Equilibria in Aqueous Solutions of Some Chromium(2+) Complexes

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The stepwise formation constants of the complexes formed in the Cr^{2+}–ethylenediamine (en), –malonate (mal), –glycinate (glyO), –β-alaninate (alaO), –iminodiacetate (imda), –nitrilotriacetate (nta), and –ethylenediaminetetra-acetate (edta) systems in aqueous 1 mol dm^{-3} KCl at 25 °C, determined pH-metrically, are as follows: $\log K_1^{en} = 5.48$, $\log K_2^{en} = 4.15$, $\log K_1^{mal} = 3.57$, $\log K_2^{mal} = 1.92$, $\log K_1^{glyO} = 4.21$, $\log K_2^{glyO} = 3.06$, $\log K_1^{alaO} = 3.89$, $\log K_1^{imda} = 5.01$, $\log K_2^{imda} = 3.17$, $\log K_1^{nta} = 6.52$, $\log K_2^{nta} = 3.14$, $\log K_1^{edta} = 12.70$. The logarithm of the equilibrium constant for the $Cr^{2+} = Cr(OH)^+ + H^+$ process is -5.30; the formation of a protonated complex was detected in the Cr^{2+}–malonate and –ethylenediaminetetra-acetate systems and the formation of a binuclear $[Cr_2(nta)]^+$ complex in the Cr^{2+}–nitrilotriacetate system. The log (K_1/K_2) values for the Cr^{2+} and Cu^{2+} complexes are roughly the same in the case of bidentate ligands, but they are much lower for Cr^{2+} than for Cu^{2+} in the case of multidentate ligands. The ratios of 'excess' stabilities of the Cr^{2+} and Cu^{2+} complexes are also roughly the same (0.54) in the case of bidentate ligands, but no excess stability (even destabilization) of the Cr^{2+} complexes was found in the case of the multidentate ligands. These phenomena are interpreted in terms of the difference in ionic radii of the two metal ions.

The results of studies on the dynamics of equilibria in aqueous solutions of a number of Cu^{2+} and vanadyl complexes have recently been published.[1] These studies (based on an n.m.r. relaxation method) are now extended to Cr^{2+} complexes, for which only a few equilibrium data and even fewer complex formation and exchange kinetic data are available; such data would be important for comparing and interpreting the equilibrium and kinetic behaviour of complexes of the first row transition metal ions.

For interpretation of the n.m.r. relaxation data, the composition and stability of the complexes formed under exactly the same conditions as used for the relaxation studies must be known. In the case of Cr^{2+}, however, few equilibrium data are published (mainly by Pecsok and co-workers [2–5] and Fukuda *et al.*[6]). Data published up to 1976 were summarized by Cannon,[7] who suggested an empirical relationship to predict the formation constants of the Cr^{2+} complexes, based on the Irving–Williams series.

The results of Fukuda *et al.*[6] seem to be in serious error, although the source of error was not apparent from their paper. They found that Cr^{2+} formed more stable bis-complexes with glycine than did Cu^{2+}, with $K_1/K_2 < 4$, which is evidently unrealistic. They determined formation constants even for Cr^{2+}–oxalate complexes, although it is known that a redox reaction takes place between Cr^{2+} and oxalic acid. This redox reaction was thoroughly studied by Ševčik and Treindl.[8]

The lack of appropriate data, the contradictions in published results, and our need to know the composition and stability of the complexes, led us to undertake a systematic equilibrium study of the Cr^{2+} complexes formed with ligands containing amino and carboxylate donor groups with various denticities and chelate ring size; the ligands selected were ammonia, ethylenediamine (en), 1,3-diaminopropane (pd), malonate (mal), glycinate (glyO), β-alaninate (alaO), iminodiacetate (imda), nitrilotriacetate (nta), and ethylenediaminetetra-acetate (edta). The hydrolysis of Cr^{2+} was also studied, so as to obtain the formation constant of $Cr(OH)^+$ for the evaluation of the metal–ligand titration curves.

Experimental

$Cr(O_2CMe)_2$ and $CrCl_2 \cdot 4H_2O$ were prepared as described in standard textbooks. The $CrCl_2 \cdot 4H_2O$ contained about 2—3% $CrCl_3$. This contamination was removed by thorough mixing of the solution with $BaCO_3$ suspension for 30 min. The supernatant solution was filtered into a vessel designed specifically to store the $CrCl_2$ stock solution at pH *ca.* 2, under argon, and from which a known volume of the solution could be taken out. The stock solution could be stored for months without oxidation to Cr^{3+}.

The Cr^{2+} concentration was determined by oxidation to Cr^{3+} with KIO_3 in the presence of an excess of KI; the excess of iodine was titrated with $Na_2S_2O_3$ solution. The total chromium concentration was determined iodometrically also, after conversion of the Cr^{2+} into CrO_4^{2-} in alkaline solution with H_2O_2. The excess of H_2O_2 was boiled off; an excess of KI was added after acidification and the liberated iodine was titrated with $Na_2S_2O_3$ solution. The Cr^{2+} and total chromium concentration determined in this way agreed within 0.5%. The Ba^{2+} concentration of the stock solutions was determined by atomic absorption. It was less than 10% of the Cr^{2+} concentration. The HCl concentration of the stock solution was determined pH-metrically, by using the appropriate Gran function.[9]

All the experiments were carried out in specially constructed apparatus under a purified argon atmosphere. All the other solutions (KOH, KCl, and ligand stock solutions) were also prepared under oxygen-free argon, using deoxygenated water. The argon was purified by treatment with concentrated $CrCl_2$ solution before use. No oxygen could then be detected in the purified argon by mass spectrometry.

A Radiometer PHM-52 pH-meter with GK 2301B electrode, calibrated for $-\log[H^+]$ according to Irving *et al.*,[10] was used for pH-titrations in 1 mol dm^{-3} KCl at 25 °C. The protonation constants of the ligands and the formation constants of their Ba^{2+} complexes were also determined pH-metrically. These were used as auxiliary data during the evaluation of pH-titrations in the presence of Cr^{2+}. The titration curves were first transformed into formation curves, to see whether the 'rules' of stepwise complex formation were obeyed satisfactorily. The final evaluation was carried out with the program PSEQUAD.[11] The concentrations of the initial solutions used for pH-titrations in the presence of Cr^{2+} are given in Table 1.

Results and Discussion

The protonation constants of all the ligands and the formation constants of the Ba^{2+} complexes of iminodiacetate, nitrilo-

Table 1. Initial total concentrations of the solutions used for pH-metric titrations

Ligand	T_H^0	T_L^0	T_{Cr}^0
Glycine	0.5022	0.500	0.0105
	0.2016	0.200	0.0078
	0.2022	0.200	0.0105
	0.2027	0.200	0.0097
	0.2618	0.260	0.0065
β-Alanine	0.2241	0.200	0.0162
	0.1041	0.080	0.0162
	0.1885	0.160	0.0055
	0.1825	0.160	0.0110
	0.1025	0.080	0.0110
Malonic acid	0.0340	0.0160	0.0062
	0.0353	0.0160	0.0104
	0.0347	0.0160	0.0083
Ethylenediamine *	0.3936		0.0357
	0.3909		0.0220
	0.3919		0.0275
	0.2092		0.0275
	0.4009		0.0324
Iminodiacetic acid	0.0258	0.0120	0.0089
	0.0252	0.0120	0.0058
	0.0331	0.0160	0.0105
Nitrilotriacetic acid	0.0126	0.0080	0.0052
	0.0169	0.0120	0.0057
	0.0175	0.0120	0.0089
	0.0220	0.0160	0.0052
	0.0142	0.0100	0.0065
	0.0127	0.0080	0.0097
	0.0162	0.0100	0.0104
	0.0214	0.0140	0.0104
	0.0291	0.0200	0.0104
	0.0149	0.0100	0.0062
	0.0142	0.0100	0.0042
	0.0196	0.0100	0.0208
Ethylenediaminetetra-acetic acid	0.0253	0.0060	0.0027
	0.0256	0.0060	0.0041
	0.0258	0.0060	0.0055
	0.0172	0.0100	0.0065
	0.0247	0.0080	0.0097
	0.0290	0.0120	0.0097
OH^-	0.0053		0.0257
	0.0027		0.0137
	0.0045		0.0162

* The solutions were titrated with an aqueous solution of ligand.

triacetate, and ethylenediaminetetra-acetate agreed well with data published previously [12] for similar conditions.

The formation constants of the complexes formed with Cr^{2+} are collected in Table 2, together with available literature data.

Hydrolysis of Cr^{2+}.—The hydrolysis of Cr^{2+} has not been studied previously. The system could be studied up to pH *ca.* 4.2 without visible precipitate formation. Solutions above pH *ca.* 3.8, however, reached an equilibrium pH value only in 15—20 min, indicating slow precipitation of the hydrolysis products. Thus only the formation constant of $CrH_{-1}^+ = Cr(OH)^+$ is given in Table 2, calculated from the pH values up to pH *ca.* 3.8. It should be borne in mind that the maximum value of $\bar{n}_{OH}$ is less than 0.04 below pH *ca.* 3.8; thus the accuracy of the constant given is rather uncertain. This formation constant was included in all the further calculations concerning the metal–ligand systems. The calculations showed that the effect of hydrolysis was negligible in comparison with the complex formation equilibria in all cases apart from the Cr^{2+}–ammonia and Cr^{2+}–β-alanine systems.

Cr^{2+}–*Ammonia*.—No complex formation was detected in the system even in 2 mol dm^{-3} NH_4Cl before hydrolytic precipitation of Cr^{2+}.

Cr^{2+}–*Ethylenediamine*.—Pecsok and Bjerrum [2] pointed out that this system cannot be studied in the usual way by titration of the mixture of ethylenediamine dihydrochloride and $CrCl_2$ with KOH, because of the hydrolysis of Cr^{2+} even with a large ligand excess. Our preliminary experiments supported their finding. Therefore (like Pecsok and Bjerrum) we studied the system by titrating the strongly acidified solution of $CrCl_2$ with aqueous ethylenediamine free base. The p*K* values of the ligand were determined from similar titration of the same samples without $CrCl_2$. In this case the program PSEQUAD was used to calculate the p*K* and formation constants simultaneously, using both types of titration curves, by minimizing the sum of the squares of pH differences. The agreement of our data with those published by Pecsok and Bjerrum is not very good, but acceptable.

Cr^{2+}–1,3-*Diaminopropane*.—A systematic search for optimum conditions to study the system showed that at least a 30—50-fold ligand excess is necessary to avoid hydrolytic precipitation, and that complex formation takes place in that pH range where the second protonation step occurs. This means that the pH-metric method cannot be used to obtain formation constants, although a violet colour similar to that of the Cr^{2+}–ethylenediamine system, in the presence of a large excess of ligand, unambiguously indicated complex formation. Spectrophotometric measurements are in progress to study the equilibria in this and in some other systems.

Cr^{2+}–*Malonate*.—The system could be studied up to $\bar{n}$ *ca.* 1.0—1.1; a crystalline precipitate, presumably Cr^{II} malonate, was formed at higher malonate concentrations. The lower parts of the formation curves showed systematic deviation, indicating the involvement of some equilibria other than stepwise complex formation. The titration curves could be fitted well by assuming the formation of a protonated complex also. Our result agrees with the data of Fukuda *et al.*[6] only for the first complex formation step.

Cr^{2+}–*Glycinate*.—A systematic search for optimum conditions in the pH-metric study showed that at least a 10—20-fold ligand excess is necessary to avoid hydrolytic precipitation. Complex formation, however, takes place between pH 4 and 8, where the protonation processes of the ligand do not have a significant buffer effect. In this case (as proved by Fábián and Nagypál [13]) the pH-metric method can be used even with a 500-fold ligand excess to determine the formation constants. The formation curves were regular, *i.e.* the system can be fully described in terms of stepwise formation of $[Cr(glyO)]^+$ and $[Cr(glyO)_2]$. Photometric measurements are in progress to obtain the stepwise stability constant K_3, its value is essential for interpretation of the n.m.r. relaxation results.[1] Our results are completely different from those of Fukuda *et al.*[6]

Cr^{2+}–β-*Alaninate*.—The system could be studied without precipitation only up to $\bar{n}$ *ca.* 0.7—0.8, even with a 40-fold ligand excess. This part of the formation curve allowed us to calculate the formation constant of the mono-complex only.

Table 2. Stability constants of the complexes

Ligand	log β(CrL)	log β($\mathrm{CrL_2}$)	log β(CrLH)	log β($\mathrm{Cr_2L}$)
Glycine	4.21 ± 0.02	7.27 ± 0.03		
	7.72[a]	15.26[a]		
β-Alanine	3.89 ± 0.05			
	7.53[a]			
Malonic acid	3.57 ± 0.03	5.49 ± 0.05	6.45 ± 0.05	
	3.92[a]	7.13[a]		
Ethylenediamine	5.48 ± 0.05	9.63 ± 0.08		
	5.15[b]	9.19[b]		
Iminodiacetic acid	5.01 ± 0.02	8.18 ± 0.02		
Nitrilotriacetic acid	6.52 ± 0.03	9.66 ± 0.05		8.54 ± 0.05
Ethylenediaminetetra-acetic acid	12.7 ± 0.1		16.18 ± 0.15	
	13.6[c]		16.6[c]	
$\mathrm{OH^-}$	−5.3 ± 0.1[d]			

[a] See ref. 6. [b] See ref. 2. [c] See ref. 3. [d] In log β($\mathrm{CrH_{-1}}$) form.

Table 3. Comparison of log (K_1/K_2) values for $\mathrm{Cu^{2+}}$ and $\mathrm{Cr^{2+}}$ complexes

	log (K_1/K_2)	
Ligand	$\mathrm{Cu^{2+}}$	$\mathrm{Cr^{2+}}$
Glycine	1.31	1.15
Ethylenediamine	1.38	1.34
Malonic acid	1.56	1.65
Iminodiacetic acid	4.58	1.83
Nitrilotriacetic acid	8.46	3.18

This value is also completely different from that of Fukuda *et al.*[6]

$\mathrm{Cr^{2+}}$-*Iminodiacetate*.—The formation constants of the complexes are high enough to be determined in solutions containing the ligand and the metal ion in similar total concentrations (see Table 1). The formation curves are regular, *i.e.* stepwise complex formation takes place without involvement of other equilibria.

$\mathrm{Cr^{2+}}$-*Nitrilotriacetate*.—The formation curves calculated at different metal–ligand concentration ratios coincide only above $\bar{n}$ *ca.* 1.0. A definite trend was observed in the lower parts of the formation curves. The experimental results could not be described by assuming the formation of a protonated complex only. The best fit of the titration curves was observed if the formation of a $\mathrm{[Cr_2(nta)]^+}$ complex was assumed as well as stepwise complex formation. The formation of this binuclear complex is surprising; no sign of bi- or poly-nuclear complex formation was observed in any other system. Thus the constant for $\mathrm{[Cr_2(nta)]^+}$ in Table 2 can be regarded as indicating the involvement of some other equilibria, and not necessarily of binuclear complex formation only (apart from the stepwise equilibria).

$\mathrm{Cr^{2+}}$-*Ethylenediaminetetra-acetate*.—The titration curves up to pH *ca.* 4.0 could be fitted with the assumption of formation of a simple $\mathrm{[Cr(edta)]^{2-}}$ complex and its protonation (pK *ca.* 3.5).

Comparison of the Stabilities of $\mathrm{Cr^{2+}}$ *and* $\mathrm{Cu^{2+}}$ *Complexes.*—The log (K_1/K_2) values for the complexes of $\mathrm{Cr^{2+}}$ and $\mathrm{Cu^{2+}}$ are given in Table 3. The data for the $\mathrm{Cu^{2+}}$ complexes were taken from ref. 12 under those experimental conditions nearest to the ionic strength and temperature used in this work.

Table 3 shows that the log (K_1/K_2) values for the two metal ions are roughly the same in the case of bidentate ligands. If, however, the ligands have fused chelate rings, then log (K_1/K_2) values for the $\mathrm{Cr^{2+}}$ complexes are much lower. The reason for this is probably the higher ionic radius of $\mathrm{Cr^{2+}}$, resulting in much less steric hindrance against the uptake of a second multidentate ligand.

The difference between the stabilities of the complexes formed with bi- and multi-dentate ligands is even more pronounced when the ' excess ' stabilities of the $\mathrm{Cu^{2+}}$ and $\mathrm{Cr^{2+}}$ complexes are compared. These are given as differences between the logarithm of the measured formation constant and the value calculated from the stability constants of $\mathrm{Mn^{2+}}$

Table 4. Logarithms of the stability constants of $\mathrm{Mn^{2+}}$, $\mathrm{Zn^{2+}}$, $\mathrm{Cu^{2+}}$, and $\mathrm{Cr^{2+}}$ complexes; excess stabilities of $\mathrm{Cr^{2+}}$ and $\mathrm{Cu^{2+}}$ complexes and their ratios

Ligand	Equilibrium	$\mathrm{Mn^{2+}}$	$\mathrm{Zn^{2+}}$	$\mathrm{Cu^{2+}}$	$\mathrm{Cr^{2+}}$	Δlog K_{Cr}	Δlog K_{Cu}	Δlog K_{Cr}/Δlog K_{Cu}
Ethylenediamine	$\mathrm{M + L \rightleftharpoons ML}$	2.77	5.87	10.71	5.48	3.31	5.46	0.61
	$\mathrm{ML + L \rightleftharpoons ML_2}$	2.10	5.10	9.33	4.14	2.64	4.83	0.55
Malonic acid	$\mathrm{M + L \rightleftharpoons ML}$	2.30	2.47	4.63	3.57	1.30	2.19	0.59
Glycine	$\mathrm{M + L \rightleftharpoons ML}$	2.65	4.88	8.14	4.21	2.01	3.71	0.54
	$\mathrm{ML + L \rightleftharpoons ML_2}$	2.05	4.18	6.83	3.06	1.46	3.08	0.47
β-Alanine	$\mathrm{M + L \rightleftharpoons ML}$	2.52	3.90	7.07	3.90	1.66	3.45	0.48
Iminodiacetic acid	$\mathrm{M + L \rightleftharpoons ML}$	5.37	7.27	10.63	5.01	0.02	3.74	0.01
Nitrilotriacetic acid	$\mathrm{M + L \rightleftharpoons ML}$	7.46	10.66	12.94	6.52	−0.32	2.92	−0.10
	$\mathrm{ML + L \rightleftharpoons ML_2}$	3.48	3.58	4.48	3.14	−0.32	0.92	−0.35
Ethylenediaminetetra-acetic acid	$\mathrm{M + L \rightleftharpoons ML}$	13.81	16.44	18.70	12.70	−0.58	2.79	−0.21

Δlog K_{Cu} = log K_{Cu} − log K_{Mn}/5 − 4log K_{Zn}/5Δlog K_{Cr} = log K_{Cr} − 6log K_{Mn}/5 + log K_{Zn}/5 (see ref. 7) and Zn^{2+}, using linear interpolation for Cu^{2+} and extrapolation for Cr^{2+}. Table 4 contains the data necessary to calculate the ' excess ' stabilities, also taken from ref. 12. The last column of Table 4 shows that ratios of the excess stabilities are roughly the same for the bidentate ligands. The average of the ratios is 0.54 : 1, in surprisingly good agreement with Cannon's value (0.55).[7]

For imda, nta, and edta, however, there is no excess stability in the case of Cr^{2+}; the stability constants are even lower than the extrapolated values! This may also be explained by the greater ionic radius of Cr^{2+} than of Cu^{2+} (82 and 69 pm, respectively); thus the five-membered fused chelate rings cannot readily accommodate the steric requirements of co-ordination to Cr^{2+}. Further work is in progress to determine the formation constants of Cr^{2+} complexes with multidentate ligands of different chelate ring sizes.

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