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Chelation of Di - And Trivalent Cobalt With Some Polyaminopolycarboxylic Acids By

by

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22

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lit by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

Chelation of Di- and Trivalent Cobalt With Some polyaminopolycarboxylic Acids

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SUMMARY

The interaction between some polyaminopolycarboxylic acids with di- and trivalent cobalt has been studied applying some spectroscopic methods. Two cobaltous and one cobaltic chelates were identified. Metal chelate composition, formation constants and stability constants have been determined. Data for different chelates are compared and discussed.

INTRODUCTION

Complex formation between ethylenediaminetetraacetic acid (EDTA) and many metal ions was extensively studied¹⁻³. Considering other analogous chelating agents, it has been noted that metal chelates of diethylenetriaminepentaacetic acid (DTPA) are more stable than those of EDTA specially with the more highly charged ions, such as rare earth elements.⁴ Also, triethylenetetraaminehexaacetic acid (TTHA) has become increasingly valuable and interesting chelating agent due to the presence of ten coordinating groups⁵.

As a part of general investigation of cobalt chelates, the interaction of di- and trivalent cobalt with EDTA, ethyleneglycol bis (β -aminoethylether) N-N' tetraacetic acid (EGTA), DTPA and TTHA was studied and reported in this work. The results could be useful in the evaluation of these compounds as decontaminating agents in case of radioactive cobalt contamination of the environment, as well as in relating metalchelate stability to ligand structure.

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EXPERIMENTAL

EDTA, EGTA, DTPA and TTHA were analytical grade reagents. Co (II) - chelates were prepared by mixing the metal chloride, in 0.05 N HCl, with the disodium salt of the chelating agents. All the pH adjustments were made by addition of either hydrochloric acid or carbonate-free sodium hydroxide. The concentration of the complex in the final solution was kept in the range of 8×10^{-3} M to 8×10^{-2} M, depending on the molar absorbance. The cobaltic chelates were prepared by mixing the cobaltous chloride solution with each of the chelating agents, at pH 9.5, then adding few drops of hydrogen peroxide⁵. The mixture was left at least three hours to ensure complete oxidation. Lower pH values were attained by using 1 N HCl solution.

The composition of the complexes formed was determined using the following spectrophotometric methods: mole ratio⁷, slope ratio⁸ and continuous variation⁹ methods. The absorption measurements were made with Prolabo model 5238-Spectrophotometer, using 1 cm quartz cells.

pH-measurements were done with Unicum model 292-pH meter.

Stability constants (pK') were determined using the calculated formation constants (pK) and literature values of dissociation constants of the chelating agents¹⁰.

RESULTS AND DISCUSSION

L. Chelation of Divalent Cobalt:

The absorption spectra of (Co (II)-ligand) solution mixtures were found to increase, at $\lambda = 510$ nm, as a function of pH, (Fig. 1). The increase of the absorption maxima with the gradual increase in pH has a stepwise character. Within certain pH ranges, the absorbances remained constant, indicating the formation of stable complexes in these ranges, (Table 1). At lower pH values the complexes dissociated. The exact pH values at which the complexes were formed varied in the order: EGTA, EDTA > DITPA, TTHA, This is due to the strong acidic nature of the solutions of DTPA and TTHA than the corresponding EGTA and EDTA^{11,12}.

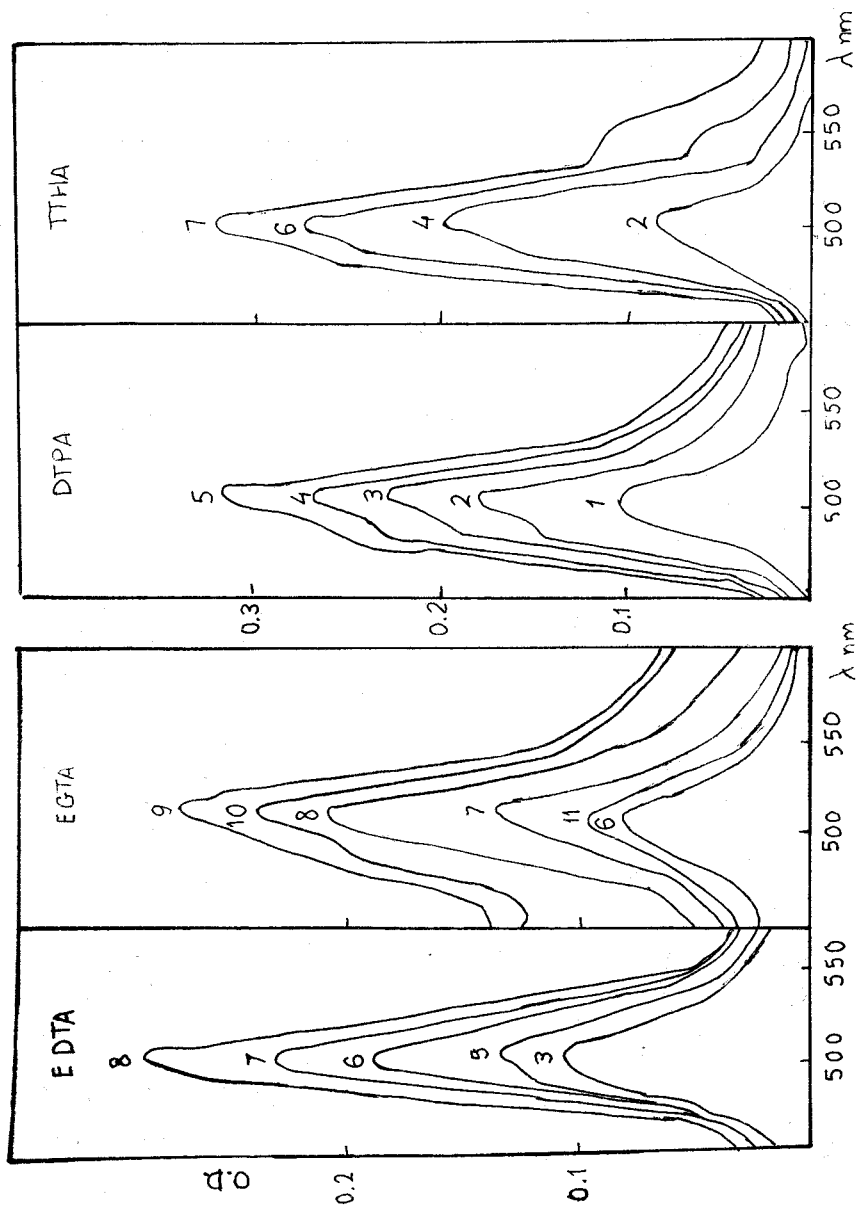


Fig. 1 Variation of the absorption spectra of a mixture of 2×10^{-2} M Co (II) and 1.6×10^{-1} M M chelating agent as a function of pH; 1) pH = 0.3, 2) pH 0.5, 3) pH 0.7, 4) pH 10., 5) pH 1.3, 6) pH 2.2, 7) pH 2.7, 8) pH 3.5, 9) pH 4.00, 10) pH 9.5 and 11) pH 1.05.

Table 1.

Characteristics of di- and trivalent cobalt-polyamino-polycarboxylic

Chelating agent	Ion	pH interval of complex	Co: chel.	(nm)	ϵ	pK	pK
EDTA	Co (II)	3.5- 5.5	2:1	505	12.5	8.2	8.22
		3.5- 9.5	1:1	505	14.5	2.7	13.72
	Co (III)	0.7-10.5	1:1	512.5	255.0	3.1	13.32
EGTA	Co (II)	4.0- 5.5	2:1	512	12.5	8.5	9.78
		4.0- 8.0	1:1	512	13.5	3.4	14.88
	Co (III)	3.5-10.5	1:1	560	100.0	3.84	14.44
DTPA	Co (II)	1.3- 5.5	2:1	508	13	8.4	15.15
		1.3- 9.5	1:1	508	15.5	3.1	20.41
	Co (III)	0.9-10.5	1:1	562.6	255.0	2.9	20.61
TTHA	Co (II)	2.7- 5.5	2:1	500	12.5	8.1	14.66
		2.7- 9.5	1:1	500	15.5	3.0	19.67
	Co (III)	1.5-10.5	1:1	532.5	255.0	2.9	19.77

To determine the composition of the complexes formed, the mole ratio method was applied. The concentration of Co (II) was kept constant at 2×10^{-2} M and the $[\text{Co (II)}]/[\text{ligand}]$ ratio was varied between 4/1 and 1/4. Optical measurements were made at the suitable pH and the proper wavelength, (Table 1). Figure 2A shows that breaks occur at $[\text{Co (II)}]/[\text{ligand}]$ ratios = 2/1 and 1/1 at pH 4, while only one break occurs at pH 7.5, at a ratio of 1/1. If the concentration of the chelating agent was kept constant and that of Co (II) was varied, the same results were obtained, suggesting the formation of two chelates at pH 4 with mole ratios of 2/1 and 1/1 of Co (II) to the ligand respectively, while at pH 7.5 the mole ratio was 1/1.

Using the slope ratio method, the concentration of one component was kept constant at 2×10^{-1} M, while that of the other was varied in the range 4×10^{-3} to 4×10^{-2} M. The maximum absorbances were plotted against the concentration of the variable component, (Fig. 2B). The ratios of the slopes of the curves 2 to 1 were found to be equal to 0.5 and 1.0, indicating the presence of two complexes of mole ratios $[\text{Co (II)}]/[\text{ligand}] = 2/1$ and 1/1.

In the continuous variation method, the concentration of the metal ion and the ligand were varied such that the total concentration of the mixture remained constant at 4×10^{-2} M. The optical measurements were

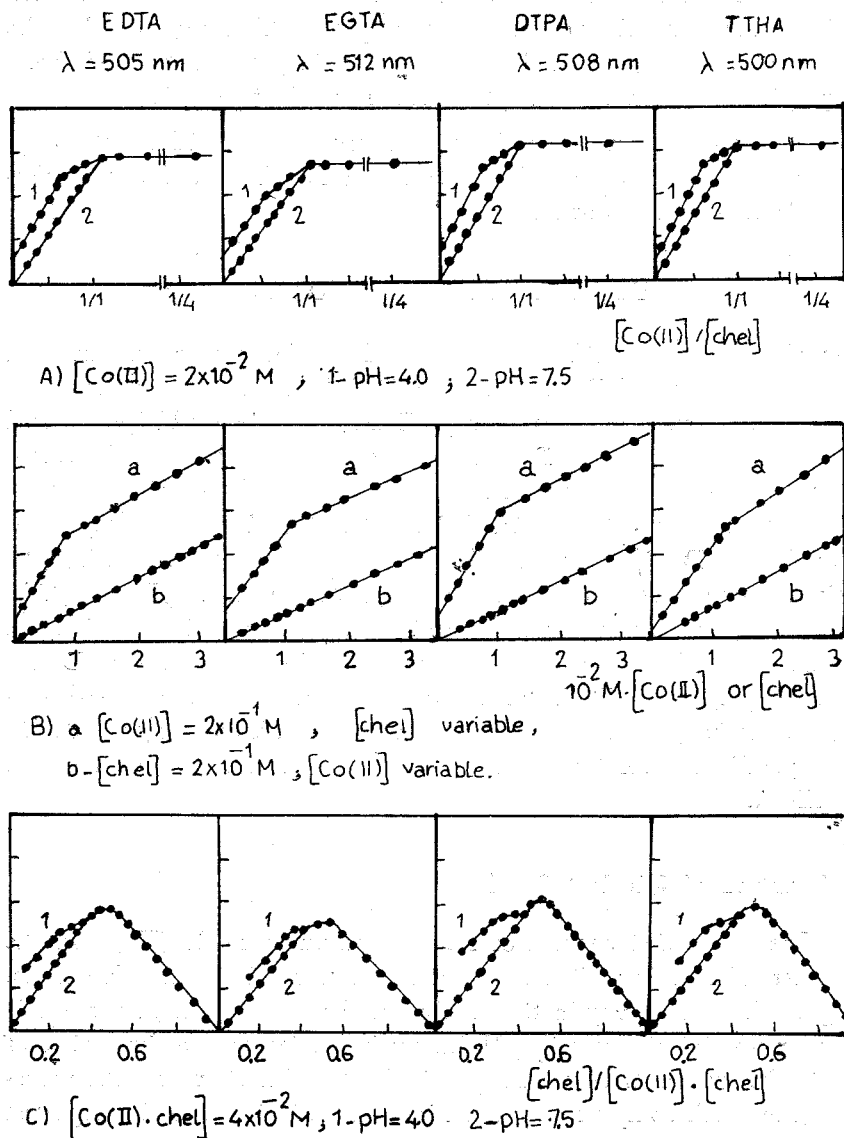


Fig. 2 Composition of Co (II) - polyaminopolycarboxylic acids chelates by: A) mole ratio method; B) slope ratio method at pH 4.0 and C) continuous variation method.

carried out at the characteristic wavelength of each complex. It could be seen that the maximum optical densities occur at metal-mole fraction of 0.33 and 0.5 at pH 4 and of 0.5 only at pH 7.5. This indicates that the composition of the formed chelates between Co (II) and the used chelating agents is 2/1 and 1/1 at pH 4 and only 1/1 at pH 7.5.

The formation and the stability constants calculated for each complex were reported in table 1. It can be shown that the stability of the chelates decreases in the order:

DTPA, TTHA, EGTA, EDTA

Regarding this order, DTPA is a potential octadentate ligand compared to the hexadentate EDTA, hence the DTPA-metal chelates should be more stable than the corresponding EDTA ones¹³. It would be expected that further extension of DTPA structure to the analogous substituted tetraamine, TTHA, produces more stable chelates. However, the stability constants of Co (II)-TTHA chelates were found to be slightly lower than those of DTPA. This may be attributed to the anion TTHA (A^{-6}), which has one more negative charge than the corresponding DTPA (A^{-5}). This excess negative charge may result in an electrostatic repulsion and accordingly in lowering the stability of TTHA-complexes than DTPA ones. EGTA, like EDTA, has six donor atoms. However, EGTA molecule contains an etheric oxygen atom, which acts as a basic center in the ligand¹⁴, thus renders the complex of EGTA more stable than that of EDTA.

II. Chelation of Trivalent Cobalt:

The absorption spectra of solution mixtures of Co (III) and the considered chelating agents were measured at different pH values, (Fig. 3). The constancy in the maximum absorption at a characteristic wavelength, within certain pH intervals, indicates the formation of stable chelates in these pH ranges, (Table 1). The characteristic wavelength for each complex and its extinction coefficient are also reported in table 1.

In order to determine the composition of the formed Co (III)-chelates, the mole ratio and the continuous variation methods, mentioned before,

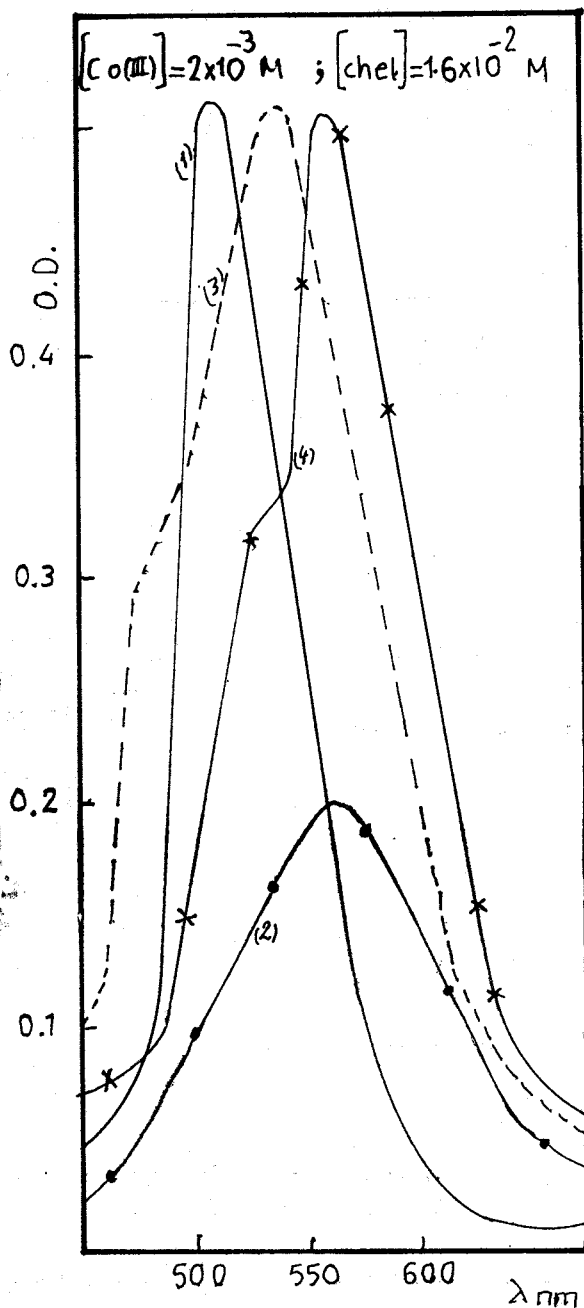


Fig. 3 Absorption spectra at pH 4.0, of: 1) Co (III) - EDTA; 2) Co (III) + EGTA; 3) Co (III) + DTPA and 4) Co (III) + TTHA mixtures.

were applied. Typical observations are shown in Figures 4A and 4B, which indicate the formation of 1/1 complex in each case.

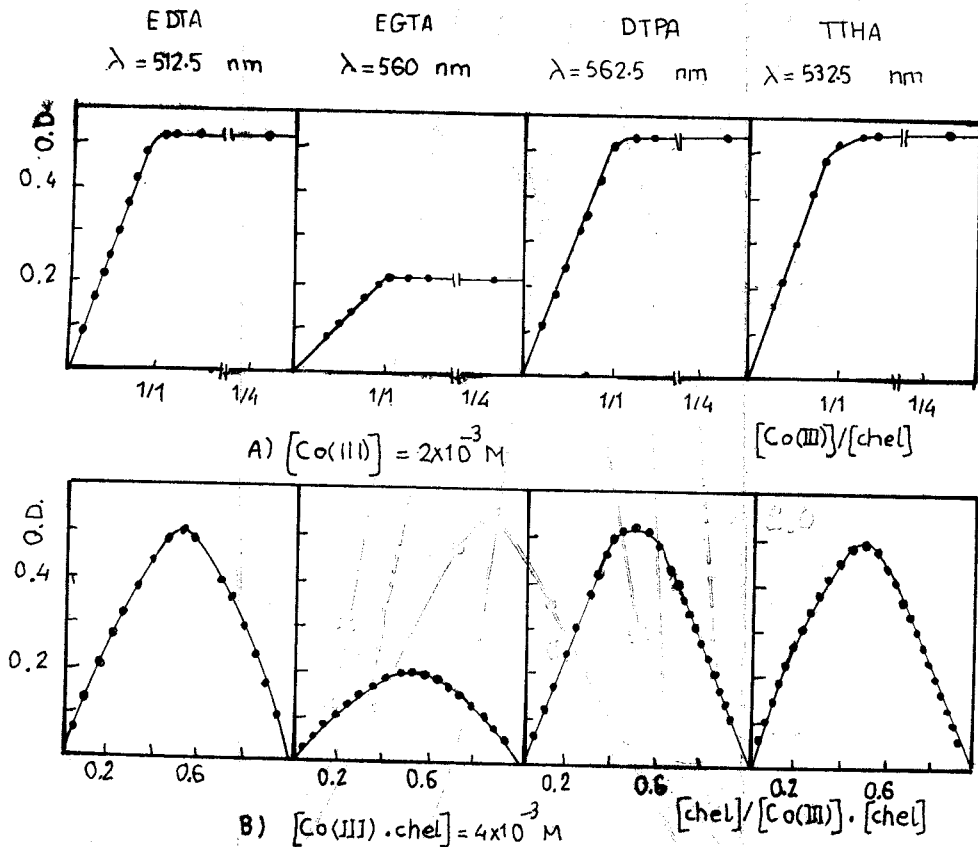


Fig. 4 Composition of Co(III) - polyaminopolycarboxylic acids chelates by: A) mole ratio method and B) continuous variation method.

The stability constants of the resulted chelates were determined and given in table 1. The values of these constant decrease also in the order:

DTPA, TTHA, EGTA, EDTA

This sequence may be ascribed, too, to the difference in the basicity of the ligands and the number of the donor atoms in the polyami nopoly-carboxylic acids.

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