APPENDIX I

TREATMENT OF DATA

The rate of a reaction is assumed to be given by the rate of passage through a transition state, and a system in the transition state is an activated complex. Under most conditions the activated complex is in equilibrium with the reactants. The transition state theory gives the rate constant \( k \) for a simple biomolecular reaction expressed in the form of \( (T-1) \),

\[
  k = \frac{P \cdot kT \cdot K^*}{h} \quad \ldots \quad (T-1)
\]

where \( k \) and \( h \) are Boltzmann's and Planck's constants respectively and \( K^* \) has the dimensions of an equilibrium constant (\( K^* \) is related to the true equilibrium constant for the activated complex \( K = [AB^*]/[A][B] \) by a factor of \( (2\pi m^* kT)^{1/2} (\delta/h) \) where \( m^* \) is the effective mass of the activated complex and defines the transition state configuration). The transmission coefficient, \( P \), is the probability of the activated complex proceeding to products and its value is taken to be unity. The parameters
free energy of activation $\Delta G^*$, activation enthalpy $\Delta H^*$ and activation entropy $\Delta S^*$ are defined as in (T-2).

$$K^* = e^{-\Delta G^*/RT} = e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R} \ldots (T-2)$$

and hence (T-3) may be derived

$$\frac{kT}{h} e^{-\Delta H^*/RT} e^{\Delta S^*/R} \ldots (T-3)$$

Rate constants, k, and activation parameters together with their errors were generally evaluated using least-squares computer programs. Similarly whenever equilibrium constants were measured by spectrophotometric methods, statistical treatments using computer programs were made.

The data for all the systems were computed using computer programs based on the Los Alamos Scientific Laboratory report. They have been adapted for use in IBM 370 computer at the Iowa State University, Ames, Iowa by Dr. J.H. Espenson and his group workers \(^{184,185}\).
APPENDIX II

II- A. DERIVATION OF THE RATE LAW FOR THE CHELATION REACTIONS OF \text{bin-}OXALATO COMPLEXES INVESTIGATED

Most of the reactions investigated in this study conformed to the kinetic scheme A given in (T-1).

\[
\begin{align*}
\text{AH}^+ & \xrightarrow{k_o} B + H^+ \\
& \xrightarrow{k_q} C + H^+ \\
A + H^+ & \xrightarrow{k_p} B \\
& \xrightarrow{k_c} C \\
\end{align*}
\]

Since the equilibrium \( \text{AH} \xleftrightarrow{K_A} A + H^+ \) is rapid and occurs prior to the rate determining steps \( k_o, k_p, k_q \) and \( k_c \), at any time the unreacted \([A]_T\) may be written as in (T-2).
\[ [A]_T = [A] + [AH^+] \quad \ldots \quad (T-2) \]

Since \( K_A \) is given by \((T-3)\),

\[ K_A = \frac{[A][H^+]}{[AH^+]} \quad \ldots \quad (T-3) \]

\([AH^+]\) and \([A]\) may be written as \((T-4)\) and \((T-5)\) respectively.

\[ [AH^+] = \frac{[H^+]}{[H^+] + K_A}[A]_T \quad \ldots \quad (T-4) \]

\[ [A] = \frac{K_A}{[H^+] + K_A}[A]_T \quad \ldots \quad (T-5) \]

Since \( k_o, k_p, k_q \) and \( k_r \) correspond to first order decomposition of \( A \) or \( AH^+ \) and equilibration of \( AH^+ \) with \( A \) is rapid, \( k_{obs} \) is given by \((7-6)\).

\[ k_{obs} = k_o[AH^+] + k_q[AH^+] + k_p[A] + k_r[A] \]

\[ \ldots \quad (T-6) \]
Substituting (T-4) and (T-5) in (T-6), rate law (T-7) is obtained.

\[ k_{\text{obs}} = \frac{k_o[H^+] + k_q[H^+] + k_pK_a + k_rK_a}{[H^+] + K_a} \]  \hspace{1cm} (T-7)

Since the reaction schemes investigated in this study denote \( k_o \) and \( k_p \) paths to be corresponding to \( X^- \) substitution and \( k_q \) and \( k_r \) to \( \text{NH}_3 \) substitution, (T-7) may be written as in (T-8).

\[ k_{\text{obs}} = k_{X^-} + k_{\text{NH}_3} = \frac{k_o[H^+] + k_pK_a}{[H^+] + K_a} + \frac{k_q[H^+] + k_rK_a}{[H^+] + K_a} \]  \hspace{1cm} (T-8)

The ratio of \( k_{X^-} / k_{\text{NH}_3} \), 'R' is given by the ratios of \( X^- \) and \( \text{NH}_3 \) substituted products at any time 't' as in (T-9).

\[ \frac{k_{X^-}}{k_{\text{NH}_3}} = R = \frac{[\text{Cr(\text{NH}_3})_3\text{C}_2\text{O}_4]}{[\text{Cr}(X)(\text{NH}_3)_3\text{C}_2\text{O}_4]} \]  \hspace{1cm} (T-9)

Therefore it may be shown that \( k_{\text{obs}} \) shows functional dependencies on \( R \) and \( H^+ \) as in (T-10) and (T-11).
\[ \frac{k_{\text{obs}}}{(R + 1)} = \frac{k_q [H^+] + k_r K_a}{[H^+] + K_a} \quad (T-10) \]

and

\[ \frac{(k_{\text{obs}})^R}{(R + 1)} = \frac{k_o [H^+] + k_p K_a}{[H^+] + K_a} \quad (T-11) \]

(T-10) and (T-11) may be rearranged as in (T-12) and (T-13).

\[ \frac{k_{\text{obs}}}{(R + 1)} ([H^+] + K_a) = k_q [H^+] + k_r K_a \quad (T-12) \]

\[ \frac{(k_{\text{obs}})^R}{(R + 1)} ([H^+] + K_a) = k_o [H^+] + k_p K_a \quad (T-13) \]

which predict linear dependences of \([H^+] + K_a \cdot k_{\text{obs}}(R+1)^{-1}\) and \([H^+] + K_a \cdot k_{\text{obs}} R (R + 1)^{-1}\) with \([H^+]\) as seen in the results reported in Chapter 4.
II-B COMPUTATIONAL METHODS USED FOR THE ANALYSIS OF EXPERIMENTAL DATA

The constants data, \( k_{\text{obs}} \), were fitted to (T-10) and (T-11) using an IBM 370 Computer and Standard non-linear least squares program in conjunction with suitable sub-routines which were originally written by Newton and Moore and implemented by Espenson and coworkers \(^{184,185}\). The subroutines used fitted the dependent variable in this case \( k_{\text{obs}}(R+1)^{-1} \) or \( k_{\text{obs}}R(R+1)^{-1} \) to the independent variable \([H^+]\) using the polynomial given in (7-14).

\[
Y = \frac{\sum_{j=1}^{n} P_j [X_1]^{P_j+1}}{\sum_{k=1}^{n} P_k [X_1]^{P_k+1}} \quad \cdots \quad (T-14)
\]

Equating \( S = 1 \) and \( 2 \) and denoting \( P_j, P_{j+1} \) etc. as \( P_1, P_2 \) etc. (T-15) may be obtained.

\[
Y = \frac{P_1[X_1]^{P_2} + P_3[X_1]^{P_4}}{P_5[X_1]^{P_6} + P_7[X_1]^{P_8}} \quad \cdots \quad (T-15)
\]
when \( Y = (k_{obs}) (R + 1)^{-1} \), \( X_l = [H^+] \) and \( P_1, P_2, P_3, P_4, P_5, P_6, P_7 \) and \( P_8 \) in (T-15) may be equated to \( k_q, 1, k_{r_a}, 0, 1, 1, K_a \) and 0 respectively. (T-16) is obtained using guestimates for \( k_q, k_{r_a} \) and \( K_a \) an iterative procedure. The values of \( k_q, k_{r_a} \) and \( K_a \) were obtained along with their standard deviations. Similarly when \( Y \) was \( k_{obs} R (R + 1)^{-1} \), the values of \( k_o \) and \( k_{p_a} \) may be obtained. In order that consistent results may be obtained, \( K_a \) values were held fixed after ensuring that the rate data fitted to the rate law used satisfactorily when \( K_a \) was a floated parameter.

Then the values of \( k_p \) and \( k_r \) were obtained after dividing \( k_{r_a} \) and \( k_{p_a} \) by \( K_a \) and the activation parameters corresponding to \( k_o, k_p, k_q \) and \( k_r \) paths were obtained using a standard non-linear least squares program.