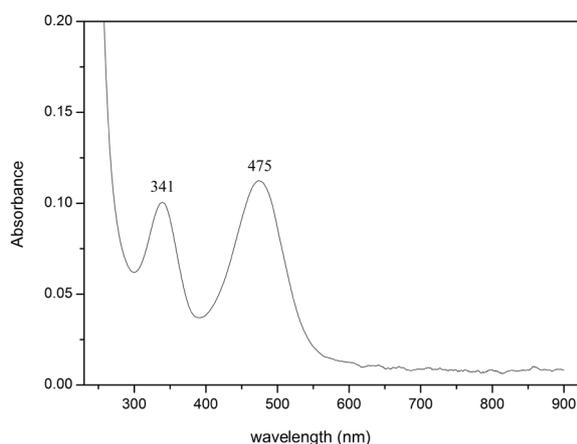


Figure 3. UV-Vis spectrum obtained for the hexamincobalt chloride (III).

Infrared spectroscopy was performed for both the product and the reagent, in order to obtain a comparison of the interactions and vibrations that occur in both substances. Figure 4 shows the results obtained for infrared spectroscopy for the product ($[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$) and for the reagent ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$).

For the analysis of the reagent (Figure 4-A), the FTIR spectrum showed three bands, and the signals at 3411 cm^{-1} and 1628 cm^{-1} are characteristics of the stretching and deformation of the O-H bond, attributed to the presence of water in the compound [27]. Such data are confirmed by Hannachi et al. [28] which describe that the presence of the water molecule is indicated by a high absorption band in the region of 3420 cm^{-1} and another band in the region $1620\text{-}1630 \text{ cm}^{-1}$. The band at 630 cm^{-1} is attributed to a possible metal-oxygen interaction [27]. These bands were also identified by Mitić et al. [29] when analyzing a Co(II) complex with pullulan.

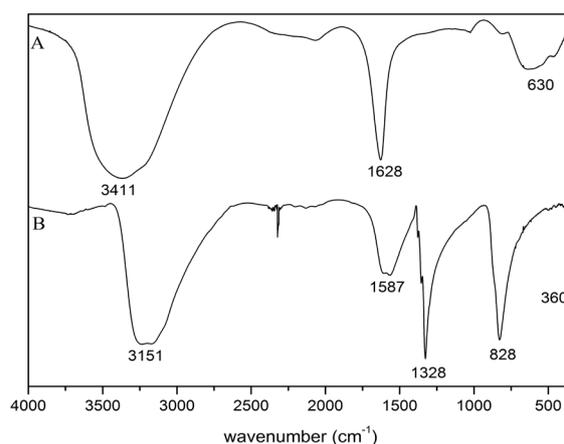


Figure 4. Infrared spectra of the samples: A) cobalt chloride (II) and B) hexamincobalt (III) chloride.

The FTIR spectrum of the obtained complex (Figure 4-B) shows that hexamincobalt (III) chloride formation occurred, because bands were obtained that were attributed to the stretching of NH_3 molecules (3151 cm^{-1} and 828 cm^{-1}) and asymmetric deformation NH at 1587 cm^{-1} and symmetric NH_3 at 1328 cm^{-1} [27,30]. Bands located in the same regions of the spectrum were obtained by Laxmi et al. [31] when studying the amine bonding to metal ions with d^5 , d^7 , d^8 and d^{10} orbitals. In addition, there is the presence of the band related to stretching of the Co-N bond in the region of 360 cm^{-1} [27,30].

3. Material and Methods

Initially, 4,5 g of cobalt chloride hexahydrate

(CoCl₂·6H₂O) (Êxodo 100%) was dissolved in 5 mL of boiling distilled water and then 3,0 g of ammonium chloride (NH₄Cl) (Dinâmica 100%) was added to form [Co(H₂O)₆]²⁺ in solution.

The solution was cooled in an ice bath and 10 ml of ammonium hydroxide (NH₄OH) (Vetec 25%) was added in order to obtain [Co(NH₃)₆]²⁺ in solution and 30 ml of hydrogen peroxide (H₂O₂) 20 volumes (Synth) were added slowly with vigorous stirring. And 1.5 g of activated charcoal (Biotec) was added and the temperature was raised to 60 °C and maintained until the complete disappearance of any trace of pink coloration.

The solution was filtered hot and the filtrate cooled in an ice bath. 6 mL of hydrochloric acid (HCl) (Vetec 37%) was dripped. The precipitate was collected, washed with acetone and dried at room temperature. In this step the complex hexamincobalt (III) chloride was obtained which was characterized by infrared and UV-Vis spectroscopy.

Infrared spectra were obtained on Perkin Elmer FTIR Spectrometer Frontier equipment with 16 scans of 4000 to 400 cm⁻¹ and resolution of 2 cm⁻¹ using KBr pellets.

In the UV-Vis analysis, quartz cuvettes were used for 200 nm to 900 nm scanning of the solution with 1x10⁻³ mol L⁻¹ concentration of hexamincobalt (III) chloride in a Thermo Fisher Scientific Scientific 60S digital spectrometer.

4. Conclusions

The reactions of complex formation can occur due to the substitution of molecules by other ligands. The abundance of NH₃ in the reaction medium and the presence of activated carbon, which acts as a catalyst, resulted in the complexation of hexamincobalt (III) chloride from cobalt chloride. For this, it was also necessary to change the NOX of the metallic center, which was initially Co²⁺ and was oxidized to Co³⁺ by the addition of an oxidizing reagent.

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