

Received: 27.4.1982 (7)

Spectroscopic and Radiolysis Studies on the Interaction
of Cobalt with Nitrilotriacetic Acid

by

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Abstract

The stoichiometry and stability of the complexes formed between Co(II) or Co(III) and nitrilotriacetic acid (NTA) were spectrophotometrically investigated. The chelation of the hydrolysed state of Co(III) with NTA was also studied. The behaviour of Co(II)-complex on irradiation with cobalt-60 γ -rays was followed spectrophotometrically.

Introduction:

The interaction between several polyaminopolycarboxylic acids and cobalt ions was extensively studied. The aminopolycarboxylic acid, nitrilotriacetic acid, NTA, was shown to form fairly stable complexes with divalent and trivalent cobalt ions.^{1,2} To our knowledge, the study was carried out only potentiometrically and within certain concentration range of both the acid and the metal ions. The present work is concerned with the study of the interaction between cobalt and NTA spectrophotometrically using different concentration ranges. Radiolysis of the formed equimolar Co(II)-NTA complex was carried out using Co-60 γ -rays. According to the results obtained, a radiolytic mechanism was suggested. Such study may be useful in the evaluation of NTA as a decontaminating agent in case of radioactive cobalt contamination of the environment.

Experimental:

All the chemicals used were A.R. reagents. Co²⁺ complexes were prepared by mixing the proper amount of CoCl₂.6H₂O solution with that of

the sodium salt of the acid. Co(III)-chelates were prepared from Co(II)-ones.³ Aqueous solutions were prepared in carbon dioxide-free double distilled water.

The chelation of the hydrolysed state of Co(II) with NTA was carried out by preparing a series of 4×10^{-2} M solutions of cobaltous chloride adjusted at different pH values and aged for various time periods, followed by the addition of equal volumes of 1.6×10^{-1} M NTA solution, adjusted at the same pH value. Optical densities were measured as a function of pH and standing time.

Spectrophotometric measurements were carried out on Veb Carl Zeiss Jena, Specord UV-Vis spectrophotometer, using 1 cm quartz cells. pH-adjustments were done using TDA, HM-7B pH-meter with a combined glass-calomel electrode.

Irradiations were carried out on 2 ml samples of mixtures of 1×10^{-3} M Co^{2+} and 4×10^{-3} M NTA with $\gamma^{60}\text{Co}$ -radiation source at a dose rate of 1.66×10^3 rad./min. The dose rate was determined with the Fricke's ferrous dosimeter. The radiolytic yields were determined spectrophotometrically⁴ in the UV region.

Results and Discussion:

A. Chelation of each of Co^{2+} and Co^{3+} with NTA:

The interaction between Co^{2+} and Co^{3+} , with NTA was studied spectrophotometrically by the continuous variation,^{5,6} mole ratio⁷ and slope ratio⁸ methods. It was found that mixtures of NTA with either cobalt ions obey Beer's law and absorb in the ultraviolet as well as in the visible regions. However, the examination of the spectra in the visible region is restricted only to concentrated solutions because the molar absorption coefficient is relatively low. An obvious shift in wave length due to complexation could be observed. These results are listed in table 1. Co(II)-NTA mixtures having different mole ratios exhibit absorption maxima at $\lambda = 220$ and 523 nm between pH 4.5 and 7.5, while Co(III) complexes show absorption maxima peaks at $\lambda = 250, 400$ and 540 nm between pH 7.5 and 9.0.

Applying the continuous variation method⁵ and its modification,⁶

the results indicated that the shape of a respective curve depends, within certain concentration range, on the total concentration of Co(II)-NTA. For a total concentration of 0.5×10^{-3} M, the representation curve has two maxima at mole fractions 0.5 and 0.66 corresponding to 1:1 and 2:1 complexes, respectively. At higher concentration, the curve has a maximum corresponding to 1:1 complex. This was confirmed by the results obtained by the mole ratio and the slope ratio methods. Guided by these results, the Co^{3+} complexes were studied using concentrated solutions (4×10^{-2} M).

Calculation of the stability constants of both Co^{2+} and Co^{3+} chelates were carried out using Job's equations.^{5,6} The values of $\log K$ are 10.8 ± 0.1 and 14.6 ± 0.2 , respectively.

B. Chelation of the hydrolysed state of Co^{2+} with NTA :

The chelation of the hydrolysed state was carried out as a function of pH and standing time. The data obtained are presented in Fig. 1. It was observed that on adjusting the pH of Co^{2+} solution at 7, 8, 9 and 10, a blue precipitate of $\text{Co}(\text{OH})_2$ is formed. For all time intervals, the precipitate formed at pH 7 and pH 8 dissolved completely and instantaneously in NTA giving clear pink and brown solutions, respectively. At pH 9 and 10, partial solubility occurs. For such samples separation of the precipitates was carried out by centrifugation directly before recording the spectra. It is to be noted that, all the spectra exhibit maximum absorption at $\lambda = 540$ nm. Compared with the optical density-pH curve for fresh solution mixture of Co^{2+} and NTA, it could be concluded that at 48 hours aging time, a remarkable decrease in optical density occurred at the pH range from 3 to 7, after which an increase started and reached a maximum value at pH= 8.5, then a sharp decrease occurred at pH ≥ 9 . The general decrease in the optical density could be due to the formation of Co(II) hydroxide, hence lowering the extent of chelation with NTA. However, on increasing the pH from 7 to 8.5, the observed increase in the optical density may be attributed to the oxidation of Co(II) with the oxygen of the air in alkaline medium to give Co(III). These latter species would then interact with NTA forming Co(III)-NTA chelate, as indicated by the maximum absorption at $\lambda = 540$ nm and at a relatively high pH value. On the other hand, the solutions aged for one, two and three weeks show a general and gradual increase in the optical density as a function of pH and reached a maximum value at 7.5. This may be explained on the basis,

that as the precipitate, Co(II)-hydroxide is more aged, the process of oxidation of Co(II) to Co(III) become more likely. Accordingly, the pH at which the maximum absorbance occurs is shifted to lower value (7.5) than the case of 48 hours-age time. From figure 1, it is obvious that nearly a constant value of optical density was obtained, in each case, for the pH values 4, 5 and 6. This pH range is characteristic, as reported previously, for the stability of Co(II)-NTA complex. Accordingly, it is supposed that the complete oxidation of Co(II) to Co(III) occurs beyond this pH range. The decrease in the optical density at higher pH values (> 8.5 in the case of 48 hours and > 7.5 in the other cases) may be due to the incomplete solubilization of the precipitate as mentioned before. For the hydrolysed state aged for 4 weeks, a slight decrease in the optical density, at pH values, than that aged three weeks could be shown in Fig. 1. This would mean that as the precipitate is aged longer, some of the hydroxide may change to polymolecular hydrolysed state,⁹ which may absorb at a different wave lengths thus causes the observed decrease in the O.D.

C. Radiolysis of Co²⁺-NTA complex in aqueous and aerated solution with γ ⁶⁰Co-radiation:

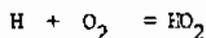
The irradiation was made on (Co²⁺-NTA) mixtures, at different pH values, namely 4.5 and 7.5. Plots of the optical density versus the dose absorbed for mixtures of different mole ratios at the two considered pH values are shown in Figure 2.

According to the experimental results, it could be postulated that at pH 4.5 decomposition of the complex occurred, while at pH 7.5 decomposition of the complex occurred, while at pH 7.5 Fig. 2 oxidation of the chelate appears to be the probable process taking place.

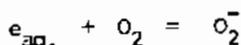
The following mechanism for both degradation and oxidation is suggested, which is identical to that discussed before for other cobalt chelates.^{10,11}

I. Degradation of the complex:

As the radiolysis is carried out in aerated solutions, the reducing species H and e_{aq.}⁻ will react with oxygen to give H₂O and O₂⁻, respectively:^{12,13}



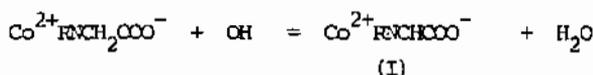
and



The two radicals H_2O and O_2^- react with each other in aqueous solutions as follows:

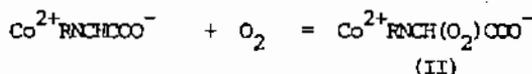


Many published work^{14,15} have reported that the aminocarboxylic acids are easily attacked via the OH radical, leading to the abstraction of a hydrogen atom from the carbon attached to the carboxylic group. Accordingly, the following reaction may take place:

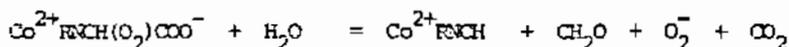


where $\text{Co}^{2+}\text{RNCH}_2\text{COO}^-$ represents the Co(II)-NIA complex.

In presence of oxygen, the species (I) may add O_2 as follows:



The oxygenated intermediate (II) is unstable and should stabilize itself through the following reaction:



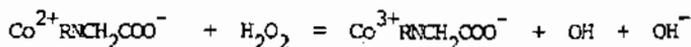
The liberated formaldehyde was detected and determined experimentally,¹⁴ its G value was found to be 0.5 ± 0.1 . For the 1:1 Co(II)-NIA chelate, the G value was determined from the slope of the straight line O.D.-Dose relationship (Fig. 2). It was found to be equal to 3.55 ± 0.2 .

According to the above mechanism, the radiolytic degradation of Co(II)-NIA complex may be due only to the OH radical, and thus $G_{\text{Co(II)}}$ should be equivalent to G_{OH} . Actually, the experimental value is much higher than that of OH radical. This could be interpreted as being due to oxidation of the complex via H_2O_2 accompanying its degradation. In such a case, the observed G value should be equivalent to the sum of G_{OH} and $G_{\text{H}_2\text{O}_2}$, which is quite fulfilled.

2. Oxidation of the complex:

The reaction between H_2O_2 , as an oxidizing agent, and Co(II)-NIA

chelate during radiolysis, specially in neutral and alkaline media, have to be considered. As a result, the divalent cobalt chelate is converted the corresponding trivalent cobalt one according to :



It was found that oxidation varies linearly with the dose absorbed. The G value of the formed Co(III) from the 1:1 Co(II)-Complex was determined from the corresponding curve. It was found to be equal to 1.6 ± 0.1 . Similar results were obtained during the radiolysis of other cobalt chelates.^{10,11}

Acknowledgment:

The authors are most indebted to Prof. Dr. Mohamed B. Hafez for his sincere assistance. The authors are also grateful to the facilities provided by the Atomic Energy Establishment lab, in which the radiolysis part of this work was executed.

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Table 1

Various values for the molar extinction coefficient, ϵ ,
at different λ_{\max} . for Co(II), NTA and the Comp-
lex (Co(II)-NTA)

Species	λ_{\max} (nm)	ϵ $M^{-1} \cdot cm^{-1}$	pH-interval
Co(II)	200, 500	25, 5	
NTA	208	5.5×10^3	
Co(II)-NTA (1:1)	220 and 523	1.9×10^3 40	} 4.5 - 7.5
Co(III)	200, 500	1.8×10^2 , 7	
Co(III)-NTA (1:1)	250, 400 and 540	46.67×10^2 , 125	} 7.5 - 9

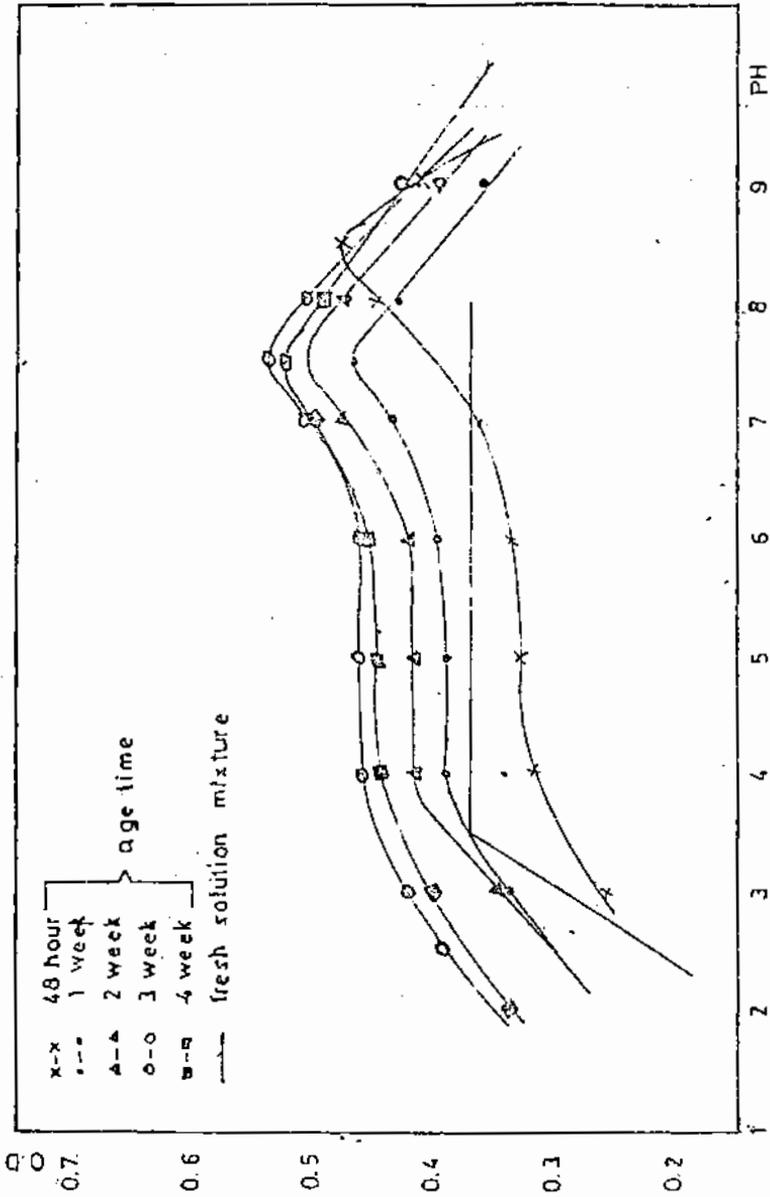


Fig. (7): Variation of the Optical Density of (Co(II)-NTA) Mixtures with pH and Aging Time

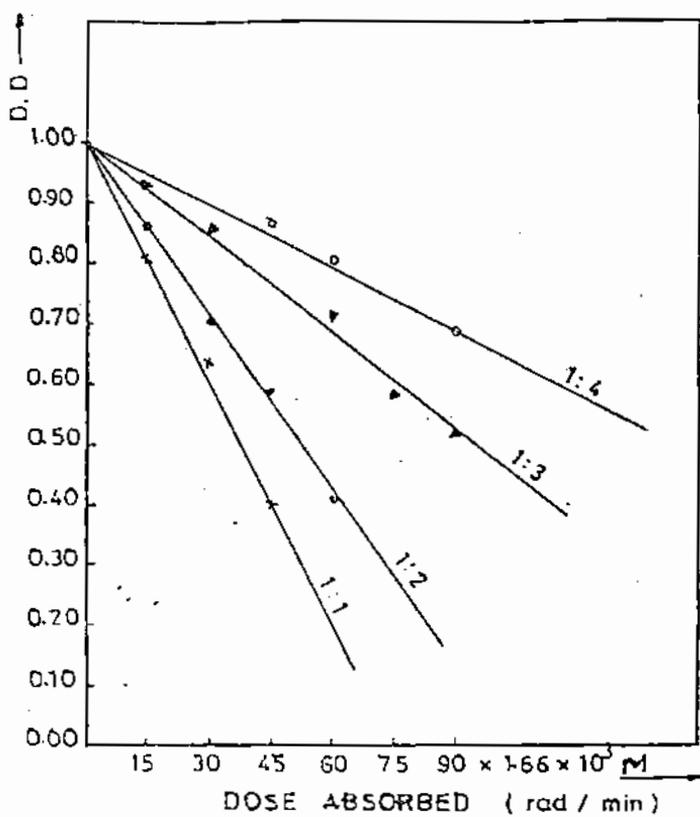


Fig. (2): Gamma radiation induced degradation of 1:1, 1:2, 1:3 and 1:4 Co(II)-NTA mixtures at pH 4.5 at $\lambda = 205$ nm.