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NMR Relaxation Studies in Solution of Transition Metal Complexes XII. Formation, Dissociation and Exchange Rate of the Cr^{2+}–Glycine Complexes in Aqueous Solution

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The results of pH-metric equilibrium studies on a number of Cr^{2+} complexes have recently been published [1]. It was found that stepwise formation of the complexes took place in the Cr^{2+}–glycine system with $\log K_1 = 4.21$ and $\log K_2 = 3.06$.

The NMR relaxation study in aqueous solution of Cu^{2+}–ammonia system is reported in part XI of this series [12]. The results could be explained by the fast formation and dissociation of the $Cu(NH_3)_i$ (i = 1–4) complexes; the formation rate constant for the first step agreed well with the results given by using T-jump method.

The stepwise stability constants of the Cu^{2+}–ammonia and Cr^{2+}–glycine complexes are near to each other. Thus, if the formation rates of the Cu^{2+} and Cr^{2+} complexes are similar, then the rate of the

$$Cr^{2+} + G^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CrG^+$$

and

$$CrG^+ + G^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CrG_2$$

processes is expected also to be in that region, which can be determined conveniently by measuring the T_2 relaxation time of water protons. Thus the systematic NMR relaxation study of the dynamics of equilibria in a number of Cu^{2+} and vanadyl complexes [2–4] is now extended to the Cr^{2+} complexes, for which only very few formation and even less exchange kinetic data are available. Such data would be important to compare and interpret the kinetic behaviour of the complexes formed with the first row transition metal ions.

The results of NMR relaxation study in aqueous solution of the Cr^{2+}–glycine system are reported in the present paper.

Experimental

The stock solutions and the samples were prepared as described earlier [1]. The T_2 relaxation times were determined from the half-width of the lines of water protons, measured by a Bruker WP-200 SY instrument.

$$T_2^{-1} = \pi \Delta\nu_{1/2}$$

The measurements were carried out at 25 ± 1 °C, and the ionic strengths of the solutions were adjusted to 1 mol dm^{-3} KCl. The concentration distribution of the species was calculated by use of the program PSEQUAD [5].

Results and Evaluation

The paramagnetic contribution to the relaxation rate of water protons

$$\frac{2[H_2O]}{T_{2p}} = 111\,\pi(\Delta\nu_{1/2} - \Delta\nu^{\circ}_{1/2})$$

are seen on Fig. 1, together with the concentration distribution of the complexes. The shape of the curve on Fig. 1 suggests that the paramagnetic relaxation rate may be given as a linear combination of the concentration of the paramagnetic species and the $[CrG_2][G^-]$ concentration product:

$$\frac{2[H_2O]}{T_{2p}} = k_{Cr}[Cr^{2+}] + k_{CrG}[CrG^+] + k_{CrG_2}[CrG_2] + $$
$$+ k_{ex}[CrG_2][G^-]$$

where k_{Cr}, k_{CrG} and k_{CrG_2} are the overall first order rate constants of the proton relaxation, including the average lifetime and the paramagnetic relaxation time of the coordinated $-NH_2$ and H_2O protons in the different species. k_{ex} stands for the second order rate constant of the

$$CrGG + \overset{*}{G}^- \rightleftharpoons CrG\overset{*}{G} + G^-$$

process.

The full line on Fig. 1 was calculated with the set of the constants given from the linear least squares treatment:

$k_{Cr} = 3.45\ 10^5\ s^{-1}$, $k_{CrG} = 5.15\ 10^5\ s^{-1}$,
$k_{CrG_2} = 5.56\ 10^5\ s^{-1}$, $k = 4.44\ 10^7\ M^{-1}\ s^{-1}$.

It is interesting to note the $k_{Cr} < k_{CrG} < k_{CrG_2}$ relation. If the proton relaxation rate would be deter-

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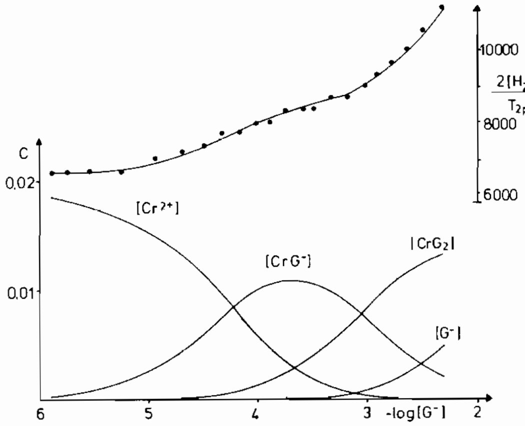

Fig. 1. Concentration distribution of the complexes formed in the Cr^{2+}–glycine system, together with the change of the relaxation rate of water protons as a function of free glycinate concentration.

mined by the water molecules remaining in the first coordination sphere, then the k values should decrease in the above order, as proved and interpreted for a number of Cu^{2+} complexes by Rossotti and Sunshine [6].

This expected relation was observed in the Cr^{2+}–malonic acid system, illustrated on Fig. 2.

The constants describing the relaxation rate of water protons in this system are as follows:

$k_{Cr} = 3.50\ 10^5\ s^{-1}$, $k_{CrmalH} = 4.3\ 10^5\ s^{-1}$, $k_{Crmal} = 1.35\ 10^5\ s^{-1}$.

The dramatic difference between k_{CrG} and k_{Crmal} – on a similar way as it is explained in the Cu^{2+}–ammonia system [12] – is interpreted by the fast formation and dissociation of the CrG^+ complex, which transfers the relaxed $-NH_2$ protons of coordinated glycine into the bulk water. A dissociation rate constant of

$$k_{-1} = \frac{5.15 - 1.35}{2} 10^5 = 1.9\ 10^5\ s^{-1}$$

can be calculated from the difference, where the number 2 in the denominator expresses that two labile $-NH_2$ protons change their environment from the *para*- to diamagnetic site when the dissociation of the CrG^+ complex takes place. From this, a formation rate constant of

$$k_1 = 3.1\ 10^9\ M^{-1}\ s^{-1}$$

can be calculated.

TABLE I. Comparison of the Formation Rate Constants ($mol^{-1}\ dm^3\ s^{-1}$) of the Cu^{2+} and Cr^{2+} Bipyridyl and Glycinate Complexes.

		Bipyridyl	Glycinate	
Cu^{2+}	k_1	4.10^7 [8]	$3.4\ 10^9$ [9], $4\ 10^9$ [10] $4.3\ 10^9$ [11]	
	k_2		$4.8\ 10^8$ [10], $1\ 10^9$ [11]	
Cr^{2+}	k_1	$3.5\ 10^7$ [8]	$3.1\ 10^9$	this work
	k2	–	$2.8\ 10^8$	

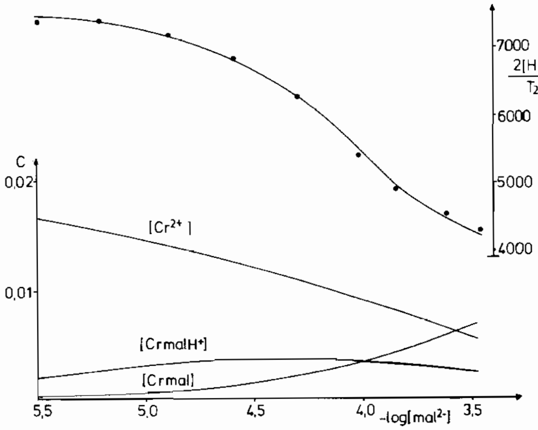

Fig. 2. Concentration distribution of the complexes formed in the Cr^{2+}–malonic acid system, together with the change of the relaxation rate of water protons, as a function of free malonate concentration.

Assuming that the contribution of water molecules to the measured relaxation rate in the bis glycinato complex is half of the contribution of the water molecules in the mono-malonato complex:

$$k_{-2} = \frac{5.56 - 0.68}{2} 10^5 = 2.4\ 10^5\ s^{-1}$$

thus

$$k_2 = 2.8\ 10^8\ M^{-1}\ s^{-1}$$

is given for the rate constant of the second complex formation step.

The significant increase of the relaxation rate at higher glycinate concentration is interpreted by the

$$\mathrm{CrGG} + \overset{*}{G}{}^- \overset{k_{ex}}{\rightleftharpoons} \mathrm{CrG}\overset{*}{G} + G^-$$

exchange reaction, with an exchange rate constant of

$$k_{ex} = 2.22\ 10^7\ M^{-1}\ s^{-1}$$

It should be kept in mind, however, that – on a similar way as it was proved for the Cu^{2+}–glycine system [7] – the exchange process may also be interpreted by the formation and dissociation of the CrG_3^- tris complex. Its formation constant, however, is not known at present, so that the exchange rate constant cannot be transformed to the formation and dissociation rate constants of CrG_3^-.

Only one formation rate constant, determined with T-jump technique, is found in the literature for Cr^{2+}, concerning to the Cr^{2+}–bipyridyl system [8]. Comparison with the formation rate constant of Cu^{2+}–bipyridyl complex, as well as the formation rate constants for the Cu^{2+}–glycine system, are seen together with our results in Table I.

The surprisingly good agreement of the rate constants concerning to the Cu^{2+} and Cr^{2+} complexes formed with bipyridyl and glycine strongly supports the theory that the present interpretation of the NMR relaxation results by the formation and dissociation of the complexes. This agreement indicates that the mechanism of the complex formation of Cu^{2+} and Cr^{2+} complexes are the same, and even the rates of the Jahn–Teller inversions responsible for the very fast complex formation kinetics are the same. Further studies are in progress to compare the complex formation kinetics of these two metal ions.

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