

Comparison of the Formation Rate Constants of some Chromium(II) and Copper(II) Complexes

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The equilibrium kinetics in aqueous solutions of the chromium(II)–ethylenediamine (en) and –iminodiacetate (ida) complexes has been studied using a n.m.r. relaxation method. The paramagnetic relaxation rate and shift of the CH₂ protons of the ligands were measured over a wide range of the complex formation. The formation rate constants (dm³ mol⁻¹ s⁻¹) of the mono and bis complexes were determined: $k_1^{\text{en}} = 6.0 \times 10^9$, $k_2^{\text{en}} = 3.2 \times 10^9$, $k_1^{\text{ida}} = 4.9 \times 10^9$, $k_2^{\text{ida}} = 2.4 \times 10^7$. Kinetic evidence is given for the formation of [Cr(Hida)]⁺ and [Cr(ida)₃]⁴⁻ complexes. The complex-formation kinetics of some complexes of Cr²⁺ and Cu²⁺ is compared; the similarities and differences are discussed.

The equilibrium data for a number of chromium(II) complexes were published and the formation constants of complexes Cr²⁺ and Cu²⁺ were compared in our earlier papers.^{1,2} Significant similarities were found in the co-ordination properties of Cr²⁺ and Cu²⁺ related to their analogous electron structures (high-spin *d*⁴ and *d*⁹ respectively). On increasing the number of the five-membered fused chelate rings, the difference in the effect of the ligand structures on the excess stabilities between the complexes of Cu²⁺ and Cr²⁺ increased. Five-membered fused chelate rings cannot readily accommodate the steric requirements of co-ordination to the larger Cr²⁺. All the differences could be explained by the relative ion size and ligand structures. The effect of the Jahn–Teller distortion, which is generally used to explain the co-ordination of Cr²⁺ and Cu²⁺, is really the same for these two metal-ion complexes, as the interpretation of their formation constants suggested.

The complex-formation kinetics in the chromium(II)–glycinate³ (glyO) and –2,2'-bipyridyl⁴ (bipy) systems has been studied earlier using n.m.r. and chemical (T-jump) relaxation methods. These data indicated considerable similarity in the formation mechanism of complexes of Cr²⁺ and Cu²⁺.

The kinetic parameters for the Cr²⁺–glyO complexes were determined by measuring the paramagnetic relaxation effect of the labile NH₂ protons of the ligands on the line broadening of water protons. The slower dissociation processes of the more stable chromium(II)–ethylenediamine (en) and –iminodiacetate (ida) complexes have been studied in this work using the n.m.r. signal of the CH₂ protons of the ligands. We report new data on the formation kinetics of the chromium(II) complexes and discuss the analogy of the formation mechanism of complexes of Cr²⁺ and Cu²⁺.

Experimental

The experimental conditions for the preparation of chromium(II) complexes were described earlier¹ together with the formation constants of the ethylenediamine (log β₁^{en} = 5.48, log β₂^{en} = 9.63) and iminodiacetate (log β₁^{ida} = 5.01, log β₂^{en} = 8.18) complexes. Using pH-metry, commensurable ligand:metal concentration ratios had to be used to get reliable equilibrium data. The n.m.r. relaxation measurements required relatively high ligand concentrations, therefore the earlier investigations were completed by spectrophotometric measurements at these ligand concentrations. However, no differences could be detected compared with the pH-metric measurements.

The n.m.r. spectra of the CH₂ protons were recorded on a

Bruker WP 200 SY spectrometer (operating at 200 MHz for protons). The experimental *T*₂ values were calculated from the half-widths of the n.m.r. signals. The chemical shifts were referenced to 3-(trimethylsilyl)propanesulphonic acid sodium salt.

For the n.m.r. relaxation measurements an oxygen-free titration method was applied. The samples (5.00 cm³) were prepared in the n.m.r. tube (1 cm in diameter and 20 cm long) and deoxygenated with argon gas. Then the tube was sealed with a special n.m.r. pressure cap ensuring a small overpressure of inert gas. The KOH solution was injected by an automatic burette piercing the pressure cap with a syringe.

The measurements were carried out at 25 ± 1 °C unless otherwise stated. The ionic strength during the titration was adjusted to *I* = 1.0 mol dm⁻³. Before the titrations the ionic strength of the samples was calculated (because of the high concentration of the charged species in the samples and the considerable dilution) and a suitable quantity of KCl was added to the sample and to the KOH solution.

The measured linewidths and shifts were corrected by the diamagnetic values (measured in absence of Cr²⁺) of the CH₂ protons, $T_{2P}^{-1} = \Pi(\Delta v_{\frac{1}{2}m} - \Delta v_{\frac{1}{2}d})$ and $\Delta\omega_p = 2\Pi(\Delta\omega_m - \Delta\omega_d)$, where T_{2P}^{-1} and $\Delta\omega_p$ = the paramagnetic contributions to the relaxation rate (s⁻¹) and shift (rad s⁻¹), $\Delta v_{\frac{1}{2}m}$ and $\Delta\omega_m$ = the measured linewidth at half-height and the measured resonance frequency (Hz) in the solution of chromium(II) complexes, and $\Delta v_{\frac{1}{2}d}$ and $\Delta\omega_d$ = the measured linewidth and the measured resonance frequency (Hz) in the absence of Cr²⁺.

The experimental data measured in the absence of Cr²⁺ (the temperature and pH dependence of the resonance of the CH₂ protons) were used for the evaluation of the metal complex systems.

The concentration distributions of the species were calculated using the program PSEQUAD.⁵ For the calculation of the kinetic parameters the generalized Swift–Connick equations⁶ were used which can evaluate the relaxation data measured in solutions containing several paramagnetic species independently of the paramagnetic relaxation properties of the complexes.

Results and Discussion

The evaluation of the measured relaxation data required knowledge of the relaxation mechanism of the CH₂ protons in the co-ordination sphere of the Cr²⁺. Therefore, the

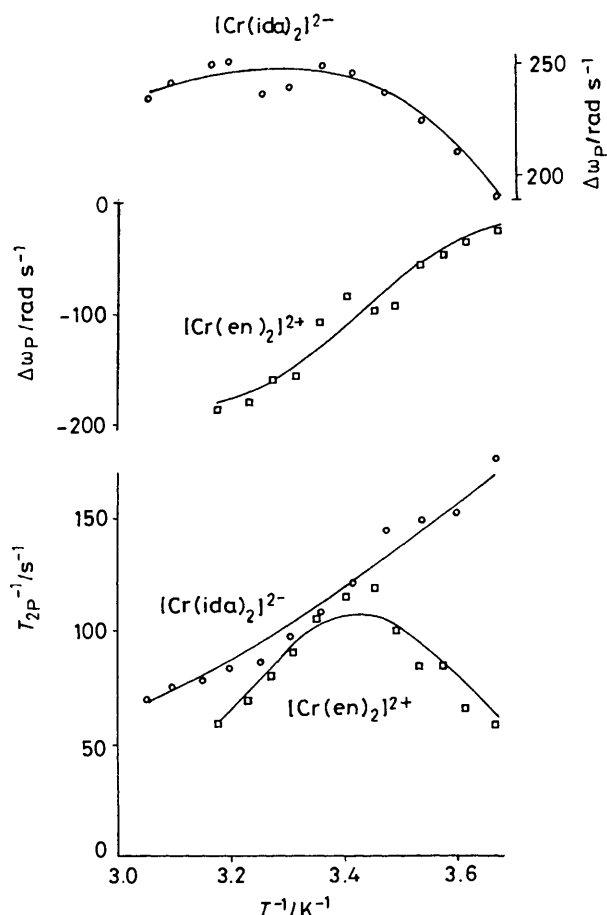


Figure 1. Temperature dependence of the paramagnetic relaxation rate and shift in the solution of $P[\text{Cr}(\text{en})_2]^{2+} = 1.652 \times 10^{-2}$ (\square) and $P[\text{Cr}(\text{ida})_2]^{2-} = 2.794 \times 10^{-2}$ (\circ) detected from the CH_2 signals

temperature dependences of the paramagnetic relaxation rate and shift of the CH_2 protons were measured as suggested by Swift and Connick,⁷ to separate the kinetic and the paramagnetic relaxation parameters.

The temperature dependences were measured in solutions of the $[\text{Cr}(\text{en})_2]^{2+}$ and $[\text{Cr}(\text{ida})_2]^{2-}$ complexes (see Figure 1) in the pH range where only these paramagnetic complexes are dominant. For the simultaneous evaluation of the relaxation rate and shift data the temperature dependences of the Swift-Connick equations were used [$\tau_M = h/kT \exp(\Delta H^\ddagger/RT - \Delta S^\ddagger/R)$; $\Delta\omega_M/\omega_0 = \alpha/T$; $T_{2M} = B \exp(C/RT)$; see ref. 7] and the best fit was reached when the $T_{2M}^{-1} \ll \Delta\omega_M$ relation was applied [equations (1) and (2)] where P_M is the molar ratio of

$$T_{2P}^{-1} = \frac{P_M \tau_M^{-1} \Delta\omega_M^2}{\tau_M^{-2} + \Delta\omega_M^2} = P_M r_{T_2} \quad (1)$$

$$\Delta\omega_P = \frac{P_M \tau_M^{-2} \Delta\omega_M}{\tau_M^{-2} + \Delta\omega_M^2} = P_M r_\omega \quad (2)$$

the co-ordinated nucleus ($P_{\text{CrLi}} = i[\text{CrLi}]/c_L$; i is the co-ordination number of the ligand, c_L is the total ligand concentration) and r_{T_2} and r_ω are the appropriate relaxation contributions of the paramagnetic species.

The calculated activation parameters and relaxation constants for the $[\text{Cr}(\text{en})_2]^{2+}$ and $[\text{Cr}(\text{ida})_2]^{2-}$ complexes are as follows: $\Delta H^\ddagger = 39 \pm 1$, 10 ± 1 kJ mol⁻¹; $\Delta S^\ddagger = -24 \pm 2$, -128 ± 3 J K⁻¹ mol⁻¹; $10^3 \alpha = 2.7 \pm 0.1$, 2.5 ± 0.1 K respec-

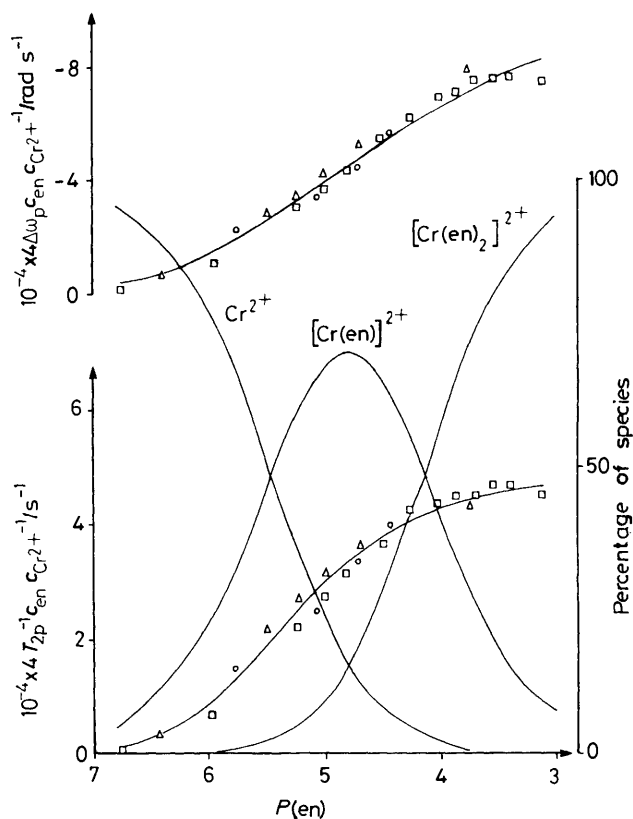
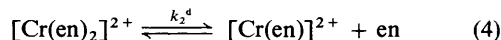
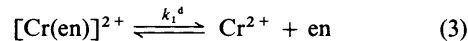


Figure 2. Normalized paramagnetic relaxation rate and shift data for the Cr^{2+} -en system measured from CH_2 protons, and the concentration distribution of the species; $c_H^0 = 1.139$, $c_L^0 = 5.000 \times 10^{-1}$, $c_{\text{Cr}^{2+}}^0 = 8.453 \times 10^{-3}$ (\square) or 1.134×10^{-2} (\triangle); $c_H^0 = 1.0825$, $c_L^0 = 4.835 \times 10^{-1}$, $c_{\text{Cr}^{2+}}^0 = 4.805 \times 10^{-3}$ (\circ) mol dm⁻³

tively. The main conclusion of the temperature-dependent investigation is that the paramagnetic relaxation of the CH_2 protons in the co-ordination sphere of the Cr^{2+} is caused by the change of the resonance frequency ($\Delta\omega$ mechanism). In this way the simplified equations can be used.

Chromium(II)-Ethylenediamine System.—The measured paramagnetic relaxation rate and shift data normalized for the total chromium(II) concentrations detected in a wide range of free-ligand concentration are shown in Figure 2 together with the concentration distribution of the species. The experimental data could be interpreted as an effect of the formation and dissociation of the parent complexes [equations (3) and (4)].



Using the curve-fitting procedure the relaxation rate and shift contributions could be calculated for the two complexes. The results of the evaluation are collected in Table 1.

Chromium(II)-Iminodiacetate System.—The experimental results of the n.m.r. titrations, using the same representation as in the case of the Cr^{2+} -en system, are shown in Figure 3. The relaxation effect of the interaction between the Cr^{2+} and Hida^- species was detected in the initial stage of the titration curve (see the measured data in range $7.0 > \text{pL} > 6.5$ and compare with Figure 2), equation (5). However, no equilibrium evidence was

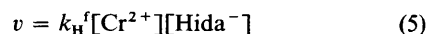


Table 1. The n.m.r. and kinetic parameters of the chromium(II) studied

Kinetic process	$10^{-3} r_{T_2}/s^{-1}$	$10^{-4} r_{\omega}/\text{rad s}^{-1}$	$10^{-4} k^d/s^{-1}$	$10^{-4} \Delta\omega_{Cr}/\text{rad s}^{-1}$
$[\text{Cr(en)}]^{2+} \rightleftharpoons \text{Cr}^{2+} + \text{en}$	9.4 ± 0.7	1.0 ± 0.1	2.0	-1.9
$[\text{Cr(en)}_2]^{2+} \rightleftharpoons [\text{Cr(en)}]^{2+} + \text{en}$	5.9 ± 0.4	1.0 ± 0.05	2.3	-1.3
$\text{Cr}^{2+} + \text{Hida}^-$	$5.2 \pm 0.2^*$	$6.8 \pm 0.1^*$	89*	6.8*
$[\text{Cr(ida)}] \rightleftharpoons \text{Cr}^{2+} + \text{ida}^{2-}$	2.2 ± 0.2	1.0 ± 0.04	4.8	1.0
$[\text{Cr(ida)}_2]^{2-} \rightleftharpoons [\text{Cr(ida)}] + \text{ida}^{2-}$	2.7 ± 0.1	0.59 ± 0.03	1.6	0.71
$[\text{Cr(ida)}_2]^{2-} + \text{ida}^{2-}$	$2.8 \pm 5^*$	$8.3 \pm 1.5^*$	27*	9.3*

* Second-order rate constants and n.m.r. parameters, because the equilibrium data are not known; only the kinetic data indicate the complex formation.

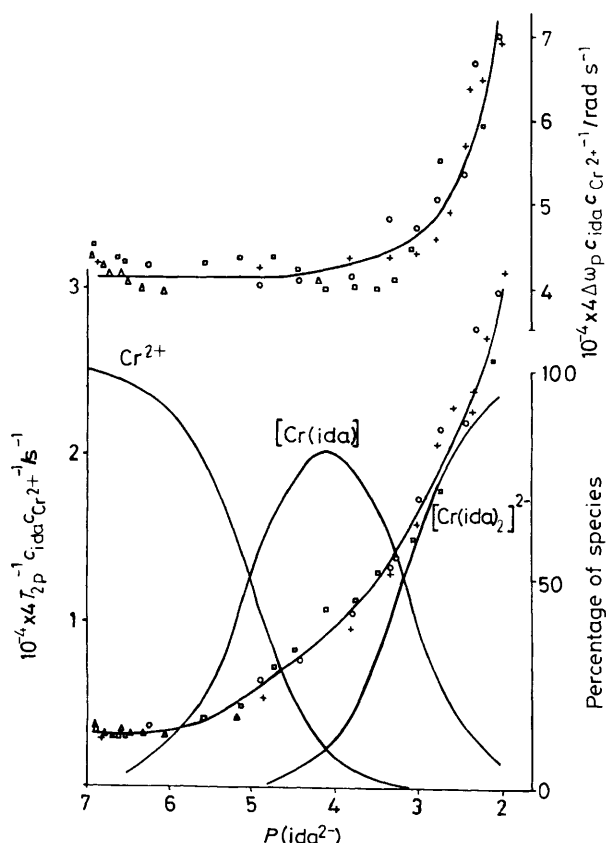
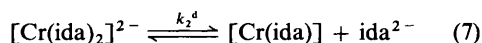
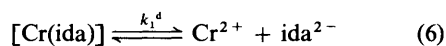


Figure 3. Normalized paramagnetic relaxation rate and shift data for the Cr^{2+} -ida system detected from the CH_2 protons, and the concentration distribution of the species; $c_{\text{H}}^0 = 5.412 \times 10^{-1}$, $c_{\text{L}}^0 = 3.107 \times 10^{-1}$, $c_{\text{Cr}^{2+}}^0 = 8.453 \times 10^{-3}$ (\square); $c_{\text{H}}^0 = 2.592 \times 10^{-1}$, $c_{\text{L}}^0 = 2.115 \times 10^{-1}$, $c_{\text{Cr}^{2+}}^0 = 4.805 \times 10^{-3}$ (\circ); $c_{\text{H}}^0 = 2.522 \times 10^{-1}$, $c_{\text{L}}^0 = 2.037 \times 10^{-1}$, $c_{\text{Cr}^{2+}}^0 = 9.243 \times 10^{-3}$ (\triangle); $c_{\text{H}}^0 = 2.217 \times 10^{-1}$, $c_{\text{L}}^0 = 2.076 \times 10^{-1}$, $c_{\text{Cr}^{2+}}^0 = 4.712 \times 10^{-3}$ (+) mol dm^{-3}

found for the formation of the protonated complex $[\text{Cr}(\text{Hida})]^+$ in our earlier investigation.¹

The dissociation of the parent complexes is responsible for the further change of the paramagnetic relaxation [equations (6) and (7)]. Increasing the free-ligand concentration after the



formation of the bis complex, a sharp change in the relaxation rate and shift was detected. The kinetic calculations indicated interaction between the bis complex and the free ligand,

Table 2. Comparison of the formation rate constants of some complexes of Cr^{2+} and Cu^{2+}

Complex or kinetic process	$k^f(\text{Cr}^{2+})/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	Ref.	$k^f(\text{Cu}^{2+})/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	Ref.
$[\text{M}(\text{bipy})]^{2+}$	3.5×10^7	4	4.0×10^7	4
$[\text{M}(\text{glyO})^+]$	3.1×10^9	3	3.4×10^9 4.0×10^9 4.3×10^9	a b c
$[\text{M}(\text{glyO})_2]$	2.8×10^8	3	4.8×10^8 1.0×10^9	b c
$[\text{M}(\text{glyO})_2] + \text{glyO}^-$	2.2×10^7	3	7.7×10^7 1.5×10^7	d e
$[\text{M}(\text{en})]^{2+}$	$(6.0 \pm 0.6) \times 10^9$		3.8×10^9	f
$[\text{M}(\text{en})_2]^{2+}$	$(3.2 \pm 0.2) \times 10^8$		1.9×10^9	f
$\text{M} + \text{Hida}^-$	$(8.9 \pm 1.5) \times 10^5$		1.2×10^4	g
$[\text{M}(\text{ida})]$	$(4.9 \pm 0.5) \times 10^9$		3.0×10^9	g
$[\text{M}(\text{ida})_2]^{2-}$	$(2.4 \pm 0.1) \times 10^7$			
$[\text{M}(\text{ida})_2]^{2-} + \text{ida}^{2-}$	$(2.7 \pm 0.5) \times 10^5$			

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equation (8). The calculated kinetic and relaxation parameters are collected in Table 1.

$$v = k_3^f [\text{Cr(ida)}_2]^{2-} [\text{ida}^{2-}] \quad (8)$$

The co-ordination of $[\text{Cr(ida)}_2]^{2-}$ is a little different from that of the mono complex. The relaxation contributions of the CH_2 protons of the bis complex (see Table 1) can be attributed only to apparent data. These values were calculated supposing eight CH_2 protons in the co-ordination sphere, but the co-ordination at the two axial positions is uncertain; the equatorial plane is certainly co-ordinatively saturated.

Nevertheless, there is a surprising interaction between the $[\text{Cr(ida)}_2]^{2-}$ and the free ligand, for which only kinetic evidence could be given. For the interpretation of the formation mechanism of the supposed tris complex the earlier suggested 'carboxyl displacement' was used.⁶ The nitrogen donor group of the free ligand can displace the more weakly bonded carboxyl group from the chelate ring, increasing the number of nitrogen bonds and of the unco-ordinated carboxyl donor groups. The entrance of the third ligand into the co-ordination sphere of Cr^{2+} really decreases the number of five-membered fused chelate rings. This is in accordance with the result of our

earlier investigations,^{1,2} whereas the placing of the five-membered fused chelate rings in the co-ordination sphere of the Cr^{2+} is rather unfavourable. The strongly distorted structure of the tris complex has low stability and large lability.

The formation rate constants of the systems studied by us together with earlier data for complexes of Cr^{2+} and Cu^{2+} are collected in Table 2. The formation rate constants of the mono complexes of Cr^{2+} and Cu^{2+} with bipyridyl, glycinate, ethylenediamine, and iminodiacetate are surprisingly the same. This similarity in kinetic behaviour, which was alluded to in our earlier work,³ together with the thermodynamic similarities^{1,2} lead to the conclusion that the mechanism of complex formation for these two metal ions is similar. However, additional data are necessary for the correct interpretation of the kinetics of the bis complexes.

The kinetic reason for the significantly different thermodynamic stability of the complexes of Cr^{2+} and Cu^{2+} is the few orders of magnitude faster dissociation of the chromium(II) complexes.

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