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### A Study of the Interaction of Cr(III) and Co(III) Complex Ions with Nucleosides and Their Bases in Aqueous Solution

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## SHORT COMMUNICATION

# A Study of the Interaction of Cr(III) and Co(III) Complex Ions with Nucleosides and Their Bases in Aqueous Solution

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The interaction of the complex ions  $\text{Cr}(\text{OH}_2)_6^{3+}$ ,  $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$ ,  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ , *trans*- $\text{Co}(\text{en})_2(\text{Cl})_2^+$  and *cis*- $\text{Co}(\text{tren})(\text{OH}_2)_2^{3+}$  with the ligands adenine, cytosine, adenosine, cytidine and 2-deoxyadenosine, were studied spectrophotometrically at 60°. The influences of variations in [metal ion], [ligand] and [H<sup>+</sup>] on the interaction processes were studied. The observed spectral changes for some interactions are considered as evidence for the formation of complexes between the metal ions and the nucleoside ligands, and possible reaction products are suggested.

## INTRODUCTION

The interaction of metal complex ions with nucleosides and their bases has received considerable attention over the past few years.<sup>3-14</sup> Such interactions vary for different metal ions and depend on the potential binding sites of the nucleosides. Only a few of the mentioned studies<sup>4,6,11,14</sup> involved Cr(III) and Co(III) ions.

In a recent study<sup>14</sup> in this laboratory, significant uv-visible spectral changes were observed during the reaction of  $\text{Cr}(\text{OH}_2)_6^{3+}$  with adenine at pH ~ 4.5, and the spectral data were employed to make a kinetic study of the interaction process. Direct evidence for the reaction of the deprotonated form of adenine with  $\text{Cr}(\text{OH}_2)_5(\text{OH})_2^{2+}$  and  $\text{Cr}(\text{OH}_2)_4(\text{OH})_2^+$ , was reported.

In the present study, we have extended the range of metal complex ions to include  $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$ ,  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ , *trans*- $\text{Co}(\text{en})_2(\text{Cl})_2^+$  (*en* ≡ ethylenediamine), and *cis*- $\text{Co}(\text{tren})(\text{OH}_2)_2^{3+}$  (*tren* ≡ β, β', β''-triaminotriethylamine). Their interaction with the ligands adenine, cytosine, adenosine, cytidine and 2-deoxyadenosine, was investigated.

## EXPERIMENTAL

**Materials:** The following complexes were prepared according to the procedures reported in the literature:  $[\text{Cr}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$ ,<sup>15,16</sup>

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$[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$ ,<sup>17</sup> *trans*- $[\text{Co}(\text{en})_2(\text{Cl})_2]\text{Cl}$ ,<sup>18</sup>  $[\text{Co}(\text{tren})(\text{OH}_2)_2](\text{ClO}_4)_3$ .<sup>19</sup> Chemical analyses were in agreement with the theoretical values and the uv-visible absorption spectra corresponded with those reported in the literature.<sup>16,19,20,21</sup> Analytically pure samples of the nucleosides (Fisher certified reagents) were used in this study. Deionized distilled water was used in preparing all solutions. Absorption spectra in the uv-visible region were recorded on a Cary 118 spectrophotometer and pH measurements were made with a Radiometer pH meter.

## RESULTS AND DISCUSSION

The interaction of  $\text{Cr}(\text{OH}_2)_6^{3+}$  with cytosine, adenosine and cytidine under conditions similar to those used to study the interaction with adenine,<sup>14</sup> showed very small spectral changes. The observed changes during prolonged heating at 60° are in fact very similar to those obtained when the pH of a solution of  $\text{Cr}(\text{OH}_2)_6^{3+}$  is raised such that partial formation of  $\text{Cr}(\text{OH}_2)_5\text{OH}_2^{2+}$  occurs.<sup>14</sup> In addition, the spectral changes are more significant in nitrate than in perchlorate media. We conclude that the observed changes are due to slow background effects and that no complexation between  $\text{Cr}(\text{OH}_2)_6^{3+}$  or  $\text{Cr}(\text{OH}_2)_5\text{OH}_2^{2+}$  and the above mentioned ligands takes place.

On the contrary, the interaction of  $\text{Cr}(\text{OH}_2)_6^{3+}$  with 2-deoxyadenosine does provide evidence for the formation of a complex. A typical example of the observed changes in spectra is given in Fig. 1.

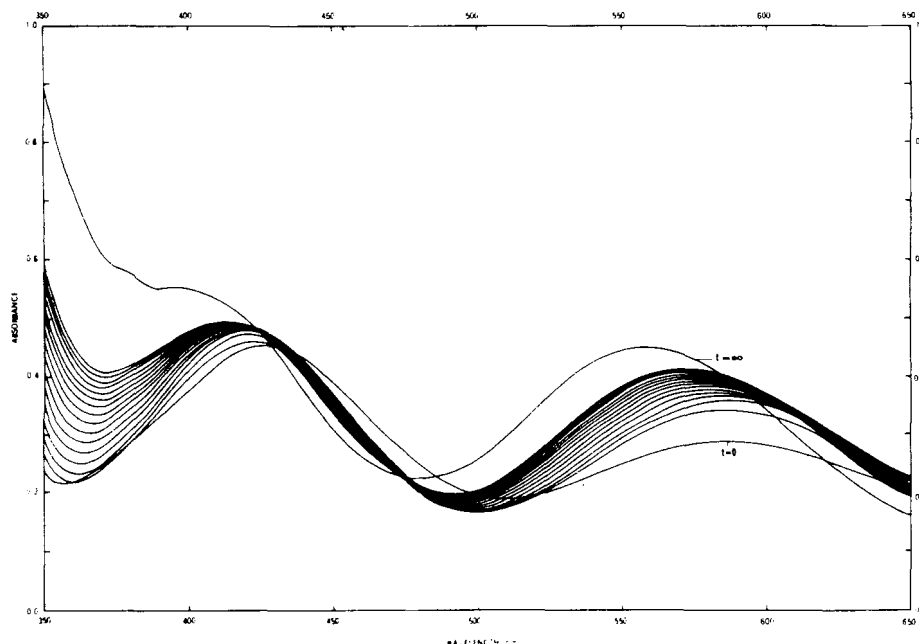


FIGURE 1 Successive scans of the spectrum of a mixture of  $\text{Cr}(\text{OH}_2)_6^{3+}$  and 2-deoxyadenosine:  $[\text{Cr}(\text{III})] = 2 \times 10^{-3} \text{ M}$ ,  $[\text{2-deoxyadenosine}] = 4 \times 10^{-2} \text{ M}$ ,  $\text{pH} = 4.5$ ,  $\text{Temp.} = 50^\circ$ , Ionic strength =  $0.5 \text{ M}$  ( $\text{KNO}_3$ ), optical path length =  $5 \text{ cm}$ , time interval =  $60 \text{ min}$ .

Increases in absorbance at ca.  $570$  and  $380 \text{ nm}$ , along with the occurrence of three isosbestic points, are observed. The spectrum at  $t = \infty$ , furthermore, shows the characteristic shoulder at  $380 \text{ nm}$ , which was also found for the  $\text{Cr}(\text{OH}_2)_6^{3+}$ -adenine interaction.<sup>14</sup> Some first-order rate constants were calculated in the usual way, and were found to be almost the same whether estimated from the change in absorbance at  $380$  or  $570 \text{ nm}$ . On going from a  $1:10$  to  $1:20$ ,  $[\text{Cr}(\text{OH}_2)_6^{3+}]:[\text{2-deoxyadenosine}]$ ,  $k_{\text{obs}}$  remains constant at  $(1.5 \pm 0.1) \times 10^{-5} \text{ sec}^{-1}$  (ionic strength =  $0.5 \text{ M}$ , temp. =  $50^\circ$ ), which is similar to the behavior of adenine under such conditions.<sup>14</sup> It is of considerable interest that an interaction between  $\text{Cr}(\text{OH}_2)_6^{3+}$  and 2-deoxyadenosine is observed, whereas no such interaction is found for adenosine. Possible explanations for this anomaly are entirely speculative for the present, and must await a more thorough and detailed study of the system.

The interaction of  $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$  with the above ligands was investigated to determine the influence of the presence of ammine ligands during such reactions. During the reaction with adenine an interesting sequence of events could be observed in the spectral changes of which an example is given in

Figure 2. Two distinct processes occur: during the first a decrease in absorbance at  $490 \text{ nm}$  is accompanied by an increase at ca.  $600 \text{ nm}$  and a shift in peak maximum from  $\sim 360$  to  $\sim 400 \text{ nm}$ ; during the second, further decreases at  $490 \text{ nm}$  and increases at ca.  $600 \text{ nm}$  are accompanied by a marked increase in absorbance at  $\lambda < 400 \text{ nm}$ , during which a new shoulder develops at  $380 \text{ nm}$ . Good isosbestic points are observed for the second process. The intermediate spectrum obtained at the end of the first process is in very good agreement with that previously reported for  $\text{Cr}(\text{OH}_2)_6^{3+}$  under such conditions<sup>14</sup> (also see Figure 1). Furthermore, the spectral changes during the second process and the first-order rate constants estimated from these changes are, within experimental error, identical to those found earlier for the reaction between  $\text{Cr}(\text{OH}_2)_6^{3+}$  and adenine.<sup>14</sup> We conclude that the first process involves loss of  $\text{NH}_3$  under these conditions<sup>22</sup> to form  $\text{Cr}(\text{OH}_2)_6^{3+}$ , which then reacts with adenine in the way outlined before.<sup>14</sup> Experiments in the absence of added adenine confirmed the first part of the process.<sup>22</sup> Consequently, reactions of  $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$  with adenosine, cytosine and cytidine, show spectral changes that confirm the formation of  $\text{Cr}(\text{OH}_2)_6^{3+}$ ,

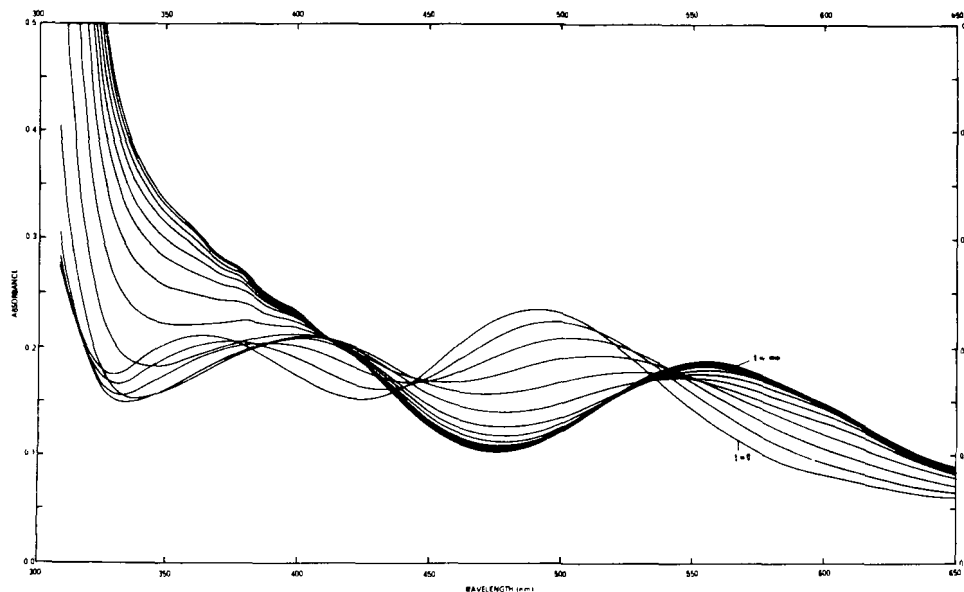


FIGURE 2 Successive scans of the spectrum of a mixture of  $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{3+}$  and adenine:  $[\text{Cr}(\text{III})] = 1 \times 10^{-3} \text{ M}$ ,  $[\text{adenine}] = 1 \times 10^{-2} \text{ M}$ ,  $\text{pH} = 4.0$ ,  $\text{Temp.} = 60^\circ$ , Ionic strength =  $0.5 \text{ M}$  ( $\text{KNO}_3$ ), optical path length =  $5 \text{ cm}$ , time interval =  $90 \text{ min}$ .

but with no significant secondary spectral changes, as expected from the findings reported above for the reactivity of  $\text{Cr}(\text{OH}_2)_6^{3+}$ .

We now turn to a discussion of the results obtained for the interaction between some  $\text{Co}(\text{III})$  complexes and the mentioned ligands. Heating a 1:10 mixture of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  and adenine at  $\text{pH} = 4.0$  and  $60^\circ$  over a period of two days, resulted in some significant spectral changes. The characteristic absorption peak of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  at  $490 \text{ nm}$  slowly decreased in intensity, whereas the peak at  $340 \text{ nm}$  increased significantly over this period of time, during which an isosbestic point was observed at  $430 \text{ nm}$ . The change in spectrum continued until the visible absorption peak had almost disappeared and the solution became nearly colorless. Analyses<sup>2,3</sup> confirmed the presence of  $\text{Co}^{2+}$  and explain the observed decoloration of the reaction solution. Some kinetic measurements were performed at  $330 \text{ nm}$  where a significant absorbance increase occurs. The reaction is indeed very slow ( $k = 3 \times 10^{-6} \text{ sec}^{-1}$  at the above-mentioned conditions) and does not occur in the presence of  $0.5 \text{ M}$   $\text{NaClO}_4$ . The exact nature of the redox reaction is unknown since the reaction rate seems to be independent of the  $[\text{adenine}]$  above the ten-fold excess used above. Very similar results were obtained for the reactions of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  with adenosine and cytidine, and

in all cases evidence for the formation of  $\text{Co}^{2+}$  was found.

In an earlier study<sup>4</sup> it was reported that *trans*- $\text{Co}(\text{en})_2(\text{Cl})_2^+$  reacts with adenine and produces *cis*- $\text{Co}(\text{en})_2(\text{Cl})(\text{adenine})^+$ , of which the x-ray structure was reported.<sup>4,6</sup> Mixtures of *trans*- $\text{Co}(\text{en})_2(\text{Cl})_2^+$  and adenine (1:2) at  $\text{pH} = 4, 8$  and  $11$ , showed some significant spectral changes when heated at  $60^\circ$ . Similar results were obtained for the reactions with adenosine and cytidine, and the final spectrum, obtained after heating for 24 hours, clearly showed the presence of  $\text{Co}(\text{III})$  nucleoside complexes, as reported for adenine.<sup>4</sup> The interpretation of the spectral changes are, however, complicated by the occurrence of three different processes, viz. loss of chloride from the coordination sphere (aquation), isomerization and complexation with the nucleoside. For this reason another  $\text{Co}(\text{III})$  system,  $\text{Co}(\text{tren})(\text{OH}_2)_2^{3+}$ , was chosen since this species is known to exist only in the *cis*-configuration.<sup>1,9</sup> Heating of  $\text{Co}(\text{tren})(\text{OH}_2)_2^{3+}$ /adenine (1:10) mixtures at  $\text{pH} \sim 4.5$  and  $60^\circ$  resulted in the spectral changes shown in Figure 3. An isosbestic point is observed at ca.  $530 \text{ nm}$ , and the reaction product is presumably  $\text{Co}(\text{tren})(\text{adenine})(\text{OH}_2)^{3+}$ . Good first-order kinetic plots are obtained from the absorbance increase at  $340 \text{ nm}$  ( $k = 1 \times 10^{-4} \text{ sec}^{-1}$  at  $60^\circ$ ). The rate data indicate that substitution is

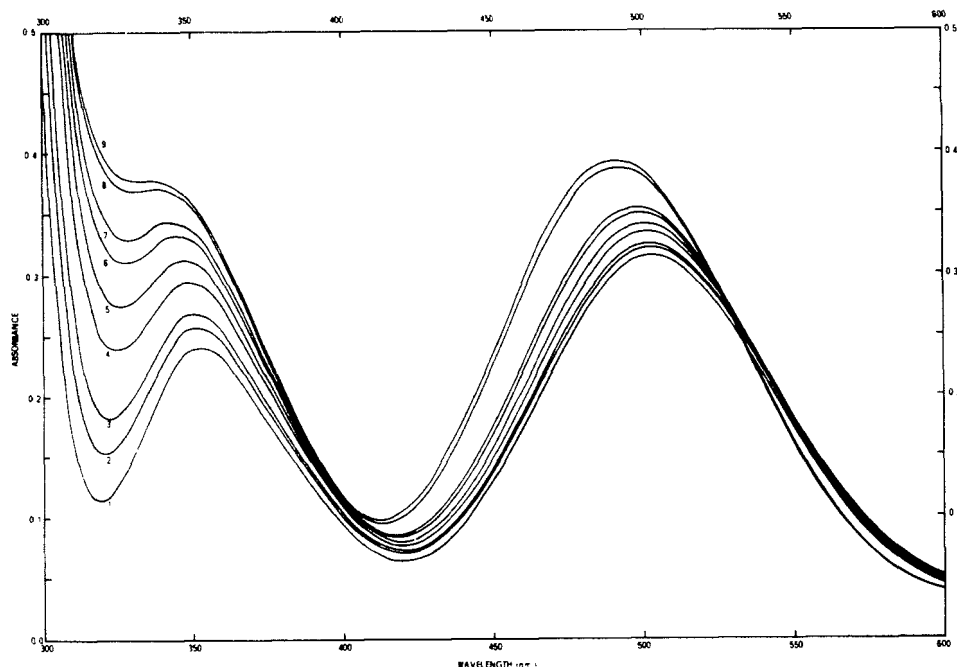


FIGURE 3 Successive scans of the spectrum of a mixture of  $\text{Co}(\text{tren})(\text{OH}_2)_2^{3+}$  and adenine:  $[\text{Co}(\text{III})] \sim 3 \times 10^{-3} \text{ M}$ ,  $[\text{adenine}] = 2 \times 10^{-2} \text{ M}$ ,  $\text{pH} = 4.5$ ,  $\text{Temp.} = 60^\circ$ , optical path length = 1 cm, spectra 1 to 9 recorded at 0, 15, 32, 89, 150, 250, 330, 1330 and 1740 min., respectively.

controlled by the loss of a water molecule, and this may be followed by a rapid ring-closing process as found in other  $\text{Co}(\text{III})$  systems<sup>2,4</sup> under such conditions. However, no evidence for this later process was observed in this study.

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