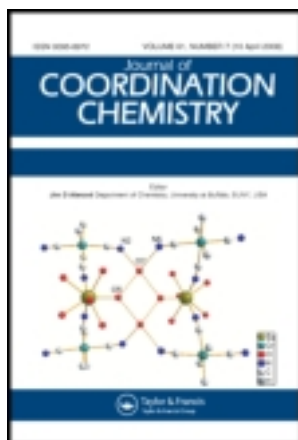


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### Kinetic studies of aquation for oxalate in $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$ and $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{H}_2\text{O})_2]^+$ induced by $\text{Fe}^{3+}$

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## Kinetic studies of aquation for oxalate in $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L}-\text{L})]^-$ and $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L}-\text{L})(\text{H}_2\text{O})_2]^+$ induced by $\text{Fe}^{3+}$

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Kinetics of oxalate substitution by water in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L}-\text{L})]^-$  and  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L}-\text{L})(\text{H}_2\text{O})_2]^+$  (where L–L denote AraNH<sub>2</sub> and BaraNH<sub>2</sub>, i.e., methyl 3-amino-2,3-dideoxy- $\alpha$ -D-arabino-hexopyranoside and methyl 3-amino-2,3-dideoxy- $\beta$ -D-arabino-hexopyranoside) induced by  $\text{Fe}^{3+}$  ions was studied. The reactions were investigated in aqueous solution from 288 to 308 K with initial concentrations of the substrates at  $2 \times 10^{-2} \text{ mol L}^{-1}$ , variable concentrations of  $\text{Fe}^{3+}$  in the range 0.02–0.08  $\text{mol L}^{-1}$ , and constant ionic strength ( $\text{H}^+$ ;  $\text{Na}^+$ ;  $\text{ClO}_4^- = 1.0$ );  $[\text{H}_3\text{O}^+] = 0.15 \text{ mol L}^{-1}$ . Investigations were carried out using the spectrophotometrical method from 350 to 700 nm. The results allowed determination of the number of steps of the reactions. Based on the kinetic equations  $(-\text{d}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L}-\text{L})]^-/\text{d}t = \{a + b[\text{Fe}(\text{H}_2\text{O})_6\}^{3+}][\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L}-\text{L})^-]$ ;  $-\text{d}[\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2(\text{L}-\text{L})]^+/\text{d}t = \{c + d[\text{Fe}(\text{H}_2\text{O})_6\}^{3+}][\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2(\text{L}-\text{L})]^+$ , rate constants were determined for each step; activation parameters were also determined. The mechanism of substitution of oxalate induced by  $\text{Fe}^{3+}$  ions in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L}-\text{L})]^-$  and  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L}-\text{L})(\text{H}_2\text{O})_2]^+$  is proposed.

**Keywords:** Chromium(III) complexes; 3-Aminodeoxysugar ligands; Kinetics and mechanism

### 1. Introduction

Metal ions play a vital role in different biological processes [1–3]. Interaction of these ions with biologically active ligands, for example in drugs, is a subject of considerable interest. Some of the biologically active compounds are chelating [4], but for most little is known about how metal binding influences their activity. The selection of chromium(III) as the center of coordination gives inert complexes which undergo relatively slow transformations at ambient temperature, enabling investigation on the kinetics and mechanism of the processes.

One class of bioactive compounds is amino sugars [5]. With features such as stereochemical modification involving both conformational and configurational transformations and the presence of electron-donating centers ( $-\text{NH}_2$  and  $-\text{OH}$ ), they can be used as ligands [6]. The presence of these functional groups in a sugar entity and their mode of interaction with metal ions open up the possibility to use them as simple amino

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sugar units in structural models [7]. In addition, these compounds play an important role in biological processes and can provide specific structural models of natural analogs. A further advantage is the possibility of utilizing UV-Vis spectroscopy to study their transformations. Taking the above-mentioned into account, we have been interested in studying the ability of biologically active ligands to complex metal ions. Substitutions of  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{histamine})]^-$  and  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{pyridoxamine})]^-$  in aqueous solutions have shown that these compounds provide convenient quasi-enzymatic biological models [8, 9]. Preparation of a specifically aligned system consisting of metal ion and a bioactive compound is likely to provide a model of an enzyme, helpful for the elucidation of an enzymatic reaction. Consequently, we show spectrophotometrically that the oxalate in  $\text{cis-}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  and  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{H}_2\text{O})_2]^+$  (where L-L denotes methyl 3-amino-2,3-dideoxy- $\alpha$ -D-*arabino*-hexopyranoside (AaraNH<sub>2</sub>) or methyl 3-amino-2,3-dideoxy- $\beta$ -D-*arabino*-hexopyranoside (BaraNH<sub>2</sub>) (figure 1)) can be substituted by water molecules via  $\text{Fe}_{(\text{aq})}^{3+}$  promoted aquation. These aquation of  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  and  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2(\text{L-L})]^+$  is faster.

## 2. Experimental

### 2.1. Reagents

Two anomers (figure 1) of methyl 3-amino-2,3-dideoxyhexopyranoside with  $\alpha$ -D-*arabino* (AaraNH<sub>2</sub>) and  $\beta$ -D-*arabino* configuration (BaraNH<sub>2</sub>) were synthesized according to the procedures described [10, 11], respectively;  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{OH}_2)_2]^+$  and  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  (where L-L denotes AaraNH<sub>2</sub> and BaraNH<sub>2</sub>) were obtained according to the literature procedures [12, 13]. The aquated  $[\text{Cr}(\text{L-L})(\text{H}_2\text{O})_4]^{3+}$  complex ions were synthesized according to a new procedure consisting of transformation of  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{OH}_2)_2]^+$  into  $[\text{Cr}(\text{L-L})(\text{H}_2\text{O})_4]^{3+}$  in 64% yield for  $[\text{Cr}(\text{AaraNH}_2)(\text{H}_2\text{O})_4]^{3+}$  and 43% yield for  $[\text{Cr}(\text{BaraNH}_2)(\text{H}_2\text{O})_4]^{3+}$ . The process was started by heating the solution containing  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{OH}_2)_2]^+$  ( $c = 10^{-2} \text{ mol L}^{-1}$ ),  $\text{Fe}^{3+}$  ions ( $c = 5 \times 10^{-2} \text{ mol L}^{-1}$ ) and  $\text{HNO}_3$  ( $0.4 \text{ mol L}^{-1}$ ) at 50°C for 2.5 h. The final aquated complex cations were separated using ion-exchange column chromatography. Dowex 50X2, 100–200 mesh ( $\text{H}^+$ ), and 2 M  $\text{HClO}_4$  as eluent were used. Next, the components of  $[\text{Cr}(\text{L-L})(\text{H}_2\text{O})_4]^{3+}$ , i.e.,  $\text{Cr}^{3+}$  and L-L ligands, were analyzed quantitatively. The complex ions were decomposed into their components in the presence of  $\text{Cr}_{(\text{aq})}^{2+}$  in an argon atmosphere [14]. Chromium(III) and two anomers of methyl 3-amino-2,3-dideoxyhexopyranoside with  $\alpha$ -D-*arabino* and  $\beta$ -D-*arabino* configurations were

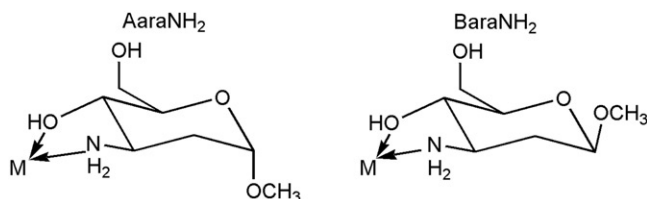


Figure 1. Bidendate ligands: AaraNH<sub>2</sub> and BaraNH<sub>2</sub>.

quantitatively characterized spectrophotometrically [15]. Consequently, molar ratios of  $\text{Cr}^{3+} : \text{L-L} = 1 : 1$  were obtained. Moreover, the positions of sugar moiety binding were studied by theoretical *ab initio* methods [16].

## 2.2. Kinetic measurements

Two steps of the  $\text{Fe}^{3+}$  promoted oxalate aquation of the  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  ions (equations 1 and 2) were studied separately. The progress of all stages of the reactions was observed spectrophotometrically. The first step of the reaction (equation 1) was monitored at 568 nm for  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{AaraNH}_2)]^-$  and at 605 nm for  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{BaraNH}_2)]^-$ , whereas the second step (equation 2) was monitored at 553 nm for  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{AaraNH}_2)(\text{OH}_2)_2]^+$  and 590 nm for  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{BaraNH}_2)(\text{OH}_2)_2]^+$ . This spectral range was not disturbed by very intense absorptions of  $\text{FeC}_2\text{O}_4^+(\text{aq})$ . The initial concentrations of the substrates were  $2 \times 10^{-2} \text{ mol L}^{-1}$ ; the concentration of  $\text{Fe}^{3+}$  ions were kept within the range 0.02–0.08  $\text{mol L}^{-1}$ ;  $[\text{H}_3\text{O}^+]$  was kept constant at 0.15  $\text{mol L}^{-1}$ . The ionic strength of solution was adjusted to 1.0 ( $\text{H}^+$ ;  $\text{Na}^+$ ;  $\text{ClO}_4^-$ ).

## 2.3. Instrumentation and simulations

Spectral measurements were carried out in the UV-Vis region using a Perkin Elmer Lambda 650 spectrophotometer equipped with Temperature Control – Peltier Systems. The systems feature high heating and cooling rates and excellent temperature accuracy, essential for measurements. The instrument had a scan accuracy of 1 nm with 1 nm slit width at a scanning rate of 120.00  $\text{nm min}^{-1}$ . The observable rate constants were computed using a “Glint” program based on global analysis [17–20].

## 3. Results and discussion

The spectra for the complex ions were recorded in the UV-Vis region. Figure 2-I presents the absorption spectra of  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{AaraNH}_2]^-$ ,  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{AaraNH}_2)(\text{H}_2\text{O})_2]^+$ , and  $[\text{Cr}(\text{AaraNH}_2)(\text{H}_2\text{O})_4]^{3+}$ , whereas figure 2-II shows the absorption spectra of  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{BaraNH}_2]^-$ ,  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{BaraNH}_2)(\text{H}_2\text{O})_2]^+$ , and  $[\text{Cr}(\text{BaraNH}_2)(\text{H}_2\text{O})_4]^{3+}$  in 0.1 M  $\text{NaClO}_4$  solutions.

Based on the spectra, wavelengths at which kinetic studies were performed for each complex ion were selected. Consequently, the first step of the aquation reaction of oxalate (substitution of oxalate by two water molecules) induced by  $\text{Fe}^{3+}$  in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  (where L-L denotes AaraNH<sub>2</sub> and BaraNH<sub>2</sub>) (equation 1) was monitored at 568 nm for  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{AaraNH}_2)]^-$  and at 605 nm for  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{BaraNH}_2)]^-$ , whereas the second step (equation 2) was monitored at 553 nm for  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{AaraNH}_2)(\text{OH}_2)_2]^+$  and at 590 nm for  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{BaraNH}_2)(\text{OH}_2)_2]^+$ .

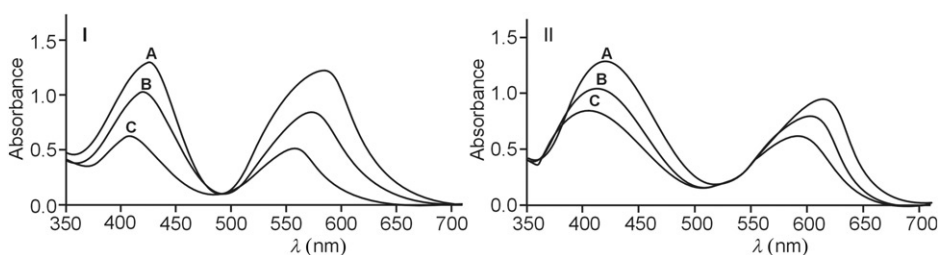
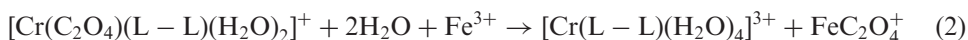


Figure 2. Electronic spectra: **I** (A)  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{AaraNH}_2]^-$ , (B)  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{AaraNH}_2)(\text{H}_2\text{O})_2]^+$ , and (C)  $[\text{Cr}(\text{AaraNH}_2)(\text{H}_2\text{O})_4]^{3+}$ ; **II** (A)  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{BaraNH}_2]^-$ , (B)  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{BaraNH}_2)(\text{H}_2\text{O})_2]^+$ , and (C)  $[\text{Cr}(\text{BaraNH}_2)(\text{H}_2\text{O})_4]^{3+}$ . Concentrations of the complexes are  $0.02 \text{ mol L}^{-1}$ .

Aquation of oxalate induced by  $\text{Fe}^{3+}$  in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  (where L-L denotes AaraNH<sub>2</sub> and BaraNH<sub>2</sub>) proceeds in aqueous solutions according to the following stoichiometric equations:



In this study, these transformations have been studied as separate reactions because of the significant difference in the rates of substitution of the first and the second oxalates. Substitution of the first oxalate by two waters (equation 1) occurs faster than substitution of the second oxalate by the next two water molecules (equation 2).

### 3.1. First aquation of oxalate by two waters $\{[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^- \rightarrow [\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{H}_2\text{O})_2]^+\}$

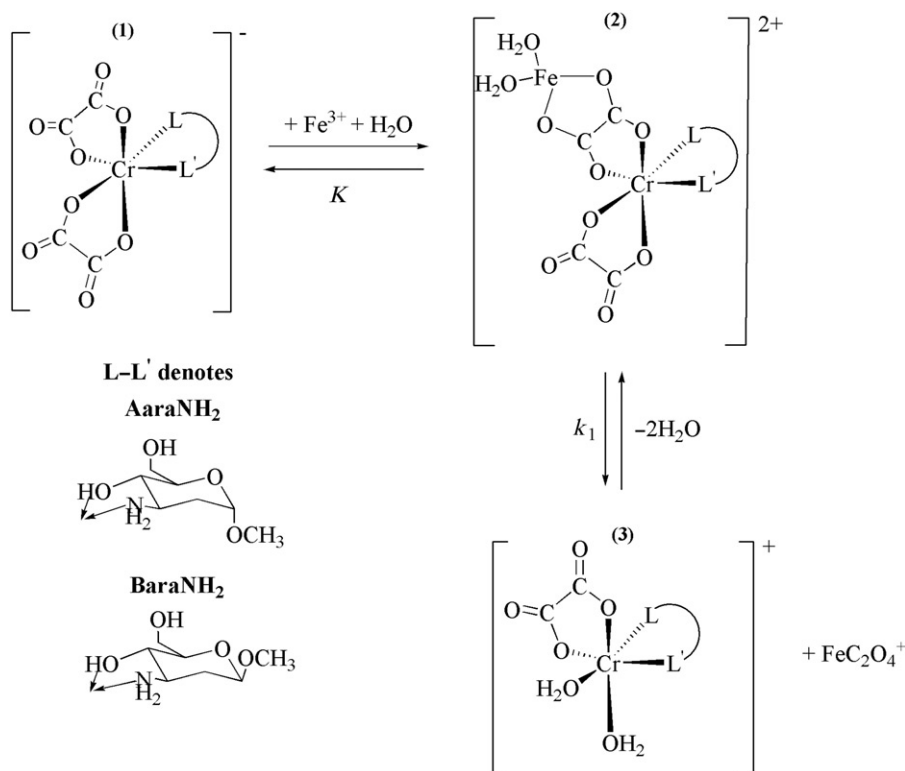
Aquation of one oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{AaraNH}_2]^-$  and  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{BaraNH}_2]^-$  occurs in one step, where the binuclear intermediate is formed and then slow decomposition of this binuclear complex with the transfer of oxalate from  $\text{Cr}^{3+}$  to  $\text{Fe}^{3+}$  occurs (scheme 1). In order to determine the rate constants based on  $\text{A} \rightarrow \text{B}$  reaction, two methods, i.e., the singular value decomposition (SVD) analysis and global analysis (GA) were used. Using the two methods gave the same results (within the range of standard deviations). The observed rate constants for the first reaction are compiled in tables 1 and 2.

Excellent fitting of experimental data gave the following reaction rate equation:

$$-d[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-/dt = k_{\text{obs}}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^- \quad (3)$$

In the next step, graphical relationships between the observable rate constants and concentrations of  $\text{Fe}^{3+}$  ( $0.01\text{--}0.08 \text{ mol L}^{-1}$ ) were created for both ligands. On the basis of the graphs obtained, pseudo-first-order rate constants depended linearly on the concentrations of  $\text{Fe}^{3+}$  in a range of temperatures studied (figure 3). Values of rate constants fulfill the terminal form of equation (4):

$$k_{1\text{obs}} = k + k_1K[\text{Fe}^{3+}] \quad (4)$$



Scheme 1. The proposed mechanism of Fe(III)-induced aquation of the first oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$ .

The pseudo-first-order rate  $k_{\text{obs}}$  is a sum of constant rates of aquation, spontaneous and catalyzed by  $\text{H}_{\text{aq}}^+$  (the concentration of  $[\text{H}^+]$ , is a constant value of  $0.15 \text{ mol L}^{-1}$ ). Factor  $k_1K$ , which cannot be separated into  $k_1$  and  $K$  because of the linear relationships presented in figure 2 for both complex ions, can be treated as apparent second-order rate constant  $k_1$   $[(\text{mol L}^{-1})^{-1} \cdot \text{s}^{-1}]$  of reaction induced by  $\text{Fe}^{3+}$ . The final forms of equations (3) and (4) have been created based on the proposed mechanism of the induced ( $\text{Fe}^{3+}$ ) substitution of one oxalate by two water molecules in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  (scheme 1). As a result of coordination of the chromium-bound oxalate by iron(III), a binuclear intermediate is created (represented in scheme 1 by (2)). The intermediate is at equilibrium with  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  (number (1) in scheme 1). In the next step, decomposition of the binuclear intermediate 2 accompanied by transfer of oxalate from chromium(III) to iron(III) takes place. The reaction proceeds in two steps during which two chromium(III)–oxygen bonds from oxalate break. On the basis of our results, these steps cannot be separated. Consequently, it is not possible to solve the step that is most important to the rate. However, for dihydroxobis(oxalato)platinum(IV) [21] and chromium(III) complexes with oxalate as ligand [22], it has been proved that chelate ring opening of chromium(III)–oxalate occurs faster than breaking of the second chromium(III)–oxalate bond.

The possibility of spectrophotometric detection of the binuclear intermediate was checked from the additivity of the spectra of solutions containing the substrates of reaction and their mixtures. No deviations from additivity were observed in the

Table 1. The observed rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) for  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{Ara}(\text{NH}_2)]^-$  for the first aquation;  $T = 288\text{--}308\text{ K}$ ;  $[\text{complex}] = 2 \times 10^{-2}\text{ mol L}^{-1}$ ;  $[\text{Fe}^{3+}] = 0.02\text{--}0.08\text{ mol L}^{-1}$ ;  $[\text{H}_3\text{O}^+] = 0.15\text{ mol L}^{-1}$ ; ionic strength 1.0.

$[\text{Fe}^{3+}]$ ( $\text{mol L}^{-1}$ )	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 288\text{ K}$	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 293\text{ K}$	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 298\text{ K}$	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 303\text{ K}$	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 308\text{ K}$
0.02	$1.01 \times 10^{-4} \pm 2 \times 10^{-6}$	$3.04 \times 10^{-4} \pm 5 \times 10^{-6}$	$6.04 \times 10^{-4} \pm 3 \times 10^{-6}$	$1.51 \times 10^{-3} \pm 4 \times 10^{-5}$	$3.23 \times 10^{-3} \pm 8 \times 10^{-5}$
0.03	$2.52 \times 10^{-4} \pm 4 \times 10^{-6}$	$6.12 \times 10^{-4} \pm 2 \times 10^{-6}$	$1.23 \times 10^{-3} \pm 4 \times 10^{-5}$	$2.53 \times 10^{-3} \pm 7 \times 10^{-5}$	$5.42 \times 10^{-3} \pm 3 \times 10^{-5}$
0.04	$3.81 \times 10^{-4} \pm 1 \times 10^{-6}$	$9.67 \times 10^{-4} \pm 8 \times 10^{-6}$	$1.87 \times 10^{-3} \pm 2 \times 10^{-5}$	$3.65 \times 10^{-3} \pm 8 \times 10^{-5}$	$7.74 \times 10^{-3} \pm 5 \times 10^{-5}$
0.05	$5.44 \times 10^{-4} \pm 7 \times 10^{-6}$	$1.33 \times 10^{-3} \pm 7 \times 10^{-5}$	$2.50 \times 10^{-3} \pm 7 \times 10^{-5}$	$4.82 \times 10^{-3} \pm 3 \times 10^{-5}$	$9.93 \times 10^{-3} \pm 4 \times 10^{-5}$
0.06	$7.17 \times 10^{-4} \pm 4 \times 10^{-6}$	$1.69 \times 10^{-3} \pm 3 \times 10^{-5}$	$3.19 \times 10^{-3} \pm 3 \times 10^{-5}$	$5.88 \times 10^{-3} \pm 8 \times 10^{-5}$	$1.21 \times 10^{-2} \pm 7 \times 10^{-4}$
0.07	$8.63 \times 10^{-4} \pm 2 \times 10^{-6}$	$1.95 \times 10^{-3} \pm 6 \times 10^{-5}$	$3.74 \times 10^{-3} \pm 7 \times 10^{-5}$	$6.82 \times 10^{-3} \pm 5 \times 10^{-5}$	$1.46 \times 10^{-2} \pm 5 \times 10^{-4}$
0.08	$1.11 \times 10^{-3} \pm 4 \times 10^{-5}$	$2.31 \times 10^{-3} \pm 4 \times 10^{-5}$	$4.30 \times 10^{-3} \pm 8 \times 10^{-5}$	$7.97 \times 10^{-3} \pm 2 \times 10^{-5}$	$1.72 \times 10^{-2} \pm 4 \times 10^{-4}$



Table 2. The observed rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) for  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{BaraNH}_2]^-$  for reaction (1);  $T = 288\text{--}308\text{ K}$ ;  $[\text{complex}] = 2 \times 10^{-2}\text{ mol L}^{-1}$ ;  $[\text{Fe}^{3+}] = 0.02\text{--}0.08\text{ mol L}^{-1}$ ;  $[\text{H}_3\text{O}^+] = 0.15\text{ mol L}^{-1}$ , ionic strength 1.0.

$[\text{Fe}^{3+}]$ ( $\text{mol L}^{-1}$ )	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 288\text{ K}$	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 293\text{ K}$	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 298\text{ K}$	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 303\text{ K}$	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 308\text{ K}$
0.02	$8.03 \times 10^{-5} \pm 5 \times 10^{-7}$	$1.92 \times 10^{-4} \pm 5 \times 10^{-6}$	$3.83 \times 10^{-4} \pm 3 \times 10^{-6}$	$7.03 \times 10^{-4} \pm 4 \times 10^{-6}$	$1.22 \times 10^{-3} \pm 5 \times 10^{-5}$
0.03	$8.32 \times 10^{-5} \pm 4 \times 10^{-7}$	$2.32 \times 10^{-4} \pm 2 \times 10^{-6}$	$4.42 \times 10^{-4} \pm 2 \times 10^{-6}$	$9.73 \times 10^{-4} \pm 7 \times 10^{-6}$	$2.05 \times 10^{-3} \pm 2 \times 10^{-5}$
0.04	$8.54 \times 10^{-5} \pm 8 \times 10^{-7}$	$2.79 \times 10^{-4} \pm 8 \times 10^{-6}$	$5.76 \times 10^{-4} \pm 1 \times 10^{-6}$	$1.33 \times 10^{-3} \pm 5 \times 10^{-5}$	$2.75 \times 10^{-3} \pm 4 \times 10^{-5}$
0.05	$8.74 \times 10^{-5} \pm 9 \times 10^{-7}$	$3.22 \times 10^{-4} \pm 6 \times 10^{-6}$	$6.65 \times 10^{-4} \pm 6 \times 10^{-6}$	$1.71 \times 10^{-3} \pm 7 \times 10^{-5}$	$3.63 \times 10^{-3} \pm 8 \times 10^{-5}$
0.06	$8.93 \times 10^{-5} \pm 4 \times 10^{-7}$	$3.79 \times 10^{-4} \pm 2 \times 10^{-6}$	$7.83 \times 10^{-4} \pm 4 \times 10^{-6}$	$1.98 \times 10^{-3} \pm 3 \times 10^{-5}$	$4.43 \times 10^{-3} \pm 2 \times 10^{-5}$
0.07	$9.34 \times 10^{-5} \pm 1 \times 10^{-7}$	$3.98 \times 10^{-4} \pm 6 \times 10^{-6}$	$8.78 \times 10^{-4} \pm 3 \times 10^{-6}$	$2.34 \times 10^{-3} \pm 2 \times 10^{-5}$	$5.12 \times 10^{-3} \pm 5 \times 10^{-5}$
0.08	$1.02 \times 10^{-4} \pm 7 \times 10^{-6}$	$4.05 \times 10^{-4} \pm 1 \times 10^{-6}$	$9.23 \times 10^{-4} \pm 3 \times 10^{-6}$	$2.62 \times 10^{-3} \pm 2 \times 10^{-5}$	$6.04 \times 10^{-3} \pm 8 \times 10^{-5}$

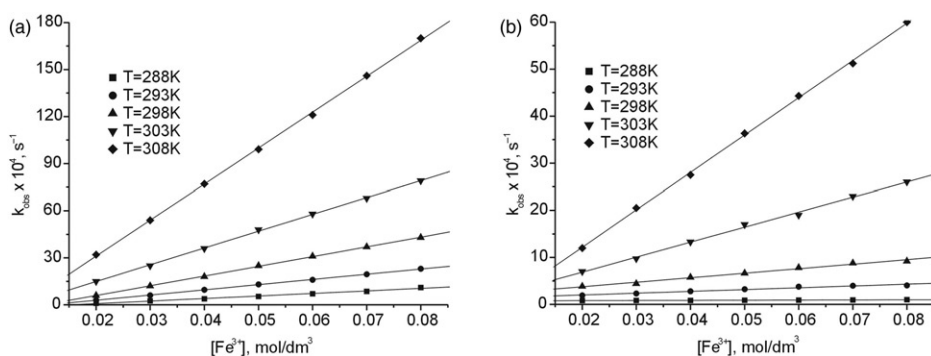


Figure 3. Dependence of pseudo-first-order rate constants for reaction (1) on  $\text{Fe}^{3+}$  concentrations at ionic strength ( $\text{H}^+$ ;  $\text{Na}^+$ ;  $\text{ClO}_4^-$ ) = 1.0;  $T = 288\text{--}308\text{ K}$ ;  $[\text{complex}] = 2 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[\text{Fe}^{3+}] = 0.02\text{--}0.08 \text{ mol L}^{-1}$ ;  $[\text{H}_3\text{O}^+] = 0.15 \text{ mol L}^{-1}$ . (A)  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{AaraNH}_2]^-$ ; (B)  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{BaraNH}_2]^-$ .

analyzed spectra, which can be treated as consistent with a low concentration of the intermediate in the reaction system, and a very low value of equilibrium constant of the reaction studied. The low value of equilibrium constant  $K$  (stability constant for the formation of the Fe–Cr binuclear complex) is consistent with the observed linear dependence of the rate constant  $k_{\text{obs}}$  on the concentration of  $\text{Fe}^{3+}$ . Furthermore, the constant value of absorbance in all isosbestic points is consistent with the practical absence of the intermediate in the system studied. The final product of the first aquation is  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{H}_2\text{O})_2]^+$ . The values of apparent second-order rate constants of this reaction for coordination compounds of the  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  type are presented in table 3.

### 3.2. The aquation of the second oxalate by two waters $\{[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{H}_2\text{O})_2]^+\}$

As mentioned before, the substitution reactions (1) and (2) were studied separately because of the significant difference in the rates of substitution of the first and second oxalates. Nevertheless, the second substitution proceeded according to the same mechanism as in the first step (scheme 2).

The values of  $k_{2\text{obs}}$  obtained using two methods (SVD and GA) are shown in tables 4 and 5. The experimental data obtained fully fitted to reaction rate in the following equation:

$$-\text{d}[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{H}_2\text{O})_2]^+/\text{d}t = k_{\text{obs}}\{[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{H}_2\text{O})_2]^+\} \quad (5)$$

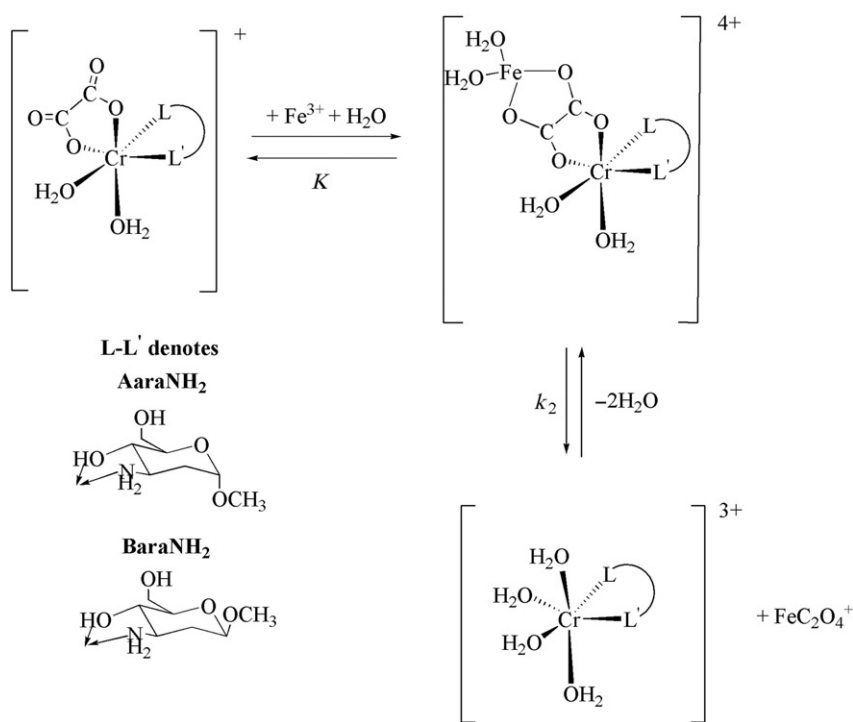
Linear relationships between the observable rate constants  $k_{2\text{obs}}$  and concentrations of  $\text{Fe}^{3+}$  (in the range 0.01–0.08 mol L<sup>-1</sup>) were observed for both AaraNH<sub>2</sub> and BaraNH<sub>2</sub> for the range of temperatures studied (figure 4). The results shown in figure 3 fully fit the following equation.

$$k_{2\text{obs}} = k + k_2K[\text{Fe}^{3+}] \quad (6)$$

As for aquation of oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$ ,  $k_2K$  cannot be separated into  $k_2$  and  $K$  for  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{AaraNH}_2)(\text{OH}_2)_2]^+$  and  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{BaraNH}_2)(\text{OH}_2)_2]^+$ . The apparent

Table 3. Rate constants and activation parameters for the first aquation of oxalates in chromium(III) complexes;  $T = 288\text{--}308\text{ K}$ ;  $[\text{complex}] = 2 \times 10^{-2}\text{ mol L}^{-1}$ ;  $[\text{Fe}^{3+}] = 0.02\text{--}0.08\text{ mol L}^{-1}$ ;  $[\text{H}_3\text{O}^+] = 0.15\text{ mol L}^{-1}$ ; ionic strength 1.0.

$T$ (K)	$k_1$ $[(\text{mol L}^{-1})^{-1} \cdot \text{s}^{-1}]$ for $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{AaraNH}_2]^-$	$k_1$ $[(\text{mol L}^{-1})^{-1} \cdot \text{s}^{-1}]$ for $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{BaraNH}_2]^-$
288	$1.62 \times 10^{-2} \pm 4 \times 10^{-4}$	$1.01 \times 10^{-2} \pm 6 \times 10^{-4}$
293	$3.33 \times 10^{-2} \pm 3 \times 10^{-4}$	$3.12 \times 10^{-2} \pm 2 \times 10^{-4}$
298	$6.21 \times 10^{-2} \pm 2 \times 10^{-4}$	$5.61 \times 10^{-2} \pm 4 \times 10^{-4}$
303	$1.07 \times 10^{-1} \pm 2 \times 10^{-3}$	$7.43 \times 10^{-2} \pm 5 \times 10^{-4}$
308	$2.29 \times 10^{-1} \pm 2 \times 10^{-3}$	$8.89 \times 10^{-2} \pm 5 \times 10^{-4}$
$\Delta H^\ddagger$ (KJ mol $^{-1}$ )	$53 \pm 1$	$62 \pm 1$
$\Delta S^\ddagger$ (JK $^{-1}$ mol $^{-1}$ )	$-36 \pm 1$	$-29.5 \pm 0.5$



Scheme 2. The proposed mechanism of Fe(III)-induced aquation of oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{OH}_2)_2]^+$ .

second-order rate constants of the induced ( $\text{Fe}^{3+}$ ) aquation of  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{OH}_2)_2]^+$  are shown in table 6.

### 3.3. The aquation of two oxalates by four waters $\{[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^- \rightarrow [\text{Cr}(\text{L-L})(\text{H}_2\text{O})_4]^{3+}\}$

Based on the results obtained for both steps of aquation (tables 3 and 6), the rate constants  $k_1$   $[(\text{mol L}^{-1})^{-1} \cdot \text{s}^{-1}]$  of aquation in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  are much larger than for their cationic analogs  $-\text{[Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{OH}_2)_2]^+$ . In aqueous solution, substitution of the first oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{AaraNH}_2]^-$  is about eight times faster than substitution

Table 4. The observable rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) for reaction (2) with  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{Ara}\text{NH}_2)(\text{OH}_2)_2]^+$ ;  $T = 288\text{--}308\text{ K}$ ;  $[\text{complex}] = 2 \times 10^{-2}\text{ mol L}^{-1}$ ;  $[\text{Fe}^{3+}] = 0.02\text{--}0.08\text{ mol L}^{-1}$ ;  $[\text{H}_3\text{O}^+] = 0.15\text{ mol L}^{-1}$ ; ionic strength 1.0.

$[\text{Fe}^{3+}]$ ( $\text{mol L}^{-1}$ )	$k_{2,\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 288\text{ K}$	$k_{2,\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 293\text{ K}$	$k_{2,\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 298\text{ K}$	$k_{2,\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 303\text{ K}$	$k_{2,\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 308\text{ K}$
0.02	$1.11 \times 10^{-5} \pm 6 \times 10^{-7}$	$3.01 \times 10^{-5} \pm 4 \times 10^{-7}$	$6.02 \times 10^{-5} \pm 5 \times 10^{-7}$	$1.54 \times 10^{-4} \pm 4 \times 10^{-6}$	$3.25 \times 10^{-4} \pm 2 \times 10^{-6}$
0.03	$2.51 \times 10^{-5} \pm 8 \times 10^{-7}$	$8.03 \times 10^{-5} \pm 3 \times 10^{-7}$	$2.02 \times 10^{-4} \pm 6 \times 10^{-6}$	$5.24 \times 10^{-4} \pm 6 \times 10^{-6}$	$9.95 \times 10^{-4} \pm 3 \times 10^{-6}$
0.04	$3.82 \times 10^{-5} \pm 4 \times 10^{-7}$	$1.67 \times 10^{-4} \pm 7 \times 10^{-6}$	$3.73 \times 10^{-4} \pm 4 \times 10^{-6}$	$8.46 \times 10^{-4} \pm 3 \times 10^{-6}$	$1.62 \times 10^{-3} \pm 6 \times 10^{-5}$
0.05	$5.43 \times 10^{-5} \pm 5 \times 10^{-7}$	$2.23 \times 10^{-4} \pm 6 \times 10^{-6}$	$5.37 \times 10^{-4} \pm 6 \times 10^{-6}$	$1.24 \times 10^{-3} \pm 5 \times 10^{-5}$	$2.33 \times 10^{-3} \pm 6 \times 10^{-5}$
0.06	$7.11 \times 10^{-5} \pm 8 \times 10^{-7}$	$3.04 \times 10^{-4} \pm 5 \times 10^{-6}$	$6.65 \times 10^{-4} \pm 7 \times 10^{-6}$	$1.59 \times 10^{-3} \pm 8 \times 10^{-5}$	$2.99 \times 10^{-3} \pm 5 \times 10^{-5}$
0.07	$8.60 \times 10^{-5} \pm 3 \times 10^{-7}$	$3.74 \times 10^{-4} \pm 5 \times 10^{-6}$	$8.03 \times 10^{-4} \pm 2 \times 10^{-6}$	$1.94 \times 10^{-3} \pm 4 \times 10^{-5}$	$3.59 \times 10^{-3} \pm 1 \times 10^{-5}$
0.08	$1.10 \times 10^{-4} \pm 4 \times 10^{-6}$	$4.31 \times 10^{-4} \pm 1 \times 10^{-6}$	$9.30 \times 10^{-4} \pm 1 \times 10^{-6}$	$2.29 \times 10^{-3} \pm 6 \times 10^{-5}$	$4.28 \times 10^{-3} \pm 4 \times 10^{-5}$

Table 5. The observable rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) for reaction (2) with  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{BaraNH}_2)(\text{OH}_2)_2]^+$ ;  $T = 288\text{--}308\text{ K}$ ;  $[\text{complex}] = 2 \times 10^{-2}\text{ mol L}^{-1}$ ;  $[\text{Fe}^{3+}] = 0.02\text{--}0.08\text{ mol L}^{-1}$ ;  $[\text{H}_3\text{O}^+] = 0.15\text{ mol L}^{-1}$ ; ionic strength 1.0.

$[\text{Fe}^{3+}]$ ( $\text{mol L}^{-1}$ )	$k_{2,\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 288\text{ K}$	$k_{2,\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 293\text{ K}$	$k_{2,\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 298\text{ K}$	$k_{2,\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 303\text{ K}$	$k_{2,\text{obs}}$ ( $\text{s}^{-1}$ ) $T = 308\text{ K}$
0.02	$3.03 \times 10^{-6} \pm 5 \times 10^{-8}$	$7.76 \times 10^{-6} \pm 5 \times 10^{-8}$	$2.22 \times 10^{-5} \pm 7 \times 10^{-7}$	$4.02 \times 10^{-5} \pm 6 \times 10^{-7}$	$7.22 \times 10^{-5} \pm 6 \times 10^{-7}$
0.03	$4.13 \times 10^{-6} \pm 4 \times 10^{-8}$	$1.21 \times 10^{-5} \pm 7 \times 10^{-7}$	$3.36 \times 10^{-5} \pm 5 \times 10^{-7}$	$6.23 \times 10^{-5} \pm 3 \times 10^{-7}$	$1.15 \times 10^{-4} \pm 8 \times 10^{-6}$
0.04	$5.32 \times 10^{-6} \pm 7 \times 10^{-8}$	$1.76 \times 10^{-5} \pm 6 \times 10^{-7}$	$4.37 \times 10^{-5} \pm 8 \times 10^{-7}$	$8.35 \times 10^{-5} \pm 2 \times 10^{-7}$	$1.59 \times 10^{-4} \pm 5 \times 10^{-6}$
0.05	$6.65 \times 10^{-6} \pm 3 \times 10^{-8}$	$1.99 \times 10^{-5} \pm 4 \times 10^{-7}$	$5.22 \times 10^{-5} \pm 5 \times 10^{-7}$	$9.89 \times 10^{-5} \pm 2 \times 10^{-7}$	$2.05 \times 10^{-4} \pm 3 \times 10^{-6}$
0.06	$7.97 \times 10^{-6} \pm 8 \times 10^{-8}$	$2.39 \times 10^{-5} \pm 1 \times 10^{-7}$	$6.35 \times 10^{-5} \pm 2 \times 10^{-7}$	$1.22 \times 10^{-4} \pm 7 \times 10^{-6}$	$2.48 \times 10^{-4} \pm 9 \times 10^{-6}$
0.07	$9.54 \times 10^{-6} \pm 3 \times 10^{-8}$	$2.89 \times 10^{-5} \pm 5 \times 10^{-7}$	$7.32 \times 10^{-5} \pm 2 \times 10^{-7}$	$1.43 \times 10^{-4} \pm 5 \times 10^{-6}$	$2.98 \times 10^{-4} \pm 3 \times 10^{-6}$
0.08	$1.32 \times 10^{-5} \pm 5 \times 10^{-7}$	$3.45 \times 10^{-5} \pm 7 \times 10^{-7}$	$8.2 \times 10^{-5} \pm 6 \times 10^{-7}$	$1.62 \times 10^{-4} \pm 7 \times 10^{-6}$	$3.45 \times 10^{-4} \pm 8 \times 10^{-6}$

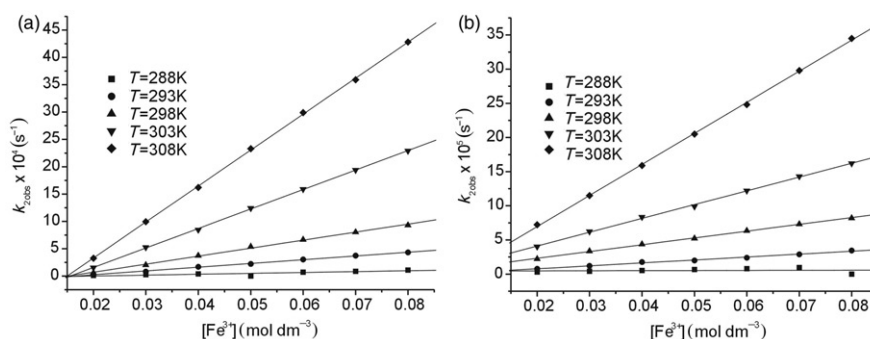


Figure 4. The dependence of pseudo-first-order rate constants for reaction (1) on  $\text{Fe}^{3+}$  concentration at ionic strength ( $\text{H}^+$ ;  $\text{Na}^+$ ;  $\text{ClO}_4^-$ ) = 1.0;  $T = 288\text{--}308\text{ K}$ ;  $[\text{complex}] = 2 \times 10^{-2}\text{ mol L}^{-1}$ ;  $[\text{Fe}^{3+}] = 0.02\text{--}0.08\text{ mol L}^{-1}$ ;  $[\text{H}_3\text{O}^+] = 0.15\text{ mol L}^{-1}$ . (a)  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{AaraNH}_2)(\text{OH}_2)_2]^+$ ; (b)  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{BaraNH}_2)(\text{OH}_2)_2]^+$ .

Table 6. Rate constants and activation parameters for the second aquation of oxalates in chromium(III) complexes;  $T = 288\text{--}308\text{ K}$ ;  $[\text{complexes}] = 2 \times 10^{-2}\text{ mol L}^{-1}$ ;  $[\text{Fe}^{3+}] = 0.02\text{--}0.08\text{ mol L}^{-1}$ ;  $[\text{H}_3\text{O}^+] = 0.15\text{ mol L}^{-1}$ ; ionic strength 1.0.

$T$ (K)	$k_2$ $[(\text{mol L}^{-1})^{-1} \cdot \text{s}^{-1}]$ for $[\text{Cr}(\text{C}_2\text{O}_4)(\text{AaraNH}_2)(\text{OH}_2)_2]^+$	$k_2$ $[(\text{mol L}^{-1})^{-1} \cdot \text{s}^{-1}]$ for $[\text{Cr}(\text{C}_2\text{O}_4)(\text{BaraNH}_2)(\text{OH}_2)_2]^+$
288	$2.45 \times 10^{-3} \pm 4 \times 10^{-5}$	$8.89 \times 10^{-4} \pm 7 \times 10^{-6}$
293	$4.76 \times 10^{-3} \pm 6 \times 10^{-5}$	$2.89 \times 10^{-3} \pm 9 \times 10^{-5}$
298	$9.64 \times 10^{-3} \pm 8 \times 10^{-5}$	$7.74 \times 10^{-3} \pm 5 \times 10^{-5}$
303	$4.64 \times 10^{-2} \pm 8 \times 10^{-4}$	$9.89 \times 10^{-3} \pm 8 \times 10^{-5}$
308	$8.53 \times 10^{-2} \pm 2 \times 10^{-4}$	$5.22 \times 10^{-2} \pm 4 \times 10^{-4}$
$\Delta H^\ddagger$ (K J mol $^{-1}$ )	$72.3 \pm 0.8$	$79.5 \pm 0.9$
$\Delta S^\ddagger$ (J K $^{-1}$ mol $^{-1}$ )	$-49 \pm 1$	$-42 \pm 1$

of the oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{AaraNH}_2)(\text{OH}_2)_2]^+$ ; substitution of oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)_2\text{BaraNH}_2]^-$  is about 11 times faster than in  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{BaraNH}_2)(\text{OH}_2)_2]^+$ . This can be explained in terms of the electrostatic factor, attraction of the charged substrates in reaction (1) and repulsion of substrates in reaction (2). The value of the rate constant for these total reactions is lower than those determined for AaraNH<sub>2</sub> and BaraNH<sub>2</sub> in this study. Comparing these data, the reaction rate depends on the kind of ligand substituted, increasing in the following series:  $\text{H}_2\text{O} < \text{BaraNH}_2 < \text{AaraNH}_2$ , i.e., in accord with the ligand field strength. Different behaviors of coordination ions substituted by two sugar ligands on aquation can be explained based on the crystal structure of both 3-aminosugars [10, 11]. The dissimilarities in the sugar ligands, especially location of the 1-methoxy substituent, seem to be of major importance. In the  $\alpha$ -anomer (faster kinetic path), the methoxy group at C1 is bonded in the axial position in contrast to equatorial in anomer  $\beta$  (slower kinetic path). Steric hindrance is caused by the position of substituents and strengthened by the coplanar arrangement of N–C3–C2–C1–O2–C7 in the  $\beta$ -anomer (figure 1). This influences the neighboring ligand exchange mechanism during the second step of substitution of oxalate by water (table 6). A characteristic feature of reactions catalyzed by  $\text{Fe}^{3+}$  is that they have low apparent activation enthalpies (hence the resulting small changes in the reaction rate with

temperature) and negative values of apparent activation entropy. Similar values of apparent activation entropies for the compounds indicate that the structure of the bridge linking  $\text{Cr}^{3+}$  with  $\text{Fe}^{3+}$  may depend on the structure of initial complex ion.

Competitive pathways for the aquation of (ethylenediamine)bis(oxalate) chromate(III) in acidic media were studied [22]. The  $[\text{Cr}(\text{ox})_2(\text{enH})(\text{H}_2\text{O})]$  complex ion is the major intermediate at pH 1 and aquates to  $\text{cis-}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$  with first-order rate constant of  $1.9 \times 10^{-5} \text{ s}^{-1}$  at 298 K. Two other intermediates,  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{H}_2\text{O})_2]^+$  and  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{enH})(\text{H}_2\text{O})_3]^{2+}$ , result from oxalate aquation at lower pH and lead to  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]^{4+}$ . Observed rate constants for the process are described by  $k_{\text{obsd}} = k_a + k_b[\text{H}^+] + k_c[\text{H}^+]^2$  where  $k_a = 1.7 \times 10^{-5} \text{ s}^{-1}$ ;  $k_b = 7.69 \times 10^{-5} [(\text{mol L}^{-1})^{-1} \text{ s}^{-1}]$ ;  $k_c = 6.15 \times 10^{-5} [(\text{mol L}^{-1})^{-2} \text{ s}^{-1}]$  at 298 K. Activation parameters for all reactions were determined. The activation enthalpies for  $k_a$ ,  $k_b$ , and  $k_c$  calculated from data at 298, 308, and 318 K are  $20.6 \pm 0.6$ ,  $17.6 \pm 0.2$ , and  $16.6 \pm 0.6 \text{ kcal mol}^{-1}$ , while the activation entropies are  $-11 \pm 2$ ,  $-18.3 \pm 0.5$ , and  $-22 \pm 2 \text{ cal mol}^{-1} \cdot \text{deg}^{-1}$ , respectively. Aquation reaction of oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  and  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{H}_2\text{O})_2]^+$  induced by  $\text{Fe}^{3+}$  occurs faster than the aquation of oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]$  and  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)(\text{H}_2\text{O})]$ . Furthermore, for the aquation of oxalate in coordination complexes, low apparent activation enthalpies and negative values of apparent activation entropies are characteristic.

#### 4. Conclusions

In this study, results of the investigations of the  $\text{Fe}^{3+}$ -induced aquation reaction of oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  and  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{OH}_2)_2]^+$ , where L-L denotes methyl 3-amino-2,3-dideoxy- $\alpha$ -D-arabino-hexopyranoside (AaraNH<sub>2</sub>) or methyl 3-amino-2,3-dideoxy- $\beta$ -D-arabino-hexopyranoside (BaraNH<sub>2</sub>), are described. Two steps of  $\text{Fe}^{3+}$  promoted substitution of oxalate by water have been studied separately. It can be concluded that the reaction rate for  $\text{Fe}^{3+}$  promoted aquation of oxalate in  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{L-L})]^-$  is approximately one order of magnitude higher than those observed for its cationic analogs,  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{L-L})(\text{OH}_2)_2]^+$  is dependent on the kind of ligand used (AaraNH<sub>2</sub> or BaraNH<sub>2</sub>). Activation parameters for both aquation reactions were determined and mechanisms for both aquation reactions have been proposed.

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