Synthesis, Characterisation, and Aquation Kinetics of [*N*-(*o*-Carboxyphenyl)-iminodiacetato](glycinato)chromate(III) Complex Ion in Acidic Media†

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The potassium salt of the [*N*-(*o*-carboxyphenyl)iminodiacetato](glycinato)chromate(III) complex has been synthesised and characterised. In acidic media, the complex has been shown to aquate to diaqua[*N*-(*o*-carboxyphenyl)iminodiacetato]chromium(III) and protonated glycine as the ultimate products. The rates of aquation of the complex in aqueous perchloric acid media are reported as a function of acid concentration and temperature. The variation of the observed pseudo-first-order rate constants with acid concentration suggests the operation of two concurrent paths with $k_{obs.} = k_0 + k_H[H^+]$, where k_0 and k_H are the appropriate rate constants for uncatalysed and acid-catalysed pathways respectively. The production of a metastable bidentate glycinato-*O,O'* ligand configuration in the aquation process is proposed to explain the reactivity of the chromate(III) complex.

Kinetics of acid-catalysed aquation reactions of octahedral chromium(III) carboxylate chelates have been the subject of several investigations.[1–5] The influence of the steric and electronic effects of the carboxylate ligands on the aquation rate has been examined. In marked contrast, limited data are available for the acid-catalysed amine terminus aquation of chelated aminocarboxylate ligand.[6]

Chromium(III) chemistry has recently become more topical as a result of the isolation of a low-molecular-weight chromium(III) amino acid complex from brewers yeast,[7] potentiating insulin activity. The aminopolycarboxylate ligands have donor groups similar to more common amino acid residues. Hence the ligand substitution at the chromium(III) centre in an aminopolycarboxylate environment has considerable physiological significance. In the present study a mixed-ligand octahedral complex of chromium(III) with [*N*-(*o*-carboxyphenyl)iminodiacetic acid] (H_3cida) and glycine has been prepared and its kinetics in acidic media has been examined for the following reasons: (*a*) in order to evaluate the relative reactivity of aromatic amino acids and glycine as co-ordinating ligands, towards acid solution; (*b*) to investigate the mechanistic details and mode of dissociation of the chelating ligand.

Experimental

Materials and Reagents.—Diaqua[*N*-(*o*-carboxyphenyl)-iminodiacetato]chromium(III) trihydrate, $[Cr(cida)(OH_2)_2]\cdot3H_2O$, was prepared following the method described in the literature.[8] Chemical analysis confirmed the purity, as did a comparison with the published u.v.–visible spectral data.[8] Potassium [*N*-(*o*-carboxyphenyl)iminodiacetato](glycinato)-chromate(III) dihydrate, $K[Cr(cida)(glyO)]\cdot2H_2O$ (glyO = glycinate), was prepared by dissolving $[Cr(cida)(OH_2)_2]\cdot3H_2O$ (3.9 g, 0.01 mol) and glycine (0.75 g, 0.01 mol) in water (50 cm^3), and raising the pH of the solution to 7 by addition of potassium hydroxide. The mixture was heated under reflux for 1 h whereupon its colour changed from violet to reddish pink. The solution was concentrated to *ca.* 10 cm^3, filtered, and the pink glycine complex was precipitated by ethanol. The complex was recrystallised by dissolving in the minimum volume of water followed by filtration and precipitation by ethanol. It was washed successively with water–ethanol (1:1) and ethanol, and finally dried *in vacuo* (Found: C, 34.15; H, 4.00; Cr, 11.40; N, 6.10. Calc. for $C_{13}H_{16}CrKN_2O_{10}$: C, 34.60; H, 3.55; Cr, 11.55; N, 6.20%).

In the u.v. spectrum the positions and intensities of the ligand-field bands of the complex [$\lambda_{max.}$: 512 (ε 77.8) and 380.4 nm (ε 77.5 dm^3 mol^{-1} cm^{-1})] correspond to the $^4A_{2g} \longrightarrow {}^4T_{2g}$ and $^4A_{2g} \longrightarrow {}^4T_{1g}$ transitions, respectively. The band at 1 640 cm^{-1} in the i.r. spectrum, attributable to the ν_{asym}(C=O) mode, indicates the presence of a co-ordinated carboxy group. The characteristic doublet for the primary amine group is observed between 3 200 and 3 300 cm^{-1}. The broad peak between 3 400 and 3 500 cm^{-1} indicates the presence of lattice water or water of crystallisation. Thermal gravimetric analysis (t.g.a.) confirmed the presence of two molecules of water of crystallisation. The molar conductance of 93.2 S cm^2 mol^{-1} corresponding to a 1:1 type electrolyte and the retention of the complex on an anion-exchange resin column of Dowex-1X8 (chloride form) confirmed its anionic character.

Other chemicals used were of reagent-grade purity.

Instruments.—A Varian Superscan-3 spectrophotometer and a Julabo-SC 12 constant-temperature water bath were used.

Rate Measurements.—In the experimental acidity range ($[H^+]$ = 0.05—0.60 mol dm^{-3}) the glycine complex has been found to aquate quantitatively leading to the diaqua product $[Cr(cida)(OH_2)_2]$, accompanied by a shift of the *d–d* bands to longer wavelengths. The presence of liberated glycine was confirmed by its reaction with ninhydrin (2,2-dihydroxyindan-1,3-dione) following the method described in the literature.[9]

Figure 1 depicts the spectral changes that take place with the passage of time. The successive absorption curves pass through isosbestic points at 380, 450, and 525 nm respectively during the entire course of the spectral changes. This strongly suggests the absence of any side reaction or the presence of an intermediate with a long lifetime. The course of the aquation reaction was monitored by measuring the increase in absorbance at 546 nm, where the molar absorption coefficients of the reactant and product complexes differ appreciably.

Rate determinations were initiated by adding the complex salt (18.2 ± 0.2 mg) to 10-cm^3 portions of the reactant solutions ($HClO_4$–$NaClO_4$) which had been equilibrated at the reaction temperature for a minimum of 30 min. The reaction mixture was then mixed vigorously for 1 min and transferred to a 1.00-cm cuvette in the constant-temperature block of a Superscan-3

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† *Non-S.I. unit employed:* cal = 4.184 J.

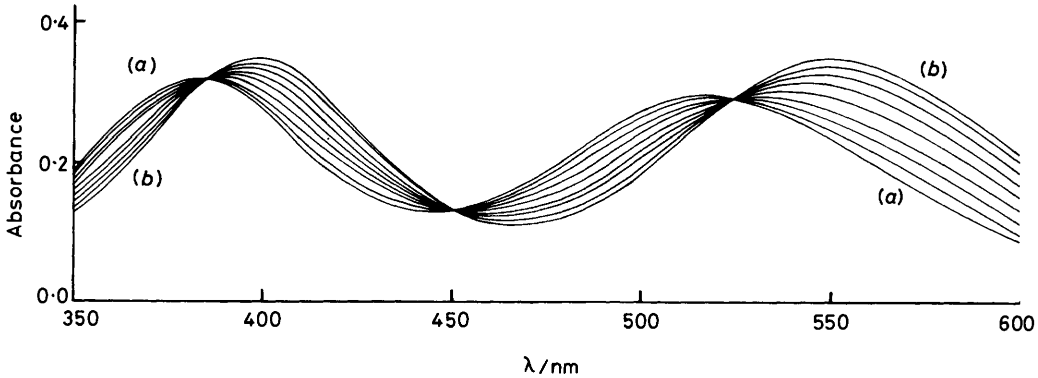
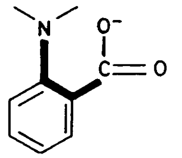


Figure 1. Spectral changes during aquation of the $[Cr(cida)(glyO)]^-$ ion (0.004 mol dm^{-3}) in 0.2 mol dm^{-3} $HClO_4$ at 25 °C after (a) 0 and (b) 90 min

spectrophotometer. The absorbance changes were measured for at least three half-lives. All experiments were carried out in an excess of perchloric acid and the pseudo-first-order rate constants, $k_{obs.}$, were computed from the gradients of the linear plots of $\ln(A_t - A_\infty)$ *versus* time by means of a least-squares program. Reported $k_{obs.}$ values represent the average of, at least, two runs which agreed within ±3%. The absorbance of the experimental solution after digesting for several half-lives (six or more) agreed with that of the diaqua complex $[Cr(cida)(OH_2)_2]$, indicating the absence of any complications due to reverse anation.

Results and Discussion

Spectral examination of the experimental solutions revealed that, under the conditions of acidity and temperature employed for this study, the metal–glycinate bond underwent dissociation in preference to the aromatic amino acid cida, leading to the product $[Cr(cida)(OH_2)_2]$. The enhanced kinetic stability of cida towards dissociation may possibly be attributed to the presence of a larger number (two five-membered and one six-membered ring) of chelate rings in the ligand cida, in comparison to only one five-membered metal–glycinate ring. In addition, the lack of free rotation of the ring carbon atoms forces the groups indicated below to lie in the same plane.



Resonance interaction of the carboxyl and tertiary nitrogen group with the phenyl ring may result in a shortening of the bond distances (indicated by the heavy lines) and may also contribute to the greater chelating power and closer approach of the chelate donor groups as compared to corresponding aliphatic ring structures.[10]

The observed pseudo-first-order rate constants, $k_{obs.}$, have been determined (Table 1) over the temperature range 20.0—40.0 °C. The hydrogen-ion concentration was varied from 0.05 to 0.60 mol dm^{-3}, while the ionic strength was maintained at 1.0 mol dm^{-3} with sodium perchlorate. The variation of $k_{obs.}$ with acid concentration at different temperatures is illustrated in Figure 2 and the results suggest the operation of two concurrent paths as shown in equation (1), where k_0 is the first-order rate constant for spontaneous aquation and k_H is the second-order rate constant describing the acid-catalysed pathway. Their values at different temperatures, as obtained from the intercepts and slopes of the plots of Figure 2, using a linear regression analysis, are summarised in Table 2 along with the activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, evaluated using the transition-state equation (2).

$$k_{obs.} = k_0 + k_H[H^+] \qquad (1)$$

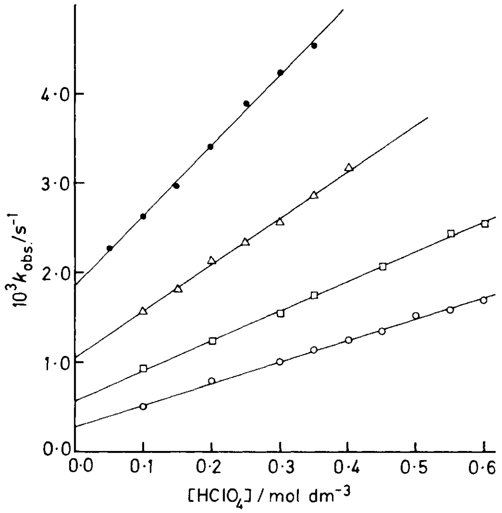
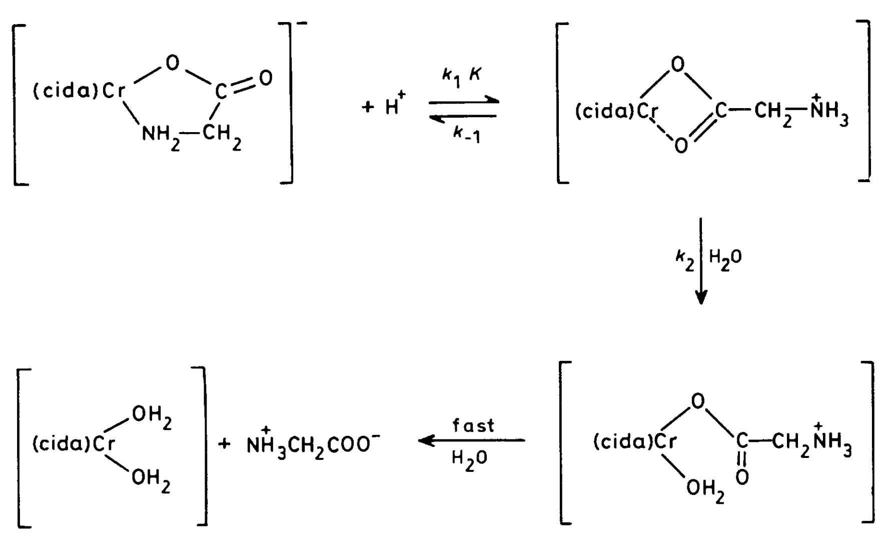


Figure 2. Effect of acid concentration on $k_{obs.}$ at different temperatures: (○) 25, (□) 30, (△) 35, and (●) 40 °C; $[Cr(cida)(glyO)]^- = 0.004$ mol dm^{-3}

$$k = (RT/Nh)\exp(-\Delta H^\ddagger/RT + \Delta S^\ddagger/R) \qquad (2)$$

A sequence of changes consistent with the kinetic results for the acid-catalysed process is depicted in the Scheme. The absence of any deviation from linearity for the $k_{obs.}$ *vs.* $[HClO_4]$ plot, even at the highest acid concentration, suggests two equilibria to lie on the side of the starting complex. The activation parameters corresponding to k_H thus involve both rate and equilibrium constants. Rate constants for the catalysed and uncatalysed amine-terminus aquation for the present system are ten to a hundred times greater than those for amine-terminus aquation of [Cr(cida)(en)] (en = ethylenediamine) and [Cr(cida)(pn)] (pn = propylenediamine) complexes.[11] This behaviour confirms general carboxylate-terminus acceleration of the aquation of bidentate amino acid ligands. The geometry and bifunctional nature of the carboxylate may possibly be regarded as a source of acceleration.



Scheme.

Table 1. Rate data for aquation of the $[Cr(cida)(glyO)]^-$ ion (4.0×10^{-3} mol dm^{-3}), I = 1.0 mol dm^{-3}

$[HClO_4]$/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}			
T/°C =	25.0 ± 0.1	30.0 ± 0.1	35.0 ± 0.1	40.0 ± 0.1
0.05				22.5 ± 0.3
0.10	5.0 ± 0.1	9.3 ± 0.1	15.5 ± 0.2	26.3 ± 0.3
0.15			18.0 ± 0.1	29.5 ± 0.5
0.20	7.8 ± 0.2	12.3 ± 0.1	21.1 ± 0.4	34.0 ± 0.4
0.25			23.3 ± 0.3	38.8 ± 0.3
0.30	10.0 + 0.1	15.2 ± 0.3	25.7 ± 0.3	42.2 ± 0.5
0.35	11.3 ± 0.3	17.4 ± 0.2	28.5 ± 0.5	45.3 ± 0.6
0.40	12.3 ± 0.3		31.5 ± 0.3	
0.45	13.4 ± 0.2	20.5 ± 0.3		
0.50	15.0 ± 0.4			
0.55	15.8 ± 0.3	24.4 ± 0.4		
0.60	16.8 ± 0.3	25.5 ± 0.4		

Table 2. Rate and activation parameters for the aquation of the $[Cr(cida)(glyO)]^-$ ion (I = 1.0 mol dm^{-3})

T/°C	10^4k_0/s^{-1}	10^3k_H/dm^3 mol^{-1} s^{-1}
25.0 ± 0.1	3.0 + 0.1	2.4 ± 0.1
30.0 ± 0.1	5.6 ± 0.15	3.3 ± 0.2
35.0 ± 0.1	10.3 ± 0.2	5.2 ± 0.1
40.0 ± 0.1	18.4 ± 0.25	7.90 ± 0.2
$\Delta H^\ddagger$/kJ mol ^{1}	92 ± 1	61 ± 5
$\Delta S^\ddagger$/J K^{-1} mol^{-1}	−5.2 ± 2.4	−93 ± 8

The protonation and dissociation steps of the amine terminus are proposed to follow a rapid rotation of the amino acid to a carboxylato-*O,O′* bonded configuration. Temporary blocking of the vacated co-ordination site by the carbonyl group facilitates the migration of the amino group from its vicinity. This is followed by the entry of a water molecule at the carbonyl co-ordination site in a rapid step of low activation energy. A similar mechanism may be visualised for the acid-independent process. However, equivalent stabilisation of the vacated co-ordination site is not possible during aquation reactions of corresponding diamine (en or pn) complexes and thus explains the reactivity difference. In a similar fashion, unidentate carboxylates have been shown to induce aquation of ammonia from carboxylato- and substituted carboxylato-penta-ammine-chromium(III) complexes.[12,13] The aquation rate was found to increase with pK_a of the carboxylic acids. Increase in ligand basicity stabilises the carboxylato-*O,O′* configuration and facilitates protonation. In view of the low but crucial order of basicity of the co-ordinated acetato ligand, the alternative pathway for the catalysed reaction may be viewed as a protonation of the carbonyl group of cida in a pre-equilibrium step followed by proton transfer from an acetate ligand to the amine terminus of the bidentate glycinate ligand. Production of a metastable, bidentate glycinato-*O,O′* ligand configuration in the rate-determining step seems to explain the amine-terminus aquation in the first step of the reaction. It is interesting that the rate constants and activation parameters for the complex $[Cr(cida)(glyO)]^-$ (Table 2) compare well with those reported for amine-terminus aquation of $[Cr(ox)_2(NH_2CH_2CO_2)]^{2-}$ (ox = oxalate) and thio-terminus aquation of $[Cr(en)_2(SCH_2CO_2)]^+$ respectively, k_H (25 °C, I = 1.0 mol dm^{-3}) = (1.11—1.57) × 10^{-3} dm^3 mol^{-1} s^{-1}, $\Delta H^\ddagger$ = 16.2—17.0 kcal mol^{-1}, and $\Delta S^\ddagger$ = 17.6 to −14.5 cal K^{-1} mol^{-1}.[6,14] This reveals that the parameters show little dependence on the nature and charge of the complexes as well as on the nature of the leaving group. Hence it can be concluded that the cardinal feature in determining the reactivity of mixed-ligand carboxylate complexes of chromium(III) rests on the potential which the carboxylate ligands possess to assume a metastable, bidentate carboxylato-*O,O′* configuration.

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