Reactivity of Co-ordinated Amino-acids. Part 2.[1] The Role of an Uncharged Intermediate in the Carbon-14-labelled-ligand-exchange Studies on the *trans*(*fac*)-Bis(*N*-methyliminodiacetato)chromate(III) Anion

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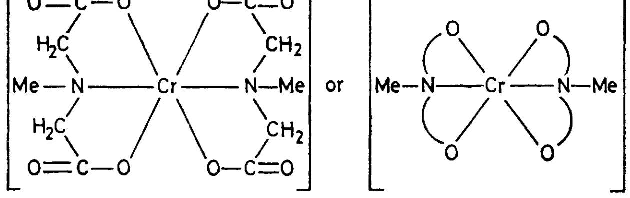
The rate of exchange of *trans*(*fac*)-bis(*N*-methyliminodiacetato)chromate(III) with free ligand which has been labelled with ^{14}C has been studied at 50 °C, and $c_{H^+} = 5.7 \times 10^{-5}$—$1.59 \times 10^{-2}$ mol dm^{-3}, and shown to be dependent on the hydrogen-ion concentration. A mechanism involving partial aquation of one of the ligands followed by re-anation has been shown to account for essentially the whole of the observed ligand-exchange rate implying that direct bimolecular exchange is negligible. The contributing rate parameters at 50 °C have been calculated. Confirmation of the mechanism is provided by an anation study of triaqua(*N*-methyliminodiacetato)-chromium(III) perchlorate at 50 °C. An uncharged intermediate in the aquation–anation equilibrium has been isolated and equilibrium constants involving the three species in solution are evaluated at 25 °C.

We recently studied [1] the carbonyl- and carboxyl-oxygen exchange of *trans*(*fac*)-bis(*N*-methyliminodiacetato)-chromate(III), $[Cr(mida)_2]^-$ (1), with ^{18}O-labelled solvent



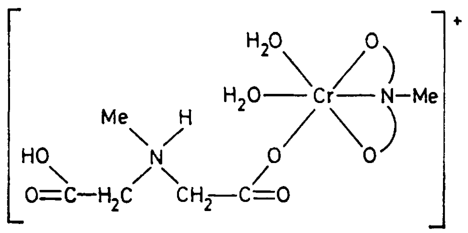
(1)

water and postulated a mechanism involving acid-dependent and acid-independent paths, both of which involve a one-ended dissociated species. This species was not isolated.

Evidence for dechelated intermediates in the acid-catalysed aquation of *cis*-bis(iminodiacetato)chromate(III), $[Cr(ida)_2]^-$, and of (1) has been reported by Weyh and Hamm [2] who separated the 1+ forms of these intermediates on cation resin columns. The products of aquation, namely $[Cr(ida)(OH_2)_3]^+$ and $[Cr(mida)(OH_2)_3]^+$, are also charged and this makes difficult the effective separation of these products. The reported [2] absorption spectrum of the protonated intermediate in the case of aquation of $[Cr(ida)_2]^-$ was indeed found to be very similar to that of the triaqua-product but with slightly higher absorption coefficients. The experimental evidence for a monoprotonated intermediate in the case of the methyl derivative, $[Cr(mida)_2]^-$, is somewhat more tentative but its structure was postulated [2] by analogy with the $[Cr(ida)_2]^-$ system as (2), *i.e.* it is the product of cleavage of both Cr–O and Cr–N bonds in (1).

Further evidence in favour of a one-ended dissociated intermediate was presented [1] in our ^{18}O-exchange studies on (1), in which the equivalence of rates of exchange of all the eight oxygen atoms require dechelation of the ligand molecule. We formulated intermediates for acid-dependent and acid-independent paths and postulated a formulation in which the Cr–N bond remained intact.

It is frequently found that a Cr^{III}–O chelate bond is labile whilst a Cr^{III}–N bond is inert. Thus ^{18}O-exchange studies between $H_2{}^{18}O$ and the tris(oxalato)chromate(III) anion and between $H_2{}^{18}O$ and oxalic acid showed comparable results,[3] indicating that 'one-ended dissociation' of a Cr–O bond was rapid compared with the rate-determining addition of water. By contrast, hexa-amminechromium(III) does not exchange its nitrogen ligands with $^{15}NH_3$ in solution,[4] and only very slowly with liquid $^{15}NH_3$ at 20 °C.[5] Penta-ammineaniono-complexes of Cr^{III} usually undergo initial aquation of the aniono-group,[6,7] but a study [8] of a series of variously substituted acetatopenta-amminechromium(III) complexes showed that NH_3 substitution by water was the primary step with progressive strengthening of the Cr–O bond and weakening of the Cr–N bond *cis* to the carboxylate, consistent with hydrogen bonding between the carbonyl oxygen and adjacent H atoms of an ammonia ligand. Similarly, a nitrate group co-ordinated to Cr^{III} activates ammine ligands in the *cis* position toward aquation.[9]



(2)

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[1] Part 1, S. Dutta-Chaudhuri, C. J. O'Connor, and A. L. Odell, *J.C.S. Dalton*, 1975, 1921.

[2] J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, 1968, **7**, 2298.

[3] C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. J. O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 1964, 4615.

[4] D. R. Llewellyn, C. J. O'Connor, and A. L. Odell, *J. Chem. Soc.*, 1964, 196.

[5] T. W. Swaddle, LaV. F. Coleman, and J. P. Hunt, *Inorg. Chem.*, 1963, **2**, 950.

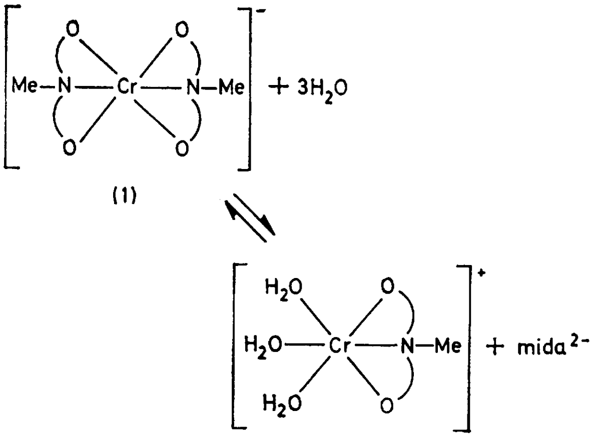
[6] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.

[7] C. S. Garner and D. A. House, *Transition Metal Chem.*, 1970, **6**, 59.

[8] E. Zinato, C. Furlani, G. Lanna, and P. Riccieri, *Inorg. Chem.*, 1972, **11**, 1746.

[9] G. Gunstalla and T. W. Swaddle, *J.C.S. Chem. Comm.*, 1973, 61.

Thus the requirement for activating cleavage of a Cr^{III}–N bond seems to be bonding from a hydrogen on the N atom to an oxygen on the ligand *cis* to it. In $[Cr(ida)_2]^-$ each NH group has four *cis*-acetato-groups and thus a structure analogous to (2) [2] might well be formed through a mechanism involving hydrogen bonding. In the present $[Cr(mida)_2]^-$ system, however, hydrogen bonding is not possible and the Cr^{III}–N bond is likely to be less labile.

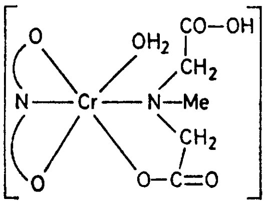


Scheme 1

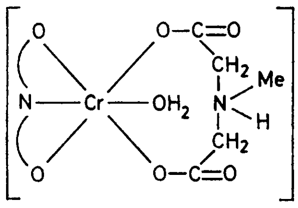
Our ^{18}O-exchange studies [1] established the presence of an equilibrium between (1) and its aquation product $[Cr(mida)(OH_2)_3]^+$ (3), as in Scheme 1. We will show that this equilibrium is important in formulating the ligand-exchange reaction.

RESULTS AND DISCUSSION

While reinvestigating the aquation of $[Cr(mida)_2]^-$ we have developed a method of separating an intermediate other than (2). The method of separation, which uses a cation resin, indicates that the intermediate is not positively charged. The experiment was made at pH 2 and it is unlikely that any dechelated species would remain unprotonated under these acid conditions. Unchanged (1) was eluted from the column and precipitated as its insoluble potassium salt. We therefore conclude that the remaining eluate, which contained 7% of the total chromium and was coloured, consists of chromium(III) species of zero charge. Two possibilities exist, (4a) and (4b).



(4a)



(4b)

Comparative visible spectra of the initial anion (1), the intermediate (4), and the triaqua-product (3) are in Figure 1 where it may be seen that, in contrast to earlier reports [2] on the $[Cr(ida)_2]^-$ system, the spectrum of the intermediate is significantly different from that of the triaqua-product. This leads us to believe that the Cr^{III}–N bond remains intact in this intermediate, and we favour structure (4a). The absence of hydrogen-bonding opportunities in (1) also leads to the prediction that (4b) is unlikely to be formed. Further protonation and hydrolysis of (4a) might then lead to the breaking of the Cr^{III}–N bond leading to formation of (2).[2] We established that our intermediate is transient in nature (see Experimental section). It is also clear that it is formed quite rapidly during the aquation of (1) (see above) and in the anation of (3) (see spectroscopic evidence below) in significant amounts. Any (2) which was formed during our identification experiment would have been held on the cation-exchange resin together with the product (3).*

Kinetics of $[^{14}C]$*-Labelled-ligand-exchange Studies of* $[Cr(mida)_2]^-$.—Preliminary studies on the rates of ligand exchange of (1) with $[^{14}C]H_2mida$ showed these to be comparable to rates of aquation of (1) and anation of (3). It is clear that meaningful determinations of rates of ligand exchange must be made under aquation equilibrium conditions so that concentrations of (1) and (3) will remain steady. These conditions were achieved by allowing a solution containing (1) and 95% of the desired amount of unlabelled free ligand to reach equilibrium and then adding the remaining 5% of the H_2mida in ^{14}C-labelled form.

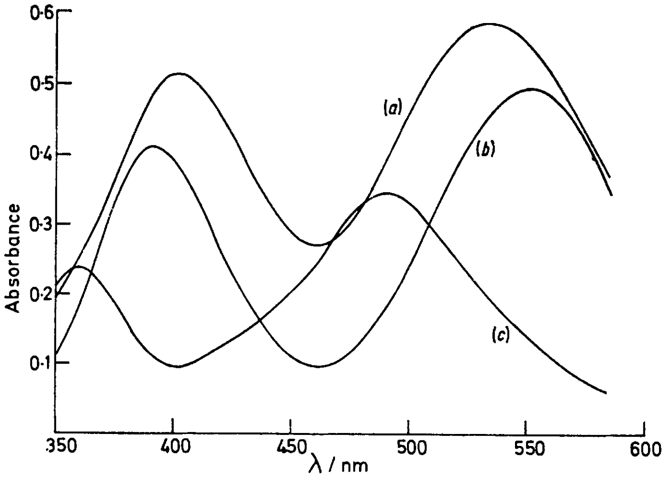


Figure 1 Visible absorption spectra of (a) 0.0085 mol dm^{-3} $[Cr(mida)(Hmida)]$, (b) 0.0084 mol dm^{-3} $[Cr(mida)(OH_2)_3]^+$, and (c) 0.0083 mol dm^{-3} $[Cr(mida)_2]^-$

Under these conditions plots of $-\log_{10}(1 - F)$, where F is the fraction exchanged, against time were linear for at least three half-lives. A typical plot is in Figure 2.

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* A full study of the anation of (3) is proceeding and will include a search for (2) using Sephadex columns. Species (2) differs from each of species (1) and (4a) by only one water molecule and one proton, and recently A. T. Thornton, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, 1976, 147, have achieved effective separation of the chromium(III) complexes, $[Cr(OH_2)_4(O_2CC_6H_4CO_2)]^+$ and $[Cr(OH_2)_5(O_2CC_6H_4CO_2H)]^{2+}$, which also differ only by one water molecule and one proton, by using Sephadex separation techniques.

TABLE 1

Calculated and experimental rates of exchange of *trans*(*fac*)-bis(*N*-methyliminodiacetato)chromate(III) anion and [^{14}C]methyliminodiacetic acid [a]

$10^2[Cr(mida)_2^-]$ [b]	$10^3[Cr(mida)(OH_2)_3^+]$ [c]	$10^4c_{H^+}$ [d]	c_{H_2mida} [e]	10^2c_{Hmida} [f]	10^7R/mol dm^{-3} s^{-1} Obs.	10^7R/mol dm^{-3} s^{-1} Calc.
5.0		0.57	0.10		0.433	
5.0	0.5 [g]	2.40	0.10	9.68	1.13	1.85
5.0	0.9	4.80	0.10	9.50	1.80	1.84
5.0	2.2	7.59	0.10	9.37	2.91	3.15
5.0	4.0	12.3	0.10	8.89	3.75	4.58
5.0	6.0	15.5	0.10	8.73	5.02	5.30
5.0	7.4	20.4	0.10	8.38	4.93	5.63
5.0	13.0	37.1	0.10	7.47	7.77	7.78
5.0	16.0	47.8	0.10	7.00	9.08	9.12
5.0	24.0	85.1	0.10	5.70	12.0	11.9
5.0	29.0	115	0.10	5.00	15.0	14.5
5.0	33.0	159	0.10	4.18	16.4	16.5
5.0	1.5 [g]	5.89	0.05	4.80	1.55	1.32
5.0	1.5 [g]	5.89	0.25	18.8	4.92	5.15
5.0	1.5 [g]	5.89	0.30	28.0	7.85	7.68
5.0	1.5 [g]	5.89	0.40	37.2	9.86	10.2
5.0	2.2	7.94	0.15	13.7	4.02	4.45
2.5		5.89	0.10		1.08	
7.5		5.89	0.10		3.10	
5.0 [h]		47.8	0.10		32.1	
5.0 [i]		47.8	0.10		93.9	

[a] At 50 °C unless stated otherwise; all concentrations are in mol dm^{-3}. [b] Initial added concentration. [c] Calculated from absorbance at 480 nm unless stated otherwise. [d] Measured after attainment of equilibrium and final adjustment. [e] Initial added concentration of [^{14}C]ligand. [f] Calculated from K_1 of H_2mida. [g] Obtained from interpolation of plot of $[Cr(mida)(OH_2)_3^+]$ against c_{H^+}. [h] At 65 °C. [i] At 80 °C.

Rates of exchange, R, were calculated using a modified McKay[10] equation (1) where c_L and c_1 represent the total

$$R = [2c_1c_L/(2c_1 + c_L)]0.693/t_{\frac{1}{2}} \tag{1}$$

concentration of free ligand and complex (1) respectively and t = time. Rates of exchange under a variety of

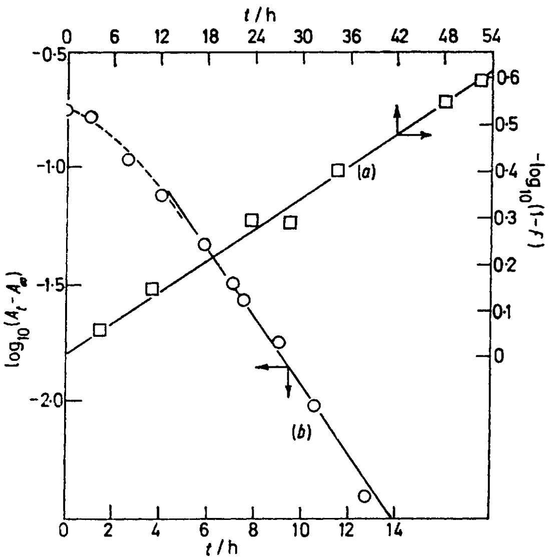

FIGURE 2 Plots showing (*a*) the rate of exchange of 5.0 × 10^{-2} mol dm^{-3} $[Cr(mida)_2]^-$ with 0.10 mol dm^{-3} [^{14}C]H_2mida (initial concentrations) and (*b*) the anation of 4.0 × 10^{-3} mol dm^{-3} $[Cr(mida)(OH_2)_3]^+$ with 10.4 × 10^{-2} mol dm^{-3} H_2mida at pH 2.91 and 50 °C

conditions are detailed in Table 1. Also shown are equilibrium concentrations of (3) (calculated from absorbances at 480 nm and using the molar absorption coefficients given in Table 2) and of Hmida$^-$ (calculated from pK_1 2.15 for H_2mida[11] and using pH measured after attainment of equilibrium).

TABLE 2

Molar absorption coefficients of $[Cr(mida)_2]^-$, [Cr(mida)(Hmida)], and $[Cr(mida)(OH_2)_3]^+$ at wavelengths of the isosbestic points

λ/nm	ε/dm^3 mol^{-1} cm^{-1} $[Cr(mida)_2]^-$	ε/dm^3 mol^{-1} cm^{-1} [Cr(mida)(Hmida)]	ε/dm^3 mol^{-1} cm^{-1} $[Cr(mida)(OH_2)_3]^+$
480	39.0	39.5	15.4
560	13.6	59.0	57.0

A plot of R at fixed initial concentrations (c_1 = 5.0 × 10^{-2} mol dm^{-3}, c_{H_2mida} = 0.10 mol dm^{-3}) against c_{H^+} showed a non-linear dependence, and curved downwards at high acidity in a manner analogous to that of the dependence of the equilibrium concentration of (3) on c_{H^+}. Plots of $k_{obs.} = R/c_3c_{Hmida}$ against c_{H^+} (*a*) and against $1/c_{H^+}$ (*b*) are shown in Figure 3. These results are consistent with a rate law of the form (2) which is identical to

$$R = [(k_0'/c_{H^+}) + k_1 + k_2'c_{H^+}]c_3c_{Hmida} \tag{2}$$

the rate law one would postulate for anation of complex (3) if this latter reaction were to occur through the presence of H_2mida, Hmida$^-$, and mida^{2-} whose respective concentrations are dependent on acidity. Thus the anation rate may be represented as (3) which reduces to

$$R(\text{anation}) = (k_0c_{mida} + k_1c_{Hmida} + k_2c_{H_2mida})c_3 \tag{3}$$

(2) if $k_0' = k_0K_2$ and $k_2' = k_2/K_1$ where K_1 and K_2 are the first and second acid-dissociation constants[11] of

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[10] H. A. C. McKay, *Nature*, 1938, **142**, 997.

[11] N. E. Ockerbloom and A. E. Martell, *J. Amer. Chem. Soc.*, 1956, **78**, 267.

H_2mida. Values for k_1 were obtained from the intercepts of curves (*a*) and (*b*) (Figure 3) using a least-squares procedure and gave $k_1 = 4.67 \times 10^{-4}$ and 4.00×10^{-4} dm^3 mol^{-1} s^{-1} respectively (weighted mean = 4.17 dm^3 mol^{-1} s^{-1}). From the gradients of the asymptotes, $k_0' = 8.2 \times 10^{-7}$ s^{-1} and $k_2' = 4.43 \times 10^{-2}$ dm^6 mol^{-2} s^{-1}.

Substituting these values and the equilibrium concentrations of complex (3) and Hmida$^-$ into equation (2) gives us the calculated values of R quoted in the last column of Table 1. The agreement with the observed rates, while not excellent, supports the proposed kinetic form and we may infer that the exchange reaction proceeds through anation of the triaqua-species. This was confirmed by a limited study of the anation of (3) under identical experimental conditions to those of the exchange reactions.

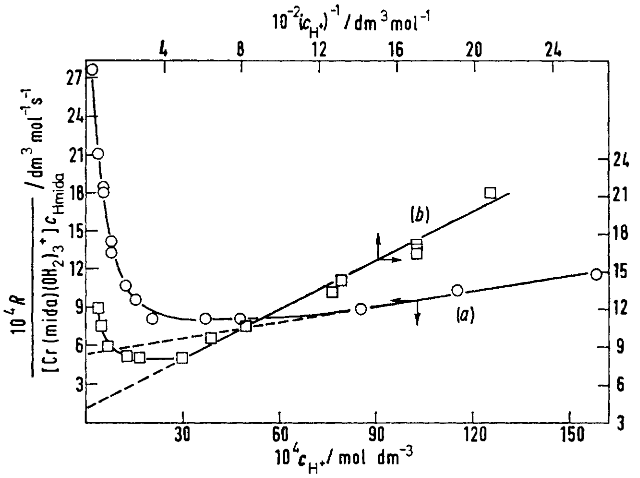
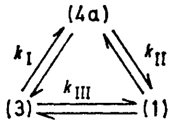


FIGURE 3 Dependence of rate of [^{14}C]ligand exchange of [Cr(mida)$_2$]$^-$ divided by [Cr(mida)(OH$_2$)$_3$$^+$] × c_{Hmida} on (*a*) hydrogen-ion concentration, and (*b*) [H$^+$]$^{-1}$

Anation Rate Studies of [Cr(mida)(OH$_2$)$_3$]$^+$.—Solutions for these rate studies were made up as follows. The triaqua-complex (3) was present in a concentration equal to that found at aquation equilibrium as detailed in Table 1. The H_2mida concentration was made equal to the sum of that used in studies of the ligand-exchange rate and the concentration of the acid liberated when the aquation proceeds to the same equilibrium position, *i.e.* equal to c_{H_2mida}(initial) + c_3. After adjusting the pH, optical-density changes at 50 °C were followed at 560 nm. At this wavelength (3) and any intermediate (4) which might be formed during the anation reaction have the same molar absorption coefficients (Table 2). Thus in the reaction shown in Scheme 2 we are measuring the total rate of formation of complex (1) whether it occurs through (4a) or directly from (3). A typical plot of $\log_{10}(A_t - A_\infty)$ against t, where A and t are the absorbance and time respectively, is given in Figure 2.



SCHEME 2

This kinetic run was made under identical conditions to the exchange run shown in the same Figure. For *ca.* 1 half-life of reaction the plot is curved and then remains linear for the next 2—3 half-lives. From the linear portion the rates for formation were calculated and are presented in Table 3. They agree well with the rate at which [^{14}C]ligand appears in complex (1). Other data are given in Table 3, and this trend appears to be generally true. The initial curvature we observe indicates that the path involving k_{II} is dominant, and that the formation of a steady-state concentration of (4) controls the rate. Preliminary investigations at 480 nm show that k_I is very comparable to k_{II}, and a full investigation of the effects of concentration of complex, ligand, and hydrogen ions on the anation reaction is in hand. This present study has shown that in contrast to the [^{14}C]ligand exchange of [Cr(O$_4$C$_2$)$_3$]$^{3-}$, which occurred primarily by a bimolecular mechanism with only a small contribution

TABLE 3

Comparison of rate constants of anation of [Cr(mida)(OH$_2$)$_3$]$^+$ by H_2mida at 50 °C with rate constants of exchange of [Cr(mida)$_2$]$^-$ with [^{14}C]H_2mida (corrected to first-order values) under identical experimental conditions

10^3[Cr(mida)(OH$_2$)$_3$$^+$]/ mol dm^{-3}	2.2	4.0	6.0	7.4
$10^2c_{H_2mida}$/mol dm^{-3}	10.22	10.40	10.60	10.74
$10^3c_{H^+}$/mol dm^{-3}	0.76	1.23	1.55	2.04
10^5k(anation)/s^{-1}	12.8	9.38	8.37	6.66
10^5k(exchange) * [Cr(mida)-(OH$_2$)$_3$$^+$]$^{-1}$/s^{-1}	13.6	9.38	8.37	6.66

* From Table 1.

from a parallel aquation–re-anation path,[12] in the present system the whole of the ligand-exchange rate may be ascribed to a process of aquation and re-anation of the complex in a reversible reaction involving the formation of an uncharged intermediate, and we may infer that any contribution to [^{14}C]ligand exchange by direct nucleophilic attack on either [Cr(mida)$_2$]$^-$ or its aquation product [Cr(mida)(OH$_2$)$_3$]$^+$ is negligible.

This difference provides yet another interesting illustration of the effect on reactivity of chromium(III) complexes when the chelating ligands are changed from dianiono-derivatives to amino-acid aniono-derivatives. We have already shown that introduction of the more robust chromium(III)–nitrogen link allowed the ^{18}O exchange of (1) with solvent water to take place by an acid-independent path, and this contrasted markedly with the results observed for the chromium(III) oxalato-systems [3] where ^{18}O exchange with water requires acid.

TABLE 4

Distribution of [Cr(mida)$_2$]$^-$, [ML$_2$], [Cr(mida)(Hmida)], [ML(HL)], [Cr(mida)(OH$_2$)$_3$]$^+$, [ML], H$_2$mida (H$_2$L), and Hmida$^-$ (HL) [a] and some equilibrium constants in a solution of total complex concentration = 2 × 10^{-3} dm^{-3}, pH = 3.05, and at 25 °C

$10^2c_{(\mathrm{H_2L}+\mathrm{HL})}$	10^2c_{HL}	10^4c_{ML}	$10^4c_{\mathrm{ML(HL)}}$	$10^4c_{\mathrm{ML_2}}$	$\frac{10^3K'}{\text{mol dm}^{-3}}$ [b]	$\frac{\beta_{\mathrm{H}}}{\text{dm}^3\text{ mol}^{-1}}$ [c]
8	7.12	6.83	2.40	10.7	4.46	4.93
14	12.5	4.72	2.92	12.4	4.24	4.96
20	17.8	3.46	3.26	13.3	4.08	5.29
25	22.3	2.62	3.85	13.5	3.50	6.60

[a] All concentrations in mol dm^{-3}. [b] $K' = c_{\mathrm{ML_2}}c_{\mathrm{H}}/c_{\mathrm{ML(HL)}}$. [c] $\beta_{\mathrm{H}} = c_{\mathrm{ML(HL)}}/(c_{\mathrm{ML}}c_{\mathrm{HL}})$.

In view of the importance of the intermediate (4) and of the aquation–re-anation equilibrium in the ligand-exchange process, we attempted to estimate the magnitude of the constants involved in defining the precise positions of the individual equilibria in Scheme 2. Due to the nature and magnitude of the spectral changes involved, such a procedure can at best be only semi-quantitative.

Spectrophotometric Determination of Equilibrium Constants involved in Formation of [Cr(mida)$_2$]$^+$.—We concluded from spectral evidence of products that a solution of [Cr(mida)$_2$]$^-$, [ML$_2$], on aquation reaches an equilibrium with the dechelated intermediate [Cr(mida)(Hmida)], [ML(HL)], and [Cr(mida)(OH$_2$)$_3$]$^+$, [ML], and have shown from kinetic evidence that the anation of [ML] to [ML$_2$] goes through the intermediate formation of [ML(HL)]. Table 2 shows that an isosbestic point exists at 480 nm between [ML(HL)] and [ML$_2$] and at 560 nm between [ML(HL)] and [ML]. The values of ϵ at these wavelengths were calculated from Figure 1.

We analysed spectrophotometrically solutions of [ML] (initial concentration = 2 × 10^{-3} mol dm^{-3}) which were allowed to come to equilibrium with H$_2$mida (H$_2$L) (0.08—0.25 mol dm^{-3}) at 25 °C and pH 3.05. At this pH any free ligand would exist as *ca.* 90% Hmida$^-$ (HL) and 10% H$_2$L. Since K_2 for H$_2$L is 10^{-10} mol dm^{-3},[11] the contribution from mida^{2-} (L) would be small. (Charges on the species involved have been omitted in the equations which follow.)

At the two isosbestic points of 480 and 560 nm and using the molar absorption coefficients given in Table 2, we have the relations (4)—(6). Using equations (4)—(6)

$$15.4\ c_{\mathrm{ML}} + 39.5\ c_{\mathrm{ML(HL)}} + 39.0\ c_{\mathrm{ML_2}} = A_{480}/d \quad (4)$$

$$57.0\ c_{\mathrm{ML}} + 59.0\ c_{\mathrm{ML(HL)}} + 13.6\ c_{\mathrm{ML_2}} = A_{560}/d \quad (5)$$

$$c_{\mathrm{ML}} + c_{\mathrm{ML(HL)}} + c_{\mathrm{ML_2}} = 0.002 \quad (6)$$

we calculated the concentrations of each of the three species containing M present at equilibrium and thereby calculated the formation constant, β_{H}, and equilibrium constant, K', for reactions (7) and (8). Results are given in Table 4.

$$[\mathrm{ML}] + \mathrm{HL} \overset{\beta_{\mathrm{H}}}{\rightleftharpoons} [\mathrm{ML(HL)}] \quad (7)$$

$$[\mathrm{ML(HL)}] \overset{K'}{\rightleftharpoons} [\mathrm{ML_2}] + \mathrm{H} \quad (8)$$

Measurements were made over a limited concentration range and the lowest concentration limit of added ligand was imposed by the necessity for pseudo-first-order conditions, *i.e.* the formation of [ML(HL)] or [ML$_2$] from [ML] did not affect the total concentration of free ligand and hence alter the pH during establishment of equilibrium. The calculations were made from small changes in small absorbances; thus at 480 and 560 nm the total change in absorbance in the equilibrium solutions we used was 0.062—0.072 and 0.068—0.056 units respectively. Although the values of K' and β_{H} are only approximate, they do indicate relative orders of magnitude for these constants. A full anation study, which is in hand, will help to clarify the kinetic importance of these paths.

Effect of Temperature on the [^{14}C]*Ligand-exchange Studies*.—Values of R observed at 50, 65, and 80 °C for the ligand exchange of $c_1 = 5 \times 10^{-2}$ mol dm^{-3} with $c_{\mathrm{H_2mida}} =$ 0.10 mol dm^{-3} at $c_{\mathrm{H^+}} = 47.8 \times 10^{-4}$ mol dm^{-3} are given in Table 1. The constant K_1 of H$_2$mida is virtually independent of temperature in the range 0—40 °C.[11] We therefore measured the pH at 50 °C and assumed that variation in these values with temperature and also a small variation in the equilibrium position will not significantly affect our calculations of activation parameters using the Eyring equation.[13] This led to $\Delta H^\ddagger =$

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[12] D. R. Llewellyn, C. J. O'Connor, A. L. Odell, and R. W. Olliff, *J. Chem. Soc.*, 1964, 4627.

[13] S. Glasstone, K. J. Laidler, and H. Eyring, 'The Theory of Rate Processes,' McGraw-Hill, New York, 1941.

84.0 kJ mol^{-1} and $\Delta S^\ddagger = -16.3$ J K^{-1} mol^{-1}. These are composite values embodying contributions from rate constants k_0', k_1, and k_2', but the value of $\Delta H^\ddagger$ differs considerably from the approximate value of 53 kJ mol^{-1} evaluated from the [^{14}C]ligand exchange [12] of the tris(oxalato)chromate(III) anion.

EXPERIMENTAL

Materials.—Sodium *trans*(*fac*)-bis(*N*-methyliminodiacetato)chromate(III), Na[Cr(mida)$_2$], triaqua(*N*-methyliminodiacetato)chromium(III) perchlorate, [Cr(mida)(OH$_2$)$_3$][ClO$_4$], and *N*-methyliminodiacetic acid, H$_2$mida, were prepared and analysed as previously described.[1] [^{14}C]H$_2$mida was prepared according to the literature [14] but using [^{14}C]methylamine. The product was diluted with H$_2$mida before use so that its silver salt gave a specific activity of *ca.* 360 disintegrations min^{-1} mg^{-1} as measured in a Geiger–Müller counter. Other reagents were AnalaR or were purified before use.

Apparatus.—pH Measurements were made on a Radiometer (Copenhagen) 4 pH meter. The pH of anation reactions was a controlled by a Radiometer Titrator TTT2 (Copenhagen). Stability-constant calculations were made from spectra obtained on a Shimadzu QV 50 spectrophotometer. The extent of aquation in the exchange studies and calculation of the equilibrium constants were obtained from visible spectra recorded on a Cary 14 spectrophotometer. Anation studies were made on a Varian Techtron 635 spectrophotometer using cells thermostatted by use of a Grant Thermocirculator. Exchange studies were made in stoppered flasks in a Grant water-bath at 50 ± 0.1 °C or in sealed ampoules in oil-baths at 65 and 80 °C. The temperature was maintained at ±0.1 °C by using a Gallenkamp contact thermometer, Klaxon stirrer, and heating element. Carbon-14 specific activities were measured in Geiger–Müller or liquid-scintillation counters.

Isolation of an Uncharged Intermediate in the Acid-catalysed Aquation of [Cr(mida)$_2$]$^-$.—A solution of [Cr(mida)$_2$]$^-$ (5×10^{-2} mol dm^{-3} at pH 2.0) was held at *ca.* 90 °C for 1 h, long enough for attainment of hydrolytic equilibrium under the conditions used. The solution was then cooled and passed down a column of Dowex 50-WX8 resin in the sodium form, followed by an equal volume of cold water, and the eluate was collected and stored at 0 °C. This procedure removed the triaqua-product quantitatively while the starting material was removed from the eluate by precipitating it as its potassium salt (which has a low solubility) by adding excess of solid potassium chloride. The supernatant liquid was coloured and contained *ca.* 7% of the initial amount of chromium present. Examination of its absorption spectrum showed peaks substantially shifted from those of the triaqua-product as shown in Table 5 (along with data from ref. 2 for comparison).

TABLE 5

Details of wavelengths (λ/nm) and absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) for spectra of various chromium(III) complexes

	$\lambda_{max.}(1)$	$\epsilon_{max.}(1)$	$\lambda_{min.}$	$\epsilon_{min.}$	$\lambda_{max.}(2)$	$\epsilon_{max.}(2)$
trans-[Cr(mida)$_2$]$^-$	363	28	405	11.6	493	42
Intermediate	403	60.2	460	31.3	537	68.8
[Cr(mida)(OH$_2$)$_3$]$^+$	393	48.4	462	11.0	555	59.4
cis-[Cr(ida)$_2$]$^-$ *	391	79	442	26	519	76
Intermediate *	394	64	461	15	543	76
[Cr(ida)(OH$_2$)$_3$]$^+$ *	393	50	460	13	564	60

* From ref. 2.

After precipitating excess of potassium ions with sodium perchlorate, the solution was allowed to stand overnight at room temperature when optical densities had decreased markedly, establishing the transient nature of this chromium species.

Determination of the Formation Constant of [Cr(mida)$_2$]$^-$.—The ligand H$_2$mida was dissolved in a solution of [Cr(mida)(OH$_2$)$_3$]$^+$ and the mixture was titrated pH-metrically to pH 3.05 before dilution to 50 cm^3. The initial concentration of complex was 2×10^{-3} mol dm^{-3}, and that of H$_2$mida was in the range 0.08—0.25 mol dm^{-3}. The solutions were thermostatted at 25 °C for 100 h before spectrophotometric analysis in the range 350—560 nm. During this time the pH remained constant.

Carbon-14 *Exchange Studies*.—Solutions of Na[Cr(mida)$_2$] and of H$_2$mida (containing 95% of the total required concentration) were mixed, diluted to nearly total volume, and the pH was adjusted to approximately the required value. After establishment of the equilibrium between [Cr(mida)$_2$]$^-$ and [Cr(mida)(OH$_2$)$_3$]$^+$ at 50 °C (this was monitored until the absorption spectrum remained constant), the remaining 5% of [^{14}C]H$_2$mida was added and a final adjustment was made to the pH by addition of not more than 0.4 cm^3 of 0.3 mol dm^{-3} HCl or Na[OH] which had been equilibrated at 50 °C. The pH was monitored throughout each run and was found to be invariant. Two aliquot samples were withdrawn immediately, one for determining the specific activity of the complex at zero time and the other for evaluating spectrophotometrically the extent of aquation. Samples (5 cm^3) were removed at time intervals, and the complex was separated from the free ligand by precipitation as insoluble K[Cr(mida)$_2$] by addition of K[NO$_3$]. The precipitate was washed and was not contaminated by either the soluble [Cr(mida)(OH$_2$)$_3$]$^+$ cation or free ligand, even in the presence of a large excess of free ligand (Found: C, 31.5; H, 3.7. Calc. for $C_{10}H_{14}CrKN_2O_8$: C, 31.5; H, 3.65%).

The effective specific activity was too low to use a Geiger–Müller counter, and was therefore measured using liquid-scintillation techniques. The powdered sample (20 ± 2 mg) was suspended in a gel of Aerosil Cab-O-sil (Hoescht, Germany) in a counting bottle and the contents were uniformly mixed. To this was added scintillation fluid [20 cm^3, made by dissolving 2,5-diphenyloxazole (6 g, Koch-Light) and 1,4-bis(phenyloxazol-2-yl)benzene (0.1 g, Koch-Light) per litre of scintillation-grade toluene (Baker)] and the mixture was uniformly mixed. In runs containing a high acid concentration and therefore a large degree of aquation it was not possible to analyse 20 mg of sample. In these cases the specific activity was corrected from a colour-quench calibration curve of disintegrations min^{-1} mg^{-1} against the weight of sample (mg).

The specific activity of Ag$_2$[mida] (*ca.* 68 disintegrations min^{-1} mg^{-1}) was determined similarly and infinite time values were generally calculated from equation (9). The

$$\text{disintegrations min}^{-1}\,\text{mg}^{-1}\text{ at } t_\infty = \left(\frac{\text{weight of [}^{14}\text{C]H}_2\text{mida}}{\text{total weight of complexed and free mida}}\right) \times \text{specific activity of [}^{14}\text{C]Ag}_2\text{[mida]} \times 1.81 \quad (9)$$

correction factor of 1.81 was necessary because the specific activity of K[Cr([^{14}C]mida)$_2$] was 1.81 times higher than that of Ag$_2$[mida] obtained from the same sample after decomposition of the complex and precipitation of the ligand

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[14] G. J. Bershet, *Org. Synth.*, 1938, **18**, 56.

as the silver salt. Values calculated thus and those measured on a sample which had been allowed to react for 10 half-lives agreed within $<1\%$. All counting samples were prepared in the absence of diffused light and counted to 1% standard deviation.

Carbon-14 exchange studies were followed in the range pH 4.25—1.80 at 50 °C. At higher pH the rates were very slow and at lower values almost complete aquation occurred. Half-times of reaction, $t_{\frac{1}{2}}$, calculated from McKay plots[10] of $-\log_{10}(1-F)$ against t were used to calculate the rates of exchange R from equation (10), where a and b are the concentrations of free and complexed mida^{2-}. The error in the estimate of R is $\pm 2\%$. Limited data were also obtained at 65 and 80 °C.

$$R = \left(\frac{ab}{a+b}\right)\cdot\frac{0.693}{t_{\frac{1}{2}}} \tag{10}$$

Kinetics of Anation at 50 °C.—The required volume of $[Cr(mida)(OH_2)_3][ClO_4]$ solution was added to a solution containing a weighted amount of H_2mida. All the solutions and equipment were allowed at least 45 min to attain temperature equilibrium before mixing. The pH was adjusted to the required value by addition of 0.5 mol dm^{-3} Na[OH] and maintained at this pH ± 0.005 using a Radiometer pH-stat–titrator, based on the pH meter 22. In order to avoid precipitation of $K[Cr(mida)_2]$ as the reaction proceeded because of continuous contact of the calomel electrode with the reaction solution, a modified Laitinen salt bridge,[15] containing 1 mol dm^{-3} $Na[ClO_4]$ and NaCl sealed within a U tube by two small (diameter 0.4—0.6 cm), porosity 4, sintered-glass discs, was used to connect the saturated calomel electrode to the glass electrode. Diffusion of Na[OH] from the injecting tube due to continuous immersion was eliminated by use of a plunging device which only operated the injector when the pH fell below the set value. Dilution effects caused by additionof Na[OH] solution were minimised by using a relatively concentrated solution. Throughout a run no more than 0.5 cm^3 Na[OH] per 50 cm^3 of reaction solution was added. Aliquot samples were withdrawn with a syringe and transferred to a dry equilibrated cell. Changes in the visible spectra were recorded as a function of time. The reference cell contained water. Pseudo-first-order rate constants of anation k_ψ were calculated from a plot of $\log_{10}(A_t - A_\infty)$ against t, where A_t and A_∞ are absorbances at 560 nm at times t and infinity respectively. 'Infinite' absorption measurements were made 12—24 h after commencement of the reaction depending on the hydrogen-ion concentration. These readings were checked intermittently for constancy. Each experimental run was duplicated and the error in the estimate of k_ψ was $\pm 2\%$.

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[15] K. A. Laitinen, *Ind. and Eng. Chem. Analyt. Edn.*, 1941, **13**, 393.