Stability Constants of Some Chromium(II) Complexes

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Equilibria between the binuclear complex $Cr_2(O_2CMe)_4$ and various chelating ligands have been studied spectrophotometrically in acetate buffer media. Combining the results with previous data on the stability of $Cr_2(O_2CMe)_4$, we obtain formation constants for mononuclear chromium(II) complexes with the following ligands: malonate, $\log \beta_2 = 6.0 \pm 0.2$; *N*-methyliminodiacetate, $\log \beta_2 = 12.3 \pm 0.5$; ethylenediamine-*N*,*N*′-diacetate, $\log K_1 = 9.1 \pm 0.2$; at $T = 25$ °C, $I = 1.0$ M (1 M = 1 mol dm^{-3}) ($NaClO_4$).

In a previous paper[1] we showed that the binuclear chromium(II) complex present in aqueous acetate buffer media has the composition $Cr_2(O_2CMe)_4$, the same as in the solid state, and from a combination of solubility and spectrophotometric measurements, we obtained equilibrium constants for the reactions

$$Cr_2(O_2CMe)_4 \overset{K_{DO}}{\rightleftharpoons} 2\,Cr(O_2CMe)_2, \quad (1)$$

$$Cr_2(O_2CMe)_2 \overset{\beta_{A2}^{-1}}{\rightleftharpoons} Cr^{2+} + 2\,MeCO_2^-. \quad (2)$$

The binuclear complex is red-brown in colour, with $\lambda_{max} = 490$ nm, while mononuclear chromium(II) complexes are generally sky-blue, with λ_{max} in the range 600 to 700 nm. The contrast in colours makes it possible to study competitive monomer-dimer equilibria spectrophotometrically, and we have now used this method to obtain stability constants of the mononuclear chromium(II) complexes of malonate, *N*-methyliminodiacetate, and ethylenediamine-*N*,*N*′-diacetate ions.

Experimental

Preparations. Chromium(II) chloride stock solutions were prepared by zinc-reduction of chromium(III), and stored under nitrogen, as described previously.[1] The solutions contained Zn^{2+} ion equal to half the chromium(II) concentration, but this had little effect on the results, as shown by experiments in which an equal additional concentration of Zn^{2+} ion was added (see, Fig. 4).†† Organic acids were Reagent grade, recrystallized twice from water, and standardized by titration with sodium hydroxide. Sodium acetate and sodium perchlorate solutions were prepared by mixing the AnalaR acids with AnalaR sodium hydroxide solution, from freshly opened ampoules.

Measurements. A Beckman DB spectrophotometer was used, with modified temperature-control system.[1] The titration procedure was as previously described.[1]

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†† The effect of zinc is expected to be a reduction in the concentration of free ligand by complex formation, thus decreasing the dissociation of the chromium(II) dimer. Since Cr^{2+} and Zn^{2+} stability constants are generally comparable, the greatest perturbation by Zn^{2+} is expected in the system for which dissociation of dimer to monomer is found to be greatest, *i.e.* the malonate system. If the zinc ions are completely complexed as ZnL_2^{2-}, the depletion of free malonate ion is about 10%, giving a reduction of about 0.1 in $\log f$ (see Eq. 15). This is within the experimental error. For the other ligands the effect is expected to be smaller.

Theory

Defining $[Cr_1]$ and $[Cr_2]$ as total concentrations of mononuclear and binuclear species, we may summarise the dimer-monomer equilibria in the solution in the equation

$$Cr_2 \overset{K_D}{\rightleftharpoons} 2\,Cr_1, \quad (3)$$

where K_D is the dimer dissociation constant averaged over all complexes, defined by

$$K_D = [Cr_1]^2/[Cr_2]. \quad (4)$$

In the absence of any ligands other than acetate ion, only one dimer species is important, hence we may write $[Cr_2] = [Cr_2(O_2CMe)_4]$ and $[Cr_1] = [Cr]_T - 2[Cr_2]$, where $[Cr]_T$ denotes the total chromium(II) concentration, giving

$$K_D = ([Cr]_T - 2[Cr_2(O_2CMe)_4])^2/[Cr_2(O_2CMe)_4]. \quad (5)$$

The concentration of $Cr_2(O_2CMe)_4$ may be calculated from the absorbance at 490 nm, using the known extinction coefficient,[1] and assuming that absorption by monomers is negligible. A plot of $[Cr_2(O_2CMe)_4]$ against $([Cr]_T - 2[Cr_2(O_2CMe)_4])^2$ is then expected to be a straight line of slope K_D^{-1}. When an additional ligand L is present which forms mononuclear complexes CrL_n, we have the additional reactions

$$(1/2)[Cr_2(O_2CMe)_4] + nL \overset{\beta_n'}{\rightleftharpoons} CrL_n + 2\,MeCO_2^-, \quad (6)$$

where $n = 1, 2, \ldots N$, $\beta_n' = (K_{DO})^{1/2}\beta_{A2}^{-1}\beta_n$, and β_n is the overall formation constant:

$$Cr^{2+} + nL \overset{\beta_n}{\rightleftharpoons} CrL_n. \quad (7)$$

(In Eqs. 6 and 7 some ionic charges are omitted). A calculation of the average dimer dissociation constant by the same method as before then yields the value K_D', where

$$K_D' = ([Cr^{2+}] + [CrO_2CMe^+] + [Cr(O_2CMe)_2] + \sum_1^N [CrL_n])^2/[Cr_2(OOCMe)_4]$$
$$= (\beta_{A2}^{-1}[MeCO_2^-]^{-2} + K_{A2}^{-1}[MeCO_2^-]^{-1} + 1 + \sum_1^N \beta_n[L]^n/\beta_{A2}[MeCO_2^-]^2)^2 K_{DO}, \quad (8)$$

where K_{A2} is the second stepwise formation constant of $Cr(O_2CMe)_2$. Equation 8 may be simplified to

$$(K_D')^{1/2} = (K_D)^{1/2} + (K_{DO})^{1/2} \sum_1^N \beta_n[L]^n/\beta_{A2}[MeCO_2^-]^2, \quad (9)$$

where K_D is the dissociation constant observed at the same acetate concentration in the absence of the ligand L. For the purpose of discussion we shall define the function

$$f = [(K_D')^{1/2} - (K_D)^{1/2}][MeCO_2^-]^2, \quad (10)$$

which in turn is related to [L] by

$$f([L]) = (K_{DO})^{1/2}\beta_{A2}^{-1}\sum_1^N \beta_n[L]^n. \quad (11)$$

The slope of a plot of log f against log ([L]) is equal to $\bar{n}$, the average value of n for complexes formed at a particular value of [L]. Knowing K_{DO} and β_{A2}, the values of β_n may be obtained.

Results

For each ligand, two sets of measurements were obtained. (1) With fixed total chromium(II), acetate, and acetic acid concentrations, the ligand concentration was varied over the range to be used in the later experiments. With increasing added ligand, the momomer and dimer absorbances increased and decreased respectively, and sharp isosbestic points were observed, *i.e.* at λ=600 nm (malonate system, Fig. 1), 620 nm (*N*-methyliminodiacetate system), 395 and 585 nm, (ethylenediamine-*N*,*N*'-diacetate system). This shows that oxidation to chromium(III) is negligible under the conditions of the experiments. (2) With fixed total acetate, acetic acid, and ligand concentrations, the chromium(II) concentration was varied, the first three all being in large excess over chromium(II). At low concentrations, the monomer absorption was dominant, but with increasing concentration the shape of the spectrum steadily changed to that of the dimer (Fig. 2). These experiments were repeated with different acetic acid, acetate and ligand concentrations. Typical plots of $[Cr_2]$ against $[Cr_1]^2$ are shown in Fig. 3.

Malonate (propanedioate) System. The total malonate concentration $[L]_T$ was varied over the range 0—0.09 M and for each malonate concentration, total chromium(II) was varied over the range 2—8 mM. The acetate and acetic acid concentrations were varied over the ranges 0.3—0.6 and 0.3—0.5 M. pK_a values of malonic acid[2] are such that in acetate buffer the first dissociation is complete, and the second partially complete (Eqs. 12—13, $L^{2-}=CH_2(CO_2)_2^{2-}$):

$$H_2L + MeCO_2^- \longrightarrow HL^- + MeCO_2H, \quad (12)$$

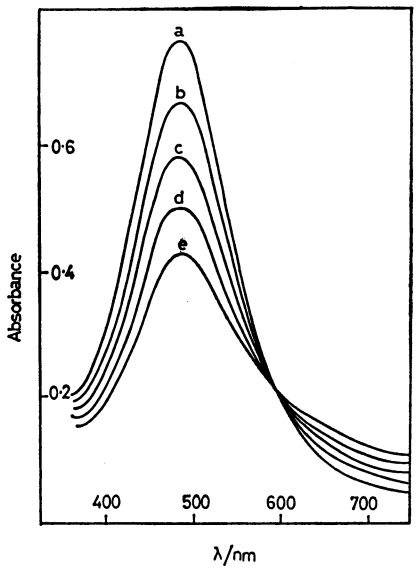

Fig. 1. Spectra of chromium(II) in acetate buffer with various concentrations of added malonic acid (H_2L). $[Cr]_T$=2.75 mM; $[L]_T$=0.0, 2.5, 5.0, 7.4, 9.9 mM (curves a to e respectively); $[MeCO_2H]=[MeCO_2^-]$= 0.2 M; I=1.0 M ($NaClO_4$). Path length 4 cm, T= 25 °C.

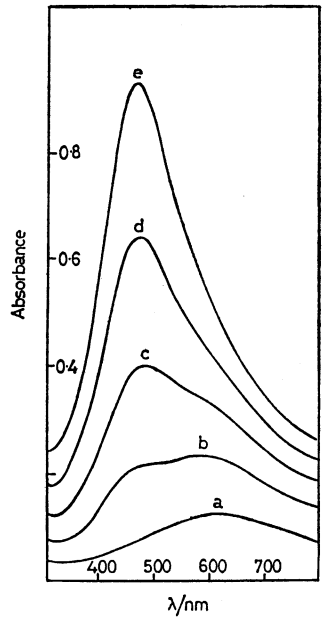

Fig. 2. Spectra of chromium(II) at various concentrations in an acetate-malonate mixture. $[L]_T$=50 mM; $[Cr]_T$=1.9, 3.7, 5.4, 7.0, 8.6 mM (curves a to e respectively); $[MeCO_2H]=[MeCO_2^-]$=0.3 M; I=1.0 M ($NaClO_4$). Path length 4 cm, T=25 °C.

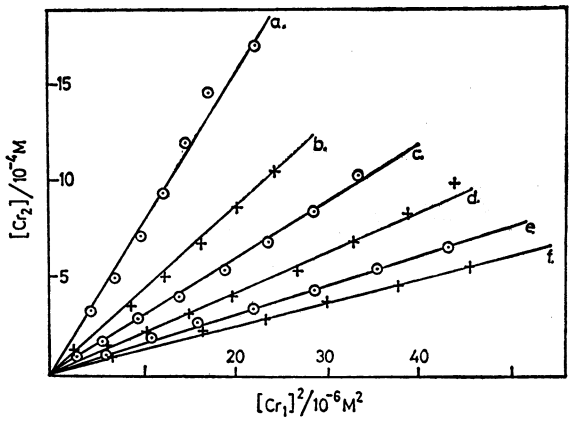

Fig. 3. Variation of chromium(II) dimer concentration with chromium(II) monomer concentration. $[Cr_2]=[Cr_2(O_2CMe)_4]$, $[Cr_1]=[Cr]_T-2[Cr_2]$. H_2L=malonic acid. $[L]_T$=40, 50, 60, 70, 80, 90 mM (curves a to f respectively); $[MeCO_2H]-2[L]_T=[MeCO_2^-]+2[L]_T$=0.3 M; I=1.0 M ($NaClO_4$). T= 25 °C.

$$HL^- + MeCO_2^- \overset{K_{Aa}^{-1}K_{La2}}{\rightleftharpoons} L^{2-} + MeCO_2H. \quad (13)$$

Hence we may write

$$[L^{2-}] = [L]_T/(1+K_{Aa}K_{La2}^{-1}[MeCO_2H]/[MeCO_2^-]), \quad (14)$$

where $[L]_T$ denotes total ligand concentration and K_{Aa} and K_{La2} are acid dissociation constants of $MeCO_2H$ and HL^-. Using $pK_{Aa}=4.58$ (the mean of three literature values at $I=1.0$ M)[2] and $pK_{La2}=5.15$,[3] we have $K_{Aa}K_{La2}^{-1}=3.7$. The plot of $\log f$ against $\log([L^{2-}])$, shown in Fig. 4(a), has the slope 2.0. This is consistent with the equation

$$f([L^{2-}]) = (K_{DO})^{1/2}\beta_{A2}^{-1}\beta_2[L^{2-}]^2, \quad (15)$$

which yields the parameters shown in Table 1.

N-Methyliminodiacetate System. The total ligand concentration was varied over the range $[L]_T=0$ to 0.12 M and total chromium(II) was varied over the range 0.8 to 3.1 mM. Acetate and acetic acid varied from 0.3 to 0.5 M. The acid H_2L has pK_a values 2.2 and 9.3,[4] hance we take $[HL^-]=[L]_T$, where HL^- denotes the ion $MeNH(CH_2CO_2)_2^-$. To show the dependence of f upon $[L^{2-}]$, we have plotted log f against $\log\{[HL^-][MeCO_2^-]/[MeCO_2H]\}$ in Fig. 4(c). The slope of 2.0 is consistent with the formation of CrL_2^{2-} as the predominant species:

$$HL^- + MeCO_2^- \overset{K_{Aa}^{-1}K_{La2}}{\rightleftharpoons} L^{2-} + MeCO_2H, \quad (16)$$

$$Cr^{2+} + 2\,L^{2-} \overset{\beta_2}{\rightleftharpoons} CrL_2^{2-}. \quad (17)$$

Using the equation

$$f([L^{2-}]) = (K_{DO})^{1/2}\beta_{A2}^{-1}\beta_2 K_{La2}^2 K_{Aa}^{-2} \times [HL^-]^2[MeCO_2^-]^2[MeCO_2H]^{-2}, \quad (18)$$

we obtain the parameters shown in Table 1.

Ethylenediamine-N,N'-diacetate System. With this ligand complexation was less than with the others, and it was necessary to use lower acetate concentrations ($[MeCO_2H]+[MeCO_2^-]=0.4$ M) in order to displace the equilibrium 6 to the right. The total ligand concentration $[L]_T$ was varied over the range 0 to 0.10 M, and total chromium(II) over the range 0.8 to 3.5 mM. The acetic acid-dependence of f was not studied. From the acid dissociation constants, $pK_{La1}=6.7$ and $pK_{La2}=9.9$,[5] we have $[L]_T=[H_2L]$. The plot of $\log f$ against $\log([H_2L])$ has a slope of 1.0 (Fig. 4(b). Hence the equation

$$f([L^{2-}]) = (K_{DO})^{1/2}\beta_{A2}^{-1}K_1K_{La1}K_{La2}K_{Aa}^{-2}[H_2L] \times [MeCO_2^-]^2[MeCO_2H]^{-2}, \quad (19)$$

was used to obtain the parameters shown in Table 1.

Other Ligands. With 5-sulfosalicylate(3-carboxy-4-hydroxybenzenesulfonate) ion, under our conditions ($[L]_T=0.01$ to 0.12 M, $[MeCO_2^-]=0.06$ to 0.3 M, $[MeCO_2H]=0.32$ to 0.62 M), dissociation of the $Cr_2(O_2CMe)_4$ complex was only slightly greater than that observed in the absence of added ligand. Assuming the complex CrL^-, we calculate an upper limit for log K_1 as shown in Table 1. With glycine, no dissociation could be detected. With edta, dissociation of the dimer into monomer was complete.

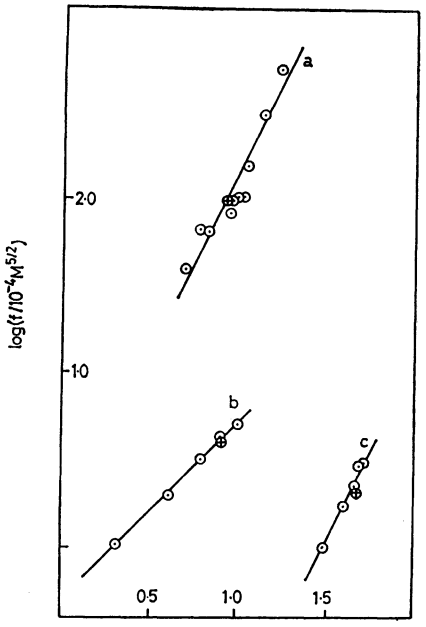

Fig. 4. Plots of log f (see text, Eqs. 10—11) against (a) $\log([L^{2-}]/10^{-3}$ M), H_2L=malonic acid; (b) $\log([H_2L]/10^{-2}$ M), H_2L=ethylenediamine-*N,N'*-diacetic acid, $[MeCO_2H]=[MeCO_2^-]$; (c) $\log([HL^-][MeCO_2^-][MeCO_2H]^{-1}/10^{-3}$ M), H_2L=*N*-methyliminodiacetic acid. Points ⊙, $[Zn]=(1/2)[Cr]_T$; points ⊕, $[Zn]_T=[Cr]_T$.

Discussion

For the chromium(II)–malonate system, Fukuda

Table 1. Summary of results

Ligand	Reaction[a]	log Q[b]	log (β_n/M^n)[c]
Malonate	$(1/2)Cr_2A_4+2L^{2-} \rightleftharpoons CrL_2^{2-}+2A^-$	2.23±0.10	log β_2 =6.0±0.2
5-Sulfosalicylate	$(1/2)Cr_2A_4+HL^{2-} \rightleftharpoons CrL^-+HA+A^-$	≤−2.64	log K_1 ≤7.8
N-Methyliminodiacetate	$(1/2)Cr_2A_4+2HL^- \rightleftharpoons CrL_2^{2-}+2HA$	−0.98±0.03	log β_2 12.3±0.5[d]
Ethylenediamine-*N,N'*-diacetate	$(1/2)Cr_2A_4+H_2L \rightleftharpoons CrL+2HA$	−2.30±0.10	log K_1 =9.1±0.2[e]

a) A^-: $MeCO_2^-$, L^{2-} or L^{3-}: the anion specified in column 1. b) Q: equilibrium constant of reaction specified in column 2; units $M^{1/2}$ or $M^{3/2}$. Temperature 25 °C, ionic strength, $I=1.0$ M ($NaClO_4$). Limits of error are root-mean-square deviations of log f from the lines shown in Fig. 4. c) β_n refers to the reaction $Cr^{2+}+nL \rightleftharpoons CrL_n$, calculated using $\log[(K_{DO}/M)^{1/2}]=-2.17$, $\log(\beta_{A2}/M^{-2})=1.70$ (Ref. 1). Limits of error are rough estimates. d) Calculated using $pK_a=4.6$ for HA (Ref. 2) and $pK_a=9.3$ for HL^- (Ref. 4). e) Calculated using $pK_a=4.6$ for HA (Ref. 2) and $pK_{a2}=6.68$ and 9.85 for H_2L (Ref. 5), neglecting the difference in ionic strength in the latter case.

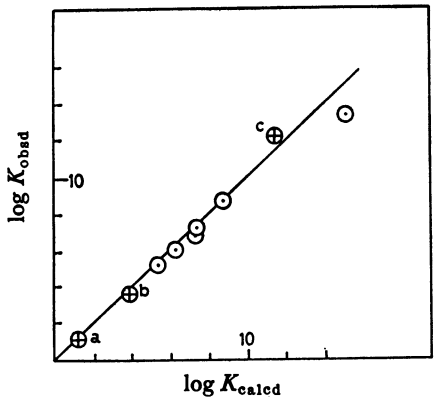

Fig. 5. Comparison of observed stability constants (log K_1) of chromium(II) complexes with those calculated from Eq. 20 of the text. Points ⊙, previous data (Ref. 8). Points ⊕, subsequent data: (a) $MeCO_2^-$ (Ref. 1); (b) malonate (Ref. 6); (c) *N*-methyliminodiacetate (this work). For point (c), log β_2 is plotted, not log K_1. Note that equation 20 yields log K_1= 7.4 (Ref. 8), and log K_2=4.2, using data from the same original sources.

et al.,[6] reported log K_1=3.92, log K_2=3.21. Our value log β_2=6.0 is more consistent with log $K_1 \cong 4$, log K_2=2, bearing in mind the usual difference between first and second stepwise stability constants of chelate complexes.[2] The formation curve reported by Fukuda *et al.*, deviates from the expected S-shape and it seems possible that their value of log K_1 is more reliable than that of log K_2. For the 5-sulfosalicylate system, the limiting value log $K_1 \leqslant 7.8$ is consistent with that of Pecsok and Schaefer (7.1)[7] but not with that of Fukuda *et al.* (9.9).[6]

Cannon[8] previously put forward an empirical expression for stability constants of chromium(II) complexes, based on the Irving-Williams series:

$$\log K_{Cr} = \alpha \log K_{Cu} + \frac{1}{5}(6-\alpha) \log K_{Mn} - \frac{1}{5}(1+4\alpha) \log K_{Zn}. \quad (20)$$

Here K_{Cr}, K_{Cu}, K_{Mn}, and K_{Zn} are stability constants of Cr^{2+}, Cu^{2+}, Mn^{2+}, and Zn^{2+} complexes with the same ligand under the same conditions (they may be step-constants K_n or overall constants β_n), and α=0.55. A comparison of predicted and observed values of log K_{Cr} is shown in Fig. 5, and it can be seen that the new data are in satisfactory agreement with the formula.

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