

## Preparation of Cobalt(II) Nitrilotriacetic Acid Complexes with Periodate in Aqueous Organic Solvent Mixtures

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### Abstract

This study reports a simple method for the preparation of cobalt (II) complexes with nitrilotriacetate (NTA), using periodate as oxidizing agent. Ternary complexes,  $[\text{Co(II)(NTA)(S)(H}_2\text{O)}_2]^{3-}$ ,  $[\text{Co(II)(NTA)(L)(H}_2\text{O)}_2]^{3-}$  and  $[\text{Co(II)(NTA)(M)(H}_2\text{O)}]^{3-}$  involving NTA-Co(II) and succinic, maleic and malonic acids in aqueous medium were prepared and characterized. The oxidation of Co(II) complexes by  $\text{IO}_4^-$  may proceed via one or two electron-transfer in the rate determining step. These complexes show that  $\text{IO}_4^-$  ion is capable of acting as a good complexing ligand. The formulae of the prepared complexes were further confirmed by IR, TGA and UV-Vis analysis. The absorbance of the complexes were conducted at wavelength 580 nm and maximal pH range from 4 to 5.

**Keywords:** Nitrilotriacetic acid, cobalt complexes, periodate, carboxylic acids.

### 1. Introduction

Cobalt exhibits a wide range of oxidation states from (+I) in the carbonyl anion to (+IV). Oxidation (+V) is also have been reported in oxide complexes of the metal. The (+II) oxidation state is the most readily available owing to the lability of the  $\text{Co(II)d}^7$  configuration. Divalent cobalt forms numerous complexes of various stereochemical types, octahedral and tetrahedral. The tetrahedral stereochemical structures are the most common, but there are a fair number of square ones as well as some which are five-coordinate. Because of the small stability difference between octahedral and tetrahedral Co(II) complexes, there are several cases in which the two types with the same ligand are both known and may be in equilibrium.

Cobalt ions also form a planar complexes with the several bidentate mono-anions such as dimethylglyoximate, amino oxalate and dithioacetylacetonate. When aqueous solutions of polydentate ligands are added to solution of cobalt (II) salts, labile cobalt (II) complexes are formed. In a large number of cases, the formation constants have been studied [1]. In

comparatively few cases, solid complexes have been isolated. In aqueous solutions, containing no other complexing agent, Co(III) ions, being sufficiently powerful oxidizing agents, which oxidized water to oxygen [2].

The amino polydentate carboxylic acids, being strongly chelating agents, are largely used for this purpose. The most famous one of these is ethylene diaminetetra acetic acid (EDTA), and its derivatives such as N-(2-hydroxyethyl) ethylene diamine-triacetic acid (TOH), in which the fundamental chelating agent unit of glycine is combined with an alcoholic ( $\text{OH}^-$ ) group [3]. Nitritotriacetic acid (NTA) is one of the most widely used chelating agents (Figure 1).

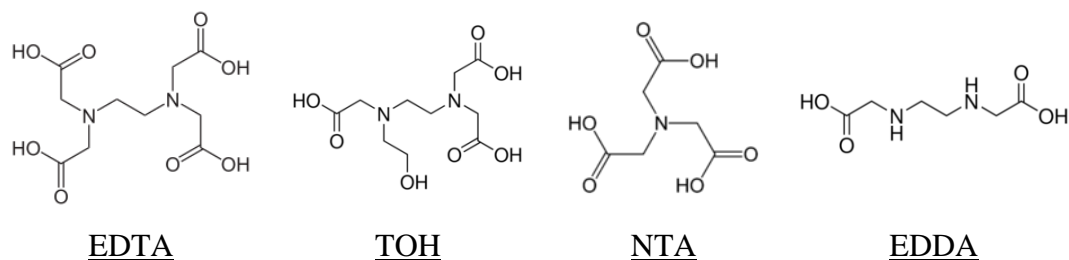
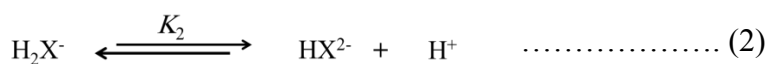
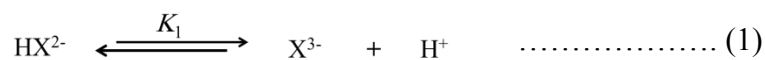
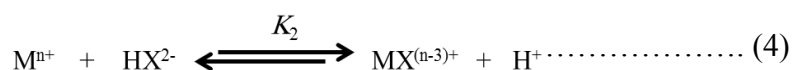


Figure 1: The structures of the most common polydentate carboxylic acids, used as chelating agents.

Nitritotriacetic acid ( $\text{H}_3\text{NTA}$ ) and its sodium salt are commercially important because of their ability to form stable ring compounds with a wide variety of metallic ions, including alkaline-earth metal and heavy metal ions in which the metallic ion becomes imprisoned or "sequestered" in a covalent ring and is no longer free to display its usual ionic character. It may be used to prevent the accumulation of deposits due to alkaline-earth and heavy metal ions in industrial chemical processes and to suppress the ionic form of a metal where the latter might have an undesired catalytic effect and may be used in chemical analysis. Several complexes of Co(II) with EDDA have already been reported, where EDDA behaves only as a quadridentate ligand towards Co(III) ion [4-6]. The complexing properties of NTA have been extensively studied [2]. Nitritotriacetic acid is a tribasic acid and the proton association constants ( $\log k_1$ ,  $k_2$ ,  $k_3$ ) for its various anionic forms are equal to 9.73, 2.49 and 1.89, respectively. These are referred to the following equilibria equations:



Over the rang of pH 4.0 - 8.0, the acid exists almost entirely in the form  $\text{HX}^{2-}$ . Then its reaction with metal ions proceed according to equation (4). The same complex will also formed in a strong alkaline conditions.



In an acidic medium, the carboxyl groups can become protonated, leading to the formation of complexes such as  $MHX^{(n-2)+}$ . In the alkaline solutions, hydroxo complexes like  $MX^{(n-4)+}$  can exist. However, studies by the slope ratio method and Job's method of continuous variations showed that a 1:1 stable complexes between NTA and Co(II) over the pH range (2.4-5.17) can be formed [7].

As stated earlier, NTA acts as a tetradentate donor in combining with metal ions [8,9]. One molecule of NTA coordinates to a Co(III) ion having a coordination number of six. It is expected that two positions around the cobalt ion, not occupied by the chelating agent, were filled by solvent molecules or other donors in the solution. On the other hand, if two molecules of NTA combined with the ion, it would be expected that the two nitrogen atoms and four of the carboxylate groups participate in the bonding, and the remaining two carboxylate groups are uncomplexed [8,9]. A ternary complexes involving nitrilotriacetatocobalt(II) and succinate, malonate as secondary ligand, were prepared and conformed by IR spectroscopy [10,11].

The equilibria existing in the solutions of periodic acid and its salts have been investigated [12,13]. Results shows the presence of paraperiodic acid,  $H_5IO_6^-$ , in a solid form and in equilibrium with its aqueous solution. The acidic Periodate solutions contain two species  $IO_4^-$  and  $H_5IO_6^-$  [14]. The proportion of  $H_5IO_6^-$  increases with decrease in pH. The ionization of the  $H_3IO_6^{2-}$  is so weak ( $pK_4 = 14$ ), that it does not give an end point in aqueous titrations. Also, it was proposed that the dianion  $H_3IO_6^{2-}$  undergoes dimerization [15,16]. However, at pH 4.2, about 99.8 % of Periodate was present as  $H_4IO_6^-$  and  $IO_4^-$  and 0.2 % as  $H_5IO_6^-$  [17]. The existence of  $H_2IO_5^-$  had been proved [18] as an intermediate in the hydration-dehydration equilibrium between hexa- and tetraoxoiodate (VII) monoanions in aqueous solution. Periodate was used for the analytical determination of glycerol by oxidizing the glycerol with excess of periodic acid or its salts forming formic acid and formaldehyde [19-21]. The direct determination of cobalt in petroleum hydrofining catalysis as Co(III)-EDTA [22] using Periodate to oxidize the first formed Co(II)-EDTA to Co(III)-EDTA can be made by spectrophotometric methods.

Finally, we have seen that, Periodate was extensively used as an oxidizing agent for both organic and inorganic compounds. These studies concluded that the electron transfer in Periodate oxidations proceeds via an inner-sphere or outer-sphere mechanism. On the light of this conclusion, use of Periodate as an oxidizing agent for inorganic complexes is very interesting for the confirmation of these mechanisms.

The aim of this work is to study the preparation of the ternary complex involving nitrilotriacetato-Co(II) and succinic, malonic and maleic acids. Also, The formulae of the prepared complexes were investigated using the IR, TGA and UV-Vis analysis.

## 2. Experimental

### *Apparatus*

The UV-Vis absorption spectra of all complexes were recorded on a SHIMADZU UV-530 and JENWAY-UV 6300 spectrophotometers. The pH of the reaction mixture was monitored using a G-C825 pH-meter. Analysis for carbon, hydrogen and nitrogen was carried out by using CHN/O analyzer. Infrared spectra ( $4000-400\text{ cm}^{-1}$ ) in KBr were recorded using Perkin-Elmer 2000 FTIR system. Thermogravimetric analysis (TGA) was performed with Perkin-Elmer thermogravimetric analyzer (TGA-7) at heating rate of  $10^\circ\text{C min}^{-1}$  under nitrogen atmosphere.

### *Chemicals and Reagents*

Trisodiumnitrilotriacetate (NTA), succinic (S), malonic (M) and maleic (L) acids were of reagent grade (Aldrich and Sigma), sodium metaperiodate (Aldrich), and sodium hydroxide, sodium nitrate, cobalt(II) nitrate and acetic acid were of reagent grade (Analar, BDH, Sigma), all were used as received without further purifications.

Standard aqueous solutions of these chemicals were prepared by accurate weighing of the appropriate compound. Similarly, stock solution of metal salt was also prepared in 250 ml deionized water. Fresh solution of sodium metaperiodate was prepared in 100 ml deionized water and the flask was wrapped with aluminum foil to avoid photochemical decomposition [23]. Stock solutions of acetic acid was made up from reagent grade acetic acid, by dilution with deionized water and standardized against freshly prepared sodium hydroxide solution. Several buffer solutions were prepared by mixing the appropriate volumes of sodium acetate and acetic acid.

### *Preparation and characterization of metal complexes.*

The ternary complexes,  $[\text{Co(II)(NTA)(M)(H}_2\text{O)}_2]^{3-}$  (**I**),  $[\text{Co(II)(NTA)(S)(H}_2\text{O)}_2]^{3-}$  (**II**) and  $[\text{Co(II)(NTA)(L)(H}_2\text{O)}]^{3-}$  (**III**) were prepared according to the reported methods [10,11]. The ternary complex involving nitrilotriacetato-cobalt(II) and maleic acid was prepared as follow: 2.92 gm (0.01 mol) of complex,  $\text{Na}[\text{Co(II)NTA(H}_2\text{O)}_2]$  as a starting material was suspended in 15 ml of water, and slightly warmed on a water bath with stirring. A 1.16 gm (0.01 mol) of maleic acid were then added. After the complete dissolving of the complex in water, the color of the solution was turned from pinkish violet to pink. About 50 ml of ethanol were then added, and the solution was cooled to room temperature. A pink crystals were formed, filtered and dried at room temperature.

## 3. Results and Discussion

### *Effect of pH.*

The dependence of the reaction rate on pH was investigated over the 4.20–5.57 pH range at constant  $[\text{IO}_4^-] = 2.0 \times 10^{-2}\text{ mol.dm}^{-3}$ , complex [**I**, **II** and **III**] =  $1.0 \times 10^{-3}\text{ mol.dm}^{-3}$ ,  $I = 0.20$

$\text{mol dm}^{-3}$  and  $T = 30^\circ\text{C}$ . Variation of the pseudo first-order rate constant ( $k_{\text{obs}}$ ) with pH is illustrated Figures 2-4. The data shows that the reaction rate increases with increasing pH values.

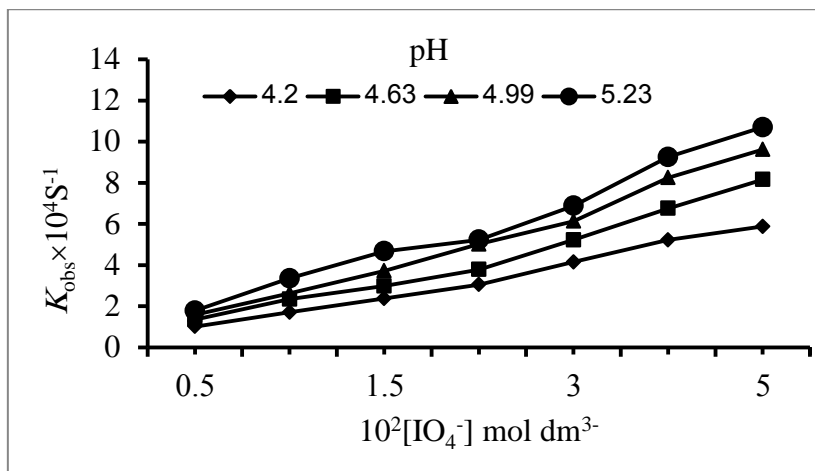


Figure 2. Effect of pH on  $K_{\text{obs}}$  for the complex (I). Complex (I) =  $[\text{Co(II)(NTA)(M)(H}_2\text{O)}]^{3-}$  =  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ , and  $T = 30^\circ\text{C}$ ,  $M = \text{Malonic acid}$ .

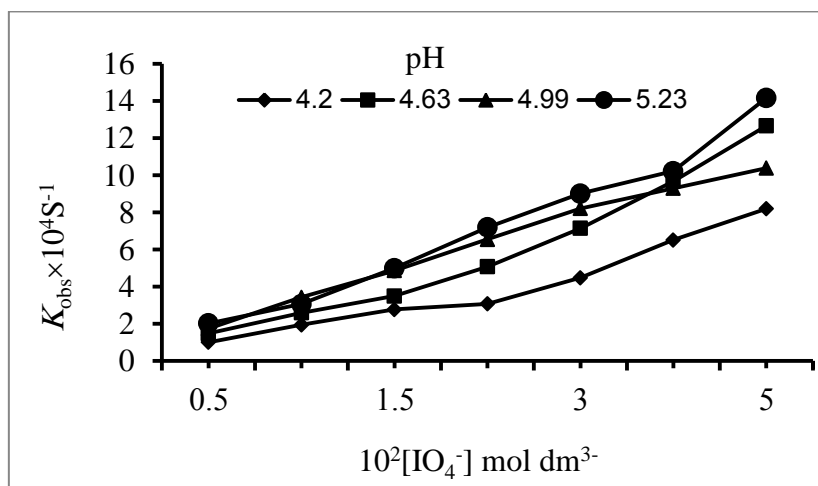


Figure 3. Effect of pH on  $K_{\text{obs}}$  for the complex (II). Complex (II) =  $[\text{Co(II)(NTA)(S)(H}_2\text{O)}]^{3-}$  =  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ , and  $T = 30^\circ\text{C}$ ,  $S = \text{Succinic acid}$ .

### Ultraviolet-visible analysis

The UV-Vis absorption spectra of the three complexes (I, II and III) after the oxidation with Periodate is illustrated Figure 5. The spectra showed the presence of the formation of the initial Co(III) products, which slowly changed to the final Co(III)-products. Both the initial and the final products were blue. There has been some controversy in the literature regarding the correct formulation of Co(III)-NTA complexes [24-27]. The blue complex has been designated by Thacker and Higginson [24] as the  $\beta$ -form. The maxima and molar absorption coefficients of the final Co(III) products recorded at pH 5.23 were  $\epsilon_{\text{max}}^{580} = 172$  and  $\epsilon_{\text{max}}^{(410)} = 166 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ ,  $\epsilon_{\text{max}}^{580} = 170$  and  $\epsilon_{\text{max}}^{400} = 168 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$  and  $\epsilon_{\text{max}}^{580} = 173$  and  $\epsilon_{\text{max}}^{408} = 167 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$  for the three (I, II, III) complexes, respectively. The Co(III)

products of oxidation by NTA were different from that obtained with Periodate. The Co(III)-NTA complexes were designated as the  $\alpha$ -form.[24].

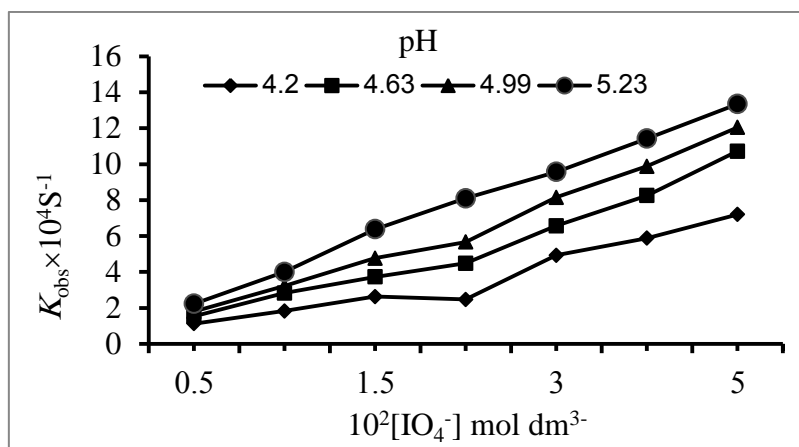


Figure 4. Effect of pH on  $K_{\text{obs}}$  for the complex (III). Complex (III)=[Co(II)(NTA)(L)(H<sub>2</sub>O)]<sup>3-</sup> =  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ , and  $T = 30^\circ\text{C}$ , L= Maleic acid.

#### CHN Analysis

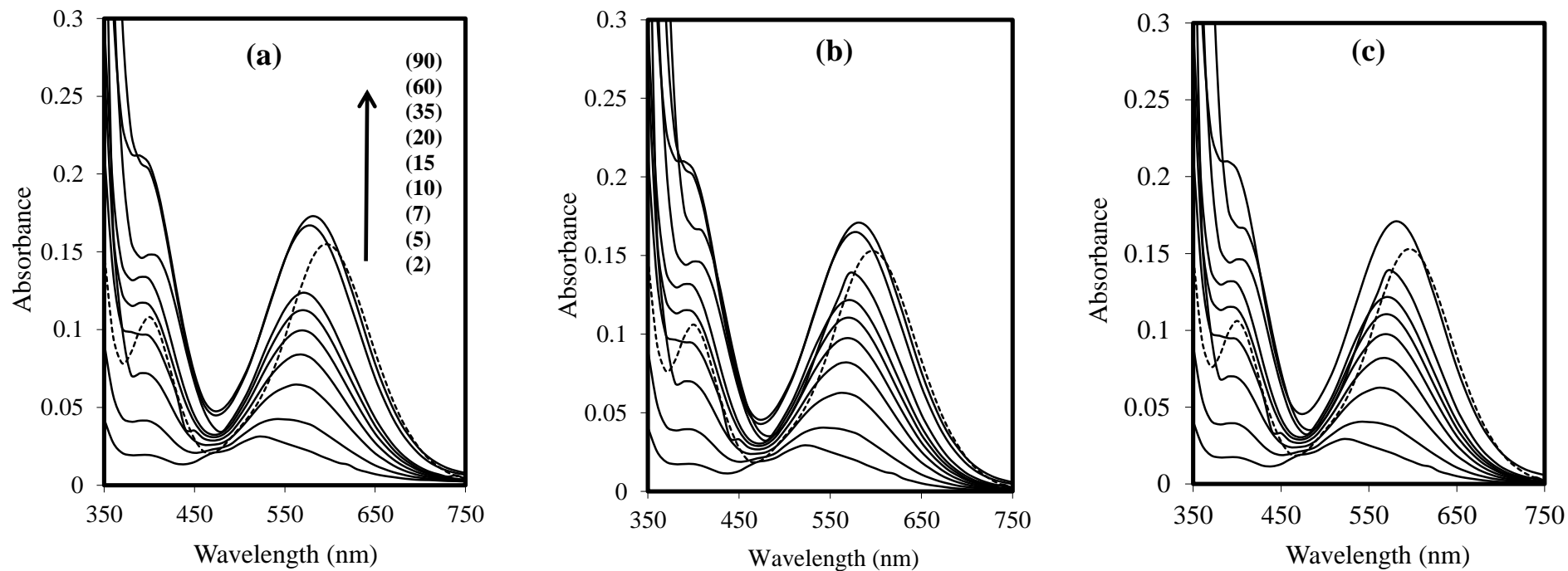
The elemental analysis of the prepared complex is illustrated as follow; Found: C, 26.72; H, 2.85; N, 2.97%. Calculated: C, 27.03; H, 2.70; N, 3.15 %. For  $\text{Na}_3[\text{Co(II)C}_{10}\text{H}_{11}\text{O}_{11}\text{N}]$  complex. The obtained data are in good agreement with the required for the suggested structure of the prepared complex.

#### Infrared Analysis

The formula of the complex was further confirmed by IR. The IR spectra of the complex, bands in the  $3367\text{--}3520 \text{ cm}^{-1}$  regions, were attributed to  $\nu\text{OH}$  of the coordinated water molecules. The ( $-\text{OH}$ ) band in the free ligand was completely disappeared and a new carboxylate band ( $\nu_{\text{COO}}$ ) was appeared in the region  $1465\text{--}1433 \text{ cm}^{-1}$ , confirming the participating of the carboxylic group of the ligand in the coordination with the metal ions through deprotonation. This is also confirmed by the presence of *asym*-( $\nu_{\text{COO}}\text{-Co}$ ) band in the range  $1585$  to  $1631 \text{ cm}^{-1}$ . The data shows that the complex started losses weight (18.45) at  $163.15^\circ\text{C}$ , corresponding to the loss of two coordinated water molecules and one acetate group (calc. 18.24). Accordingly, the proposed structure of the complex was as follows:  $[\text{Co(II)(NTA)(L)(H}_2\text{O)}_2]^{3-}$ .

#### Thermogravimetric (TGA) analysis

The thermogram of the prepared complexes shows that weight loss (18.45) begins  $163.15^\circ\text{C}$  corresponding to the loss of two coordinated water molecules and one acetate group (calc. 18.24).



**Figure 5:** Change in absorbance as a function of wavelength for the final products. (a) (I), (b) (II), and (c) (III). Data were recorded at various time (2, 5, 7, 10, 15, 20, 35, 60, and 90 min) from the time of initiation of the reaction. The dotted line represents the final product,  $[1.0 \times 10^{-3} \text{ M}]$ ,  $[\text{IO}_4^-] = 0.02 \text{ M}$ ,  $\text{I} = 0.2 \text{ M}$ ,  $(\text{NaNO}_3)$ ,  $\text{pH} = 5.23$ , and temperature =  $30^\circ \text{C}$ .

## 4. Conclusion

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The preparation of the oxidation  $[\text{Co(II)(NTA)(M)(H}_2\text{O)}]^{3-}$ ,  $[\text{Co(II)(NTA)(S)(H}_2\text{O)}_2]^{3-}$  and  $[\text{Co(II)(NTA)(L)(H}_2\text{O)}_2]^{3-}$  by periodate may proceed through an inner-sphere mechanism. This mechanism was supported by the observation that  $\text{IO}_4^-$  ion is capable of acting as a ligand. The oxidation of  $[\text{Co(II)(NTA)(M)(H}_2\text{O)}]^{3-}$  by  $\text{IO}_4^-$  may proceed via one or two electron-transfer in the rate determining step. The fact that acrylonitrile was not polymerized by the reaction mixture may support a two electron- transfer process. From the pH range and  $K_1$  value, suggests involvement of the protonated and deprotonated form of the Co(II)-complexes,  $[\text{Co(II)(NTA)(M)(H}_2\text{O)}]^{3-}$  and  $[\text{Co(II)(NTA)(L)(H}_2\text{O)}_2]^{3-}$  in the rate-determining step. The formula of the complexes were further confirmed by IR TGA and UV-Vis analysis.

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