Composition and Stability of the Dimer Tetra-acetatodichromium(II): a Spectrophotometric Study

By **Roderick D. Cannon** * and **Mohammad J. Gholami**, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

The monomer–dimer equilibrium in solutions of chromium(II) acetate has been investigated by spectrophotometric and solubility measurements. The principal dimeric species in solution is $[Cr_2(O_2CMe)_4]$. The equilibrium constant for $[Cr_2(O_2CMe)_4] \rightleftharpoons 2Cr(O_2CMe)_2$ is log $K_{DO} = -4.35$, and for $Cr^{2+} + 2MeCO_2^- \rightleftharpoons Cr(O_2CMe)_2$ is log $\beta_2 = 1.70$, at 25 °C and ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$]).

ALTHOUGH it is well established that chromium(II) acetate is predominantly dimeric in aqueous media,[1,2] the composition of the dimer has not been established with certainty. We now present evidence that this species has the same formula in solution as in the solid state, namely $[Cr_2(O_2CMe)_4]$, and some further data on the monomer–dimer equilibria. In summary, we have found evidence for reactions (1)—(3), in the acetate concentration range 0—1.0 mol dm^{-3}.

$$[Cr_2(O_2CMe)_4] \xrightleftharpoons{K_{DO}} 2Cr(O_2CMe)_2 \qquad (1)$$

$$Cr(O_2CMe)_2 \xrightleftharpoons{K_2^{-1}} [Cr(O_2CMe)]^+ + MeCO_2^- \qquad (2)$$

$$[Cr(O_2CMe)]^+ \xrightleftharpoons{K_1^{-1}} Cr^{2+} + MeCO_2^- \qquad (3)$$

EXPERIMENTAL

Preparations.—Chromium(II) stock solutions were prepared as previously described [1] except that $CrCl_3 \cdot 6H_2O$ was used instead of chromium(III) perchlorate. The resulting concentrations of chloride ion were assumed to have no effect on the measurements. Reagent concentrations were selected to give *ca.* 0.1 mol dm^{-3} Cr^{2+}, 0.1 mol dm^{-3} H^+, 0.05 mol dm^{-3} Zn^{2+} (assumed), and ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$]). Chromium(II) was determined by injecting aliquot portions into deoxygenated solutions of potassium dichromate, in excess of sulphuric acid, and back-titrating with ammonium iron(II) sulphate using Ferroin indicator. The storage vessel is shown in Figure 1. Features of the design are that the solution has no contact with greased joints, that the hypodermic syringe or pipette used for withdrawals is not introduced into the bulk of the solution, and that the nitrogen supply can be discontinued in between experiments. Using this apparatus it was found that the chromium(II) concentration remained constant within experimental error for up to 6 weeks.

---

[1] R. D. Cannon, *J. Chem. Soc.* (*A*), 1968, 1098.

[2] (*a*) R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, 1975, **14**, 2202; (*b*) *ibid.*, p. 2207.

Solid Chromium(II) *Acetate*.—In a typical preparation, chromium(II) chloride solution (25 cm^3, 0.2 mol dm^{-3}) was added to a solution (200 cm^3) of sodium acetate (2.0 mol dm^{-3}) and acetic acid (1.0 mol dm^{-3}). The crystalline precipitate was washed with deoxygenated water, ethanol, and diethyl ether, and dried under nitrogen {Found: C, 24.8; H, 4.25, Cr^{II} (by titration, as above), 25.8. $[Cr_2(O_2CMe)_4(OH_2)_2]$ requires C, 25.5; H, 4.25; Cr, 27.8%}. For the solubility measurements, and for spectrophotometric measurements at low acetate concentrations where solid chromium(II) acetate was used, the solid was not isolated and dried, but merely precipitated and washed several times with the appropriate acetate buffer solution and then allowed to equilibrate with the solution under a stream of nitrogen.

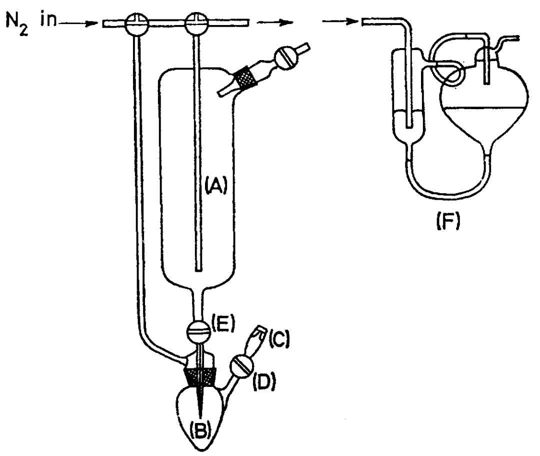

FIGURE 1 Apparatus for storing and dispensing air-sensitive solutions. The solution is stored in vessel (A). To withdraw solution, vessel (B) is flushed with nitrogen, using a hypodermic needle at (C) as the exit; the pressure in (A) and (B) is then equalised and the desired volume of solution is run into vessel (B). From there it is withdrawn by means of a hypodermic syringe inserted through the rubber sealing cap (C) and stopcock (D). Stopcock (E) is of Kel-F, the others glass, lubricated with silicone grease. All stopcocks are spring-loaded and the two joints are secured with springs. Nitrogen pressure is adjusted by means of the mercury valve (F)

Sodium acetate and sodium perchlorate solutions were prepared by neutralising standard sodium hydroxide, from freshly opened ampoules, with the corresponding acids.

Equilibrium Measurements.—Optical densities were measured on a Beckman DB spectrophotometer with output to a Beckman 10-in chart recorder. The spectrophotometer was modified in two ways to provide effective temperature control. (*i*) A heat barrier was placed between the lamphouse and the cell compartment, consisting of an aluminium box, with light passage, through which cold tap water was continuously circulated. (*ii*) The cell holder itself was reconstructed as a double-walled box for circulating water from an external thermostat. To ensure maximum circulation, and to make full use of the restricted space available, the box was constructed of thin (2 mm) stainless steel, with electric-welded joints, and the connecting tubes were of the widest possible diameter (10-mm internal diameter at the points of junction). Using a Churchill circulating thermostat, the flow rate was found to be 5.5 dm^3 min^{-1} and the temperature difference between the water at the inlet and outlet did not exceed 0.05 °C.

Most of the measurements were spectrophotometric titrations, with a sodium acetate–acetic acid–sodium perchlorate mixture in the sample cell and chromium(II) solution injected from an 'Agla' syringe. After each injection, the solution was stirred by bubbling nitrogen through the cell (the inlet needle being bent out of the light path). The titrant solution was prepared by either of three procedures. (*i*) When the solution in the cell contained $\geqslant 0.15$ mol dm^{-3} acetate ion, the stock chromium(II) perchlorate was used, having ionic strength 1.0 mol dm^{-3} but contained up to 0.1 mol dm^{-3} H$^+$ and 0.05 mol dm^{-3} Zn^{2+}. (*ii*) For acetate concentrations below 0.15 mol dm^{-3}, the titrant was a solution of chromium(II) acetate in acetate buffer having the same acetate and acetic acid concentrations and the same ionic strength as the solution in the cell. It was obtained in the following way. First the solution for the cell was prepared and its pH was measured, using glass and calomel electrodes. Then two solutions were prepared under nitrogen, one containing chromium(II) chloride and the desired concentration of acetic acid, at ionic strength 1.0 mol dm^{-3} with sodium perchlorate, and the other containing the same acetic acid concentration but also 1.0 mol dm^{-3} in sodium acetate. The second solution was titrated into the first until the pH was the same as that of the cell solution. The resulting mixture was assumed to contain the same acetic acid concentration as the cell solution, and to have the same activity coefficients for hydrogen ion, and hence the same acetate concentration. (*iii*) For an experiment in the absence of chloride and zinc ion, the appropriate solutions of sodium acetate, acetic acid, and sodium perchlorate were allowed to equilibrate, under nitrogen, with freshly precipitated chromium(II) acetate.

RESULTS

Equilibria in Solution.—The results of a typical spectrophotometric titration are shown in Figure 2. As noted before [1] the optical density at 490 nm, the wavelength of maximum absorbance of the chromium(II) dimer, is a non-

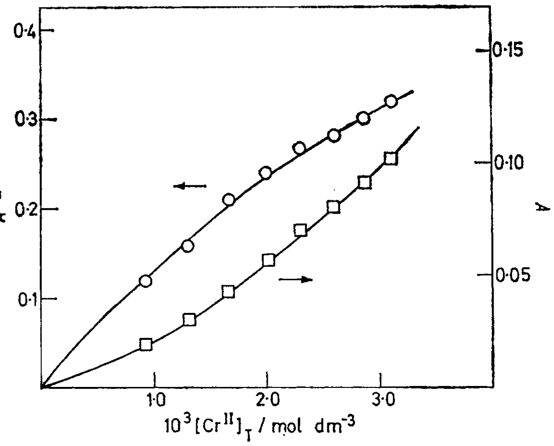

FIGURE 2 Variation of absorbance A with chromium(II) concentration: (□) dependence of A on $[Cr^{II}]_T$; (○) dependence of $A^{\frac{1}{2}}$ on $[Cr^{II}]_T$. $[MeCO_2H] = 0.10$ mol dm^{-3}, $[MeCO_2^-] = 0.057$ mol dm^{-3}, ionic strength 1.0 mol dm^{-3} ($Na[ClO_4]$), 25 °C, wavelength 490 nm, path length 1.0 cm

linear function of the chromium(II) concentration. Introducing equilibrium (4), we have (5) and (6) where $[Cr^{II}]$

$$Cr^{II}_2 \overset{K_D}{\rightleftharpoons} 2Cr^{II} \qquad (4)$$

$$[Cr^{II}_2] = K_D[Cr^{II}]^2 \qquad (5)$$

$$[Cr^{II}] + 2[Cr^{II}_2] = [Cr^{II}]_T \qquad (6)$$

and $[Cr^{II}_2]$ are the total concentrations of all monomer and dimer species respectively and $[Cr^{II}]_T$ is the total stoicheiometric chromium(II) concentration. Defining average absorption coefficients ε_1 and ε_2, the general expression for the absorbance A is (7). Assuming $\varepsilon_1 = 0$ at $\lambda = 490$ nm,

$$8A/l = 4\varepsilon_2[Cr^{II}]_T - (2\varepsilon_1 - \varepsilon_2)K_D\{1 - (1 + 8[Cr^{II}]_T/K_D)^{\frac{1}{2}}\} \qquad (7)$$

(7) may be written in the linearised form (8), so that a plot

$$[Cr^{II}]_T/A^{\frac{1}{2}} = (2A^{\frac{1}{2}}/\varepsilon_2 l) + (K_D/\varepsilon_2 l)^{\frac{1}{2}} \qquad (8)$$

of $[Cr^{II}]_T/A^{\frac{1}{2}}$ against $A^{\frac{1}{2}}$ is expected to be linear with gradient $2/\varepsilon_2 l$ and intercept $(K_D/\varepsilon_2 l)^{\frac{1}{2}}$ on the vertical axis. Typical plots are shown in Figure 3, and values of ε_2 and K_D are listed in Table 1.

TABLE 1

Results of spectrophotometric titrations [a]

$[MeCO_2H]$	$[MeCO_2^-]$	ε_2 [b]	10^4K_D
mol dm^{-3}		dm^3 mol^{-1} cm^{-1}	mol dm^{-3}
1.0	1.0	147	1.32
	1.0	147	1.53
	0.8	139	0.72
	0.6	147	0.91
	0.5	140	0.26
	0.5	141	0.27
	0.4	147	1.52
	0.4	142	0.23
	0.4	141	0.52
	0.25	145	1.18
	0.25	144	1.16
	0.20	139	1.50
	0.15	142	1.82
	0.15	142	2.98
0.10	0.132	142	6.8
	0.132	143	5.7
	0.10	143	11.2
	0.10	138	10.5
	0.10	139	9.5 [c]
	0.10	135	10.9 [c]
	0.10	135	12.1 [d]
	0.060	138	26.3
	0.060	138	27.7
	0.057	143	37.2
	0.057	138	35.9
	0.046	148	81.1
	0.046	148	76.7
		Mean: 143 ± 3	

[a] Ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$]), 25 °C. $[Zn^{2+}] = \frac{1}{2}[Cr^{II}]_T$, unless otherwise stated. [b] Figure 3 and equation (8). [c] $[Zn^{2+}] = [Cr^{II}]_T$. [d] $[Zn^{2+}] = 0$.

Solubilities.—Saturated solutions were prepared by allowing freshly precipitated chromium(II) acetate to equilibrate with appropriate acetate buffer solutions, under nitrogen and with thermostatic control. After allowing the solid to settle, samples of the clear solutions were carefully withdrawn by syringe. Optical densities A_{490}(sat), at 490 nm, and total chromium(II) concentrations, $[Cr^{II}]_T$, determined by titration as described above, are shown in Table 2.

DISCUSSION

The mean absorption coefficient, ε_2, of the dimeric species is effectively constant over the whole range of acetate concentrations used and its value $\varepsilon_2 = 143 \pm 3$ dm^3 mol^{-1} cm^{-1} is in satisfactory agreement with the

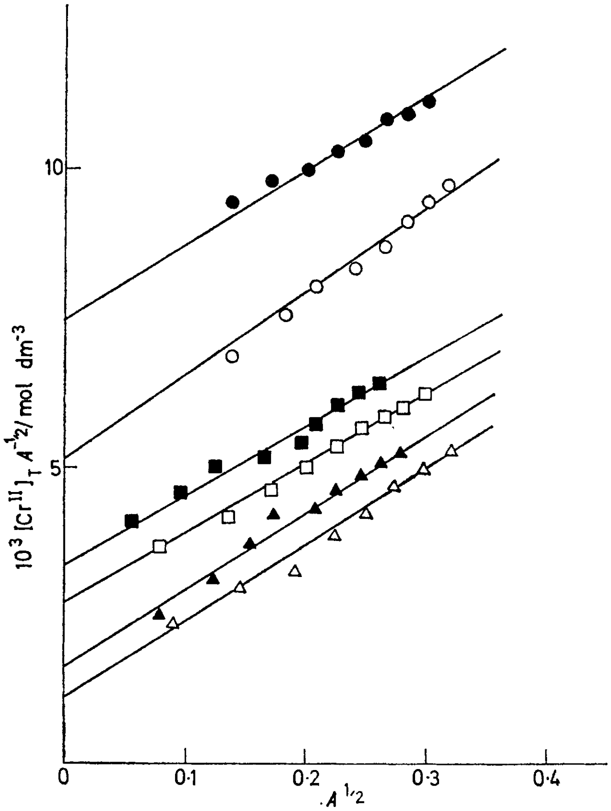

FIGURE 3 Variation of absorbance A with chromium(II) concentration $[Cr^{II}]_T$, plotted according to equation (8), at different acetate concentrations: (●) 0.046, (○) 0.057, (■) 0.10, (□) 0.132, (▲) 0.15, and (△) 0.25 mol dm^{-3}. Other concentrations as specified in Table 1

TABLE 2

Spectrophotometric and analytical data for saturated solutions of $[Cr_2(O_2CMe)_4]$ [a]

$MeCO_2^-$ / mol dm^{-3}	A_{490}(sat) [b]	$10^3[Cr^{II}]_T^{sat}$/mol dm^{-3}	
		expt. [c]	calc. [d]
1.00	0.254		
0.80	0.290		
0.60	0.295		
0.50	0.245 [e]	4.0	4.2
0.50	0.270 [f,g]		
0.40	0.284 [f]		
0.20	0.286 [f]	4.5	4.4
0.132	0.253 [e]		
0.10	0.266 [e]	5.5	5.3
0.10	0.257 [f,g]		
0.057	0.298 [f]	6.5	6.5
0.046	0.245 [g]	7.5	7.7
	Mean: 0.267 ± 0.018		

[a] $[MeCO_2H] = 1.0$ mol dm^{-3}; ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$]), 25 °C. [b] Wavelength 490 nm; path length 1 cm. [c] Analytical measurements (see text). [d] Calculated from equation (11) with values of $K_D^{\frac{1}{2}}$ interpolated from Figure 4. [e] Average of three determinations. [f] Average of two determinations. [g] Solutions were equilibrated in the presence of amalgamated zinc.

value $\varepsilon_2 = 142$ dm^3 mol^{-1} cm^{-1} found in the earlier work.[1] Since the optical density of the saturated solution also remains constant over this range ($A/l = 0.267 \pm 0.018$ cm^{-1}) it follows that the concentration of dimeric complex is independent of acetate ion. The dimer which is present in solution therefore has the same stoicheiometric formula as the solid, and the dissolution equilibrium (9) may be written with $K_{S42} = (1.87 \pm 0.13) \times 10^{-3}$ mol dm^{-3} at 24.3 °C and ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$]). (The notation K_{S42} used here is in conformity with ref. 3.)

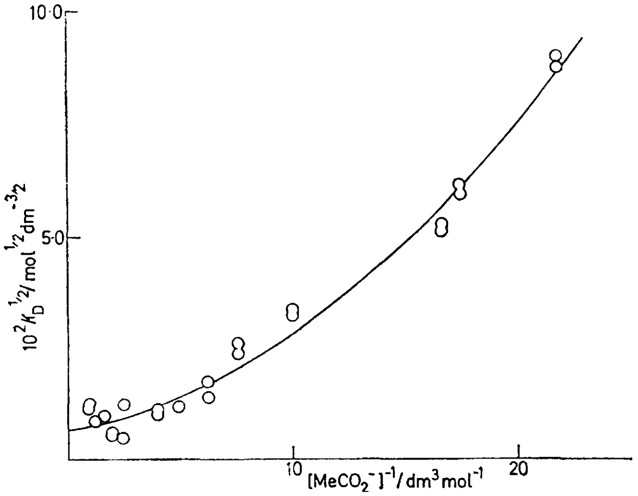

FIGURE 4 Variation of K_D with acetate-ion concentration (data of Table 1). The curve was calculated from equation (12) with parameters given in the text

$$[\mathrm{Cr_2(O_2CMe)_4}](\mathrm{s}) \xrightleftharpoons{K_{S42}} [\mathrm{Cr_2(O_2CMe)_4}](\mathrm{aq}) \qquad (9)$$

From this value and from the dissociation constant K_D as measured spectrophotometrically, we may calculate the total chromium(II) concentration, $[\mathrm{Cr^{II}}]_T^{\mathrm{sat}}$, in the saturated solution at various acetate concentrations, as in equations (10) and (11). As shown in Table 2, the

$$[\mathrm{Cr^{II}}]_T^{\mathrm{sat}} = [\mathrm{Cr^{II}}]^{\mathrm{sat}} + 2[\mathrm{Cr^{II}}_2]^{\mathrm{sat}} \qquad (10)$$

$$= K_D^{-\frac{1}{2}} K_{S42}^{\frac{1}{2}} + 2K_{S42} \qquad (11)$$

calculated values are in satisfactory agreement with experiment.

Measurements at 0.10 mol dm^{-3} acetate concentration (Table 1) show that zinc ion in the concentrations present in our experiments has no significant effect on either ε_2 or K_D.

The variation of K_D with acetate concentration is shown in Figure 4 in the form of a plot of $K_D^{\frac{1}{2}}$ against $[\mathrm{MeCO_2^-}]^{-1}$. This shows the marked increase in dissociation of the dimer as the acetate concentration is decreased, but it also shows a significant curvature. This is consistent with dissociation equilibria in which more than one acetate ion is liberated per ion of Cr$^{\mathrm{II}}$; that is, with equations (2) and (3) above. From equations (1)—(3) the theoretical form of the curve of Figure 4 is (12). In theory it is possible to deduce the

$$K_D^{\frac{1}{2}} = K_{DO}^{\frac{1}{2}}\{1 + K_2^{-1}[\mathrm{MeCO_2^-}]^{-1} + (K_1K_2)^{-1}[\mathrm{MeCO_2^-}]^{-2}\} \qquad (12)$$

values of the stepwise stability constants K_1 and K_2, but in practice this can only be done within quite wide limits of variation. Fitting the data to equation (12) by the method of least squares, and using $[\mathrm{MeCO_2^-}]^{-1}$ and $[\mathrm{MeCO_2^-}]^{-2}$ as independent variables,[4] we obtain $K_{DO}^{\frac{1}{2}} = (6.7 \pm 1.7) \times 10^{-3}$ mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$, $K_{DO}^{\frac{1}{2}}K_2^{-1} = (8.2 \pm 4.6) \times 10^{-4}$ mol$^{\frac{3}{2}}$ dm$^{-\frac{9}{2}}$, and $K_{DO}^{\frac{1}{2}}K_1^{-1}K_2^{-1} = (1.3 \pm 0.2) \times 10^{-4}$ mol$^{\frac{5}{2}}$ dm$^{-\frac{15}{2}}$, where the limits for each parameter are set at ± one standard error of estimate. Evidently the product $K_1K_2 = \beta_2$ is better defined than either K_1 or K_2 separately. Introducing logarithms and taking the standard errors as approximate limits of error, we obtain $\log K_{DO} = -4.35 \pm 0.25$, $\log \beta_2 = 1.7 \pm 0.2$, $\log K_1 = 0.8 \pm 0.4$, and $\log K_2 = 0.9 \pm 0.4$. The extent of permissible variation in K_1 and K_2 is however illustrated by the following calculation: if for simplicity we assume $K_1 = 4K_2$ (a relation that holds approximately in many analogous cases, including acetate complexes of other bivalent metals),[3] then equation (12) reduces to (13). As shown in Figure 5, the plot of $K_D^{\frac{1}{4}}$

$$K_D^{\frac{1}{4}} = K_{DO}^{\frac{1}{4}}(1 + 2K_1^{-1}[\mathrm{MeCO_2^-}]^{-1}) \qquad (13)$$

against $[\mathrm{MeCO_2^-}]^{-1}$ is in fact satisfactorily linear. A line fitted by least squares gives $K_{DO}^{\frac{1}{4}} = 0.7$ mol$^{\frac{1}{4}}$ dm$^{-\frac{3}{4}}$, $K_1 \simeq 14$ dm^3 mol^{-1}, and $K_2 = 3.5$ dm^3 mol^{-1}, *i.e.* $\beta_2 \simeq 50$ dm^6 mol^{-2} and $\log \beta_2 = 1.70$ as before.

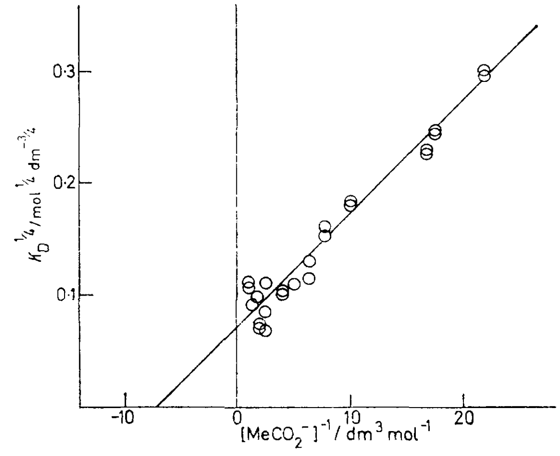

FIGURE 5 Data of Table 1, plotted according to equation (13). The straight line was fitted by a least-squares procedure

A summary of chromium(II)–acetate equilibrium data is shown in Table 3. The variation in values of K_{DO} and K_2 indicates the limits of accuracy attainable by the methods so far employed. The value of K_1 suggested here is similar to those measured by Hutchinson and Higginson[5] for acetate complexes of other bivalent

---

[3] 'Stability Constants of Metal–Ion Complexes,' eds. A. E. Martell and L. G. Sillén, *Special Publ.*, Nos. 17 and 25, The Chemical Society, London, 1964 and 1971.

[4] See, for example, 'Survey of Applicable Mathematics,' ed. K. Rektorys, Iliffe Books, London, 1969, p. 1295.

[5] M. H. Hutchinson and W. C. E. Higginson, *J.C.S. Dalton* 1973, 247.

TABLE 3

Summary of chromium(II)–acetate equilibrium data [a]

Method	ε_2 dm^3 mol^{-1} cm^{-1}	K_{DO}	K_1 dm^3 mol^{-1}	K_2	β_2 dm^6 mol^{-2}	Ref.
Spectrophotometric	154 [b]			0.8 [b]		6
Spectrophotometric	142	−3.8				1
Kinetic		−3.4		0.7		2*a*
Spectrophotometric	143	−4.35	0.8	0.9	1.7	[c]

[a] All equilibrium constants are listed as logarithms at 25 °C and ionic strength 1.0 mol dm^{-3} (Na[ClO$_4$]). [b] At 20 °C, ionic strength not controlled. (Data of K. B. Yatsimirskiĭ and T. I. Federova, *Zhur. neorg. Khim.*, 1956, **1**, 2310, recalculated in ref. 2*a*.) [c] This work.

metals and is within the range log $K_1 = 1.2 \pm 0.8$ predicted by one of the present workers on the basis of an empirical correlation with complexes of other ligands.[6]

Funds for equipment were provided by the S.R.C. and the University of East Anglia. The temperature-controlled cell housing described above was designed and built by Mr. D. Goffen and Mr. H. W. Plumbley, Engineering Workshops, University of East Anglia.

[6/431 *Received, 3rd March,* 1976]

---

[6] R. D. Cannon, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1222.