Reactivity of Co-ordinated Amino-acids. Part I. Oxygen-18 Exchange Studies on the *trans*(*fac*)-Bis(*N*-methyliminodiacetato)chromate(III) Anion and *N*-Methyliminodiacetic Acid

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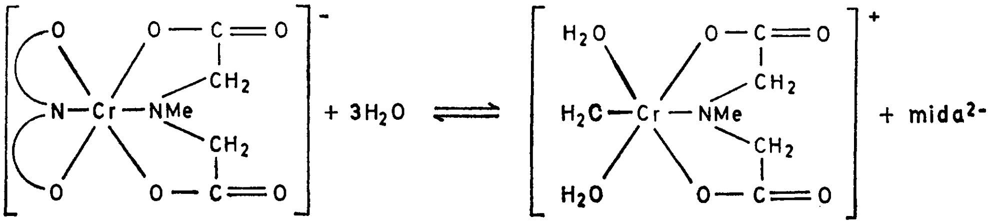
The rate of oxygen exchange of the *trans*(*fac*)-bis(*N*-methyliminodiacetato)chromate(III) anion and of *N*-methyliminodiacetic acid with solvent water varies with hydrogen-ion concentration. At 100 °C the latter reaction is 39 times faster than the former. A mechanism for ^{18}O exchange of the co-ordinated ligand through acid-independent and acid-dependent paths is postulated. Both paths appear to involve one-ended dissociated species.

SPINNER and Harris[1] have recently reviewed the chemistry of oxalatochromium(III) species. The equal rate of exchange of both carbonyl and carboxyl oxygen atoms with solvent water has been explained by a mechanism involving reversible one-ended dissociation of the bidentate ligand and breaking of the Cr–O bond. By contrast, hexa-amminechromium(III) does not exchange its nitrogen ligands with $^{15}NH_3$ in solution,[2] indicating that the Cr–N bond does not dissociate reversibly at a measurable rate. The present study was undertaken to determine whether the carbonyl and carboxyl oxygen atoms in a Cr^{III} complex, containing both N and carboxyl O atoms co-ordinated to the metal ion in the same ligand, would exchange both atoms of the carboxyl group with solvent water and at equivalent rates. Sodium *trans*(*fac*)-bis(*N*-methyliminodiacetato)-chromate(III), Na[Cr(mida)$_2$], (I), has been well characterised[3,4] and was chosen for ^{18}O exchange studies with solvent water. The results have been compared with those for ^{18}O exchange of *N*-methyliminodiacetic acid, H_2mida, with solvent water.

RESULTS AND DISCUSSION

Weyh and Hamm[5] established that the product of aquation of [Cr(mida)$_2$]$^-$, (I), was [Cr(mida)(OH$_2$)$_3$]$^+$, (II).



(I) (II)

SCHEME 1

We have now established that this reaction (Scheme 1) is reversible by the following argument. The rate of ^{18}O exchange of free ligand in the presence of (I) has been shown to be the same as that of (I) (see below) and faster than that of isolated free ligand, and therefore must go through a species in which the amino-acid is co-ordinated to a chromium centre. A spectrophotometric study of this equilibrium is in hand, but the following discussion does not require a precise knowledge of the position of this equilibrium. The rate constants, k_{ex}, for ^{18}O exchange of (I) with $H_2{}^{18}O$ at 100 °C are given in Table 1 and those of H_2mida at the same temperature in Table 2.

The values of c_{H^+} in Table 1 are the constant values attained after establishment of the aquation equilibrium which is readily attained at this temperature. The linearity of the McKay plots for >90% exchange indicates kinetic equivalence of all eight oxygen atoms in (I). The Figure shows plots of k_{ex} against c_{H^+} and the data for ^{18}O exchange of (I) fit well equation (1) where

$$k_{ex} = k_0 + k_1 c_{H^+} \qquad (1)$$

$k_0 = (3.5 \pm 0.2) \times 10^{-5}\ s^{-1}$ and $k_1 = (9.55 \pm 0.02) \times 10^{-2}\ l\ mol^{-1}\ s^{-1}$. Thus k_0 represents an acid-independent and k_1 an acid-dependent path for ^{18}O exchange. Values of k_{ex} were essentially independent of the concentration of the complex (columns 3—5 in Table 1) as expected for pseudo-first-order rate constants.

The data for ^{18}O exchange of H_2mida also fit equation (1) well (Figure) with $k_0 = (2.5 \pm 0.2) \times 10^{-6}\ s^{-1}$ and $k_1 = (2.44 \pm 0.02) \times 10^{-3}\ l\ mol^{-1}\ s^{-1}$. Thus the data indicate an acid-independent and an acid-catalysed path for exchange. It is likely that the overall rate of exchange of oxygen atoms in the free ligand is dependent on the relative concentrations of the different species of the ligand, *i.e.* mida^{2-}, Hmida$^-$, and H_2mida. Under the experimental conditions of Table 2, we need consider only Hmida$^-$ and H_2mida as reactive species (pK_1 *ca.*

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[1] T. Spinner and G. M. Harris, *Inorg. Chem.*, 1972, **11**, 1067.

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

[3] J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, 1968, **7**, 2431.

[4] A. Uehara, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Japan*, 1970, **43**, 1394.

[5] J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, 1969, **8**, 2298.

2, pK_2 *ca.* 10),[6] but there are insufficient data to justify a detailed kinetic analysis.

The ratio (at 100 °C) of the rate constants of exchange, k_1, for (I) and free ligand in this study is 39 : 1, whereas the ratio (at 25 °C) of the overall rate constants of exchange for complex and free ligand in the tris(oxalato)-chromate(III) anion and oxalic acid systems is *ca.* 2 : 1.[7] Thus chelation to Cr^{III} of mida^{2-} appears to cause acceleration of ^{18}O exchange but not chelation of $[C_2O_4]^{2-}$.

TABLE 1

Exchange of *trans*-bis(*N*-methyliminodiacetato)-chromate(III) anion [a] and $H_2{}^{18}O$ at 100.0 °C

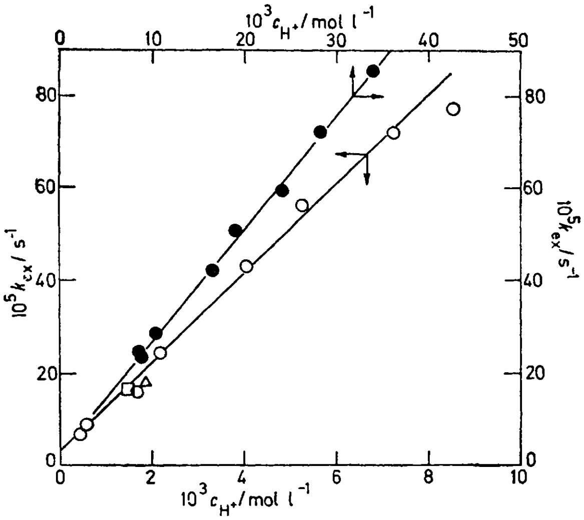
$10^3c_{H^+}$/mol l^{-1} [b]	0.43	0.54	1.48 [c]	1.66	1.82 [d]	2.14	4.07
10^5k_{ex}/s^{-1}	6.83	8.82	16.4	15.8	17.6	24.5	43.2
$10^3c_{H^+}$/mol l^{-1} [b]	5.25	7.24	8.51				
10^5k_{ex}/s^{-1}	56.3	72.1	77.2				

[a] $c_{[Cr(mida)_2]^-}$ = 0.05 mol l^{-1} unless stated otherwise. [b] Measured after establishment of aquation equilibrium. [c] $c_{[Cr(mida)_2]^-}$ = 0.075 mol l^{-1}. [d] $c_{[Cr(mida)_2]^-}$ = 0.025 mol l^{-1}.

TABLE 2

Exchange of *N*-methyliminodiacetic acid and $H_2{}^{18}O$ at 100.0 °C

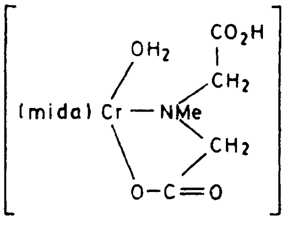
c_{mida}/mol l^{-1}	0.10	0.10	0.10	0.10	0.10	0.10	0.10
$10^2c_{H^+}$/mol l^{-1}	0.85	0.87	1.02	1.66	1.90	2.40	2.82
10^5k_{ex}/s^{-1}	2.47	2.35	2.87	4.23	5.08	5.97	7.22
c_{mida}/mol l^{-1}	0.10	0.10	0.15	0.20	0.30	0.40	
$10^2c_{H^+}$/mol l^{-1}	3.39	0.72	0.72	0.72	0.72	0.72	
10^5k_{ex}/s^{-1}	8.46	2.10	2.25	2.41	3.00	3.28	



Dependence of rate constants of ^{18}O exchange of $[Cr(mida)_2]^-$ and H_2mida with solvent water at 100.0 °C on acidity. (●), c_{H_2mida} = 0.10 mol l^{-1}; (○), (□), and (△), $c_{[Cr(mida)_2]^-}$ = 0.05, 0.025, and 0.075 mol l^{-1} respectively

Reversible one-ended dissociation in the tris(oxalato)-chromate(III) system is possible at both ends of the chelate ring, and this accounts for the kinetic equivalence of all 12 oxygen atoms in the exchange reaction with solvent water.[7] In (I) the tridentate ligand is attached to the metal by the Cr–N bond (usually inert), but a similar reversible one-ended dissociation of the two remaining Cr–O bonds of the ligand will account for the observed kinetic equivalence of all eight oxygen atoms in this exchange reaction.

We have shown that an uncharged intermediate can be isolated from the reaction mixture after establishing hydrolytic equilibrium, and have suggested a one-ended dissociated structure, (III) (with the Cr–N bond remaining intact), for this complex.[8] Formation of (III) is consistent with the above hypothesis.



(III)

We plan to study the ^{18}O exchange of (II) with solvent water, and expect, partly by analogy with the systems $[Cr(C_2O_4)_3]^{3-}$ (ref. 7) and $[Cr(C_2O_4)_2(OH_2)_2]^-$,[9] whose mechanisms of oxalate-oxygen exchange with $H_2{}^{18}O$ were similar, that (I) and (II) will react by similar mechanisms.

We propose Scheme 2 as the mechanism with one path for the acid-independent term and two alternative paths for the acid-dependent term. (Charges on the complex ions have been omitted for clarity.) Path (a) represents the acid-independent path, *i.e.* water attack on the carbonyl centre of the complex followed by one-ended dissociation. The uncatalysed path is made possible by an increase in positive charge on the carbon atom through an inductive effect from the Cr^{III} centre. This result contrasts with those observed for the Cr^{III}–oxalate systems [7,9] where there were no acid-independent paths. The presence of path (a) therefore leads us to favour (b) rather than (c) for the acid-catalysed path. Both paths (b) and (c) involve a protonation pre-equilibrium, the former on the chelated ligand and the latter on that ligand after one-ended dissociation has occurred. This is followed in the rate-determining step by water attack on the positive carbon centre. Path (b) must involve subsequent one-ended dissociation similar to that of (a) in order that the eight oxygen atoms become kinetically equivalent. For the Cr^{III}-oxalate systems we favoured [7,9] a scheme similar to path (c), *i.e.* one-ended dissociation followed by water attack. The original aim of this project was to test for kinetic equivalence of all eight oxygen atoms in (I); this we found and in addition have shown that attaching one end of the chelate ring through N led to an additional mechanism (non-acid catalysed) of exchange.

A study of the ^{18}O exchange of the free ligand showed

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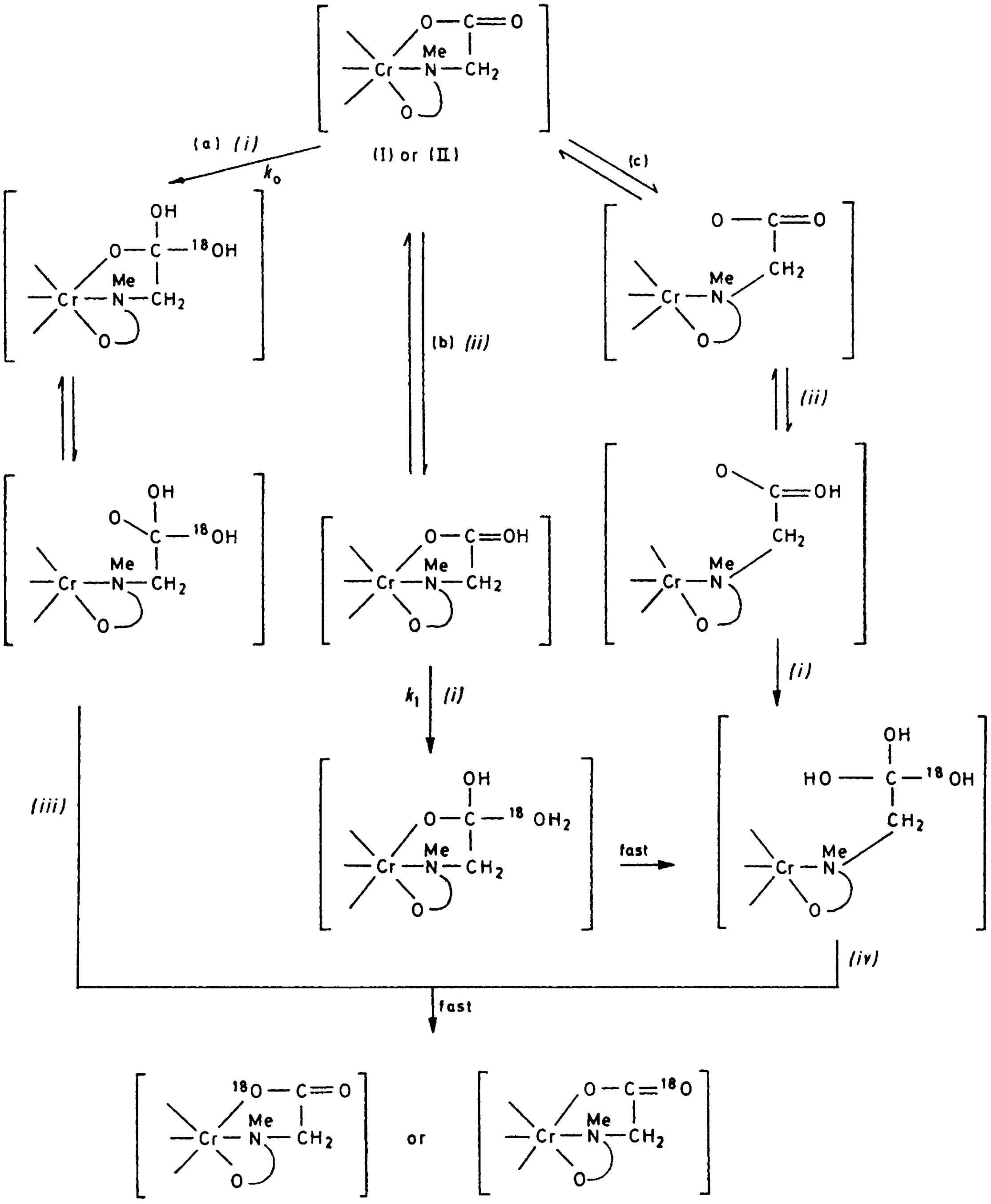
[6] N. E. Ockerbloom and A. E. Martell, *J. Amer. Chem. Soc.*, 1956, **78**, 267.

[7] 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.

[8] S. Dutta-Chaudhuri, C. J. O'Connor, and A. L. Odell, unpublished work.

[9] J. Aggett, I. Mawston, A. L. Odell, and B. E. Smith, *J. Chem. Soc.* (*A*), 1968, 1413.

that increasing the concentration of free ligand four fold increases k_{ex} by 56% (Table 2). This change is unlikely to be caused purely by an ionic-strength effect, since a ten-fold increase in ionic strength with added electrolytes caused a 30% decrease in the rate of ^{18}O exchange of aminoacetic acid with solvent water at 101 °C.[10] The reason for this increase is not clear, but perhaps at increased concentration of H_2mida the acid forms a dimeric species and there may be a contribution from a further path.



SCHEME 2 (*i*), $H_2{}^{18}O$, slow; (*ii*), $+H^+$; (*iii*), $-H_2O$; (*iv*), $-H_3O^+$

The effect of temperature on the pseudo-first-order rate constants of exchange is given in Table 3. The constant K_1 of H_2mida is virtually independent of temperature in the range 0—40 °C.[6] We therefore measured the pH values at room temperature 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

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[10] C. J. O'Connor and D. R. Llewellyn, *J. Chem. Soc.*, 1965, 2669.

parameters using the Eyring equation.[11] The activation parameters (Table 3) were calculated over three temperatures for two runs under conditions in which the hydrogen-ion term dominates. Although, for quantitative comparison, complete pH profiles at different temperatures are necessary in order to calculate the activation parameters for the k_0 and k_1 paths independently, the activation parameters quoted are presumably near to those for hydrogen-ion catalysis. Values of $\Delta H^‡$ for complex oxygen and free-ligand oxygen exchange are 79.1 ± 5.9 and 72.9 ± 0.5 kJ mol^{-1} respectively. These are close to those found for $[Cr(C_2O_4)]^{3-}$ and oxalic acid of 75.5 ± 2.1 and 77.1 kJ mol^{-1} respectively,[7] suggesting qualitatively that the systems are controlled by similar mechanisms for exchange of oxygen with solvent water, *i.e.* the rate-determining step is water attack.

TABLE 3

Effect of temperature on exchange rates of (*a*) 0.05 mol l^{-1} $[Cr(mida)_2]^-$ and $H_2{}^{18}O$ at pH 2.28 and (*b*) 0.10 mol l^{-1} H_2mida and $H_2{}^{18}O$ at pH 1.62

	$10^5k_{ex}/s^{-1}$		$\Delta H^‡$/kJ mol^{-1}		$\Delta S^‡$/J K^{-1} mol^{-1}	
θ_c/°C	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
80	12.3	1.49	79.1	72.9	−22.1	−32.0
90	27.8	2.94	±5.9	±0.5	±2.3	±0.05
100	56.3	5.96				

TABLE 4

Rate constants for aquation of *trans*-$[Cr(mida)_2]^-$ and comparison with rate constants of ^{18}O exchange and anation under comparable conditions at 100 °C

			$10^3c_{H^+}$/mol l^{-1}		
Reaction	c_X/mol l^{-1}	c_{H_2mida}/mol l^{-1}	Initial	Final	10^4k [a]
Aquation	0.025 [b]		10.0	3.16	32.5
Aquation	0.025 [b]		19.1	5.25	37.0
Aquation	0.025 [b]		23.4	7.00	48.1
Anation	0.005 [c]	0.050	8.91	9.77	32.7
Exchange	0.050 [b]		36.3	8.51	7.72

[a] In s^{-1} for k_{ex} and k_{aq}, in l mol^{-1} s^{-1} for k_{an}. [b] $X = [Cr(mida)_2]^-$. [c] $X = [Cr(mida)(OH_2)_3]^+$.

Weyh and Hamm[5] studied the aquation of (I) in moderately concentrated acid solutions and near ambient temperatures. These conditions differ greatly from those of our ^{18}O exchange experiments, and in order to compare the relative rates of ^{18}O exchange, aquation, and anation under comparable conditions of temperature and acidity we undertook a limited study of these last two reactions (Table 4). An investigation of the ^{14}C-labelled ligand exchange has been carried out[8] and further studies of the anation reaction are in hand. At 100 °C the rate constants of aquation increased slightly with increasing acidity, but the dependence on c_{H^+} was not sufficient to cause curvature in the reaction rate plots despite a three-fold change in c_{H^+} during the runs. The quoted values of k for aquation are not pseudo-first-order rate constants in the sense that $c_{H^+} < c_{[Cr(mida)_2]^-}$. However, the results show clearly that aquation is a much faster process than ^{18}O exchange under the conditions used. Moreover Table 4 shows that the second-order rate constant for anation of 0.005 mol l^{-1} (II) in the presence of 0.050 mol l^{-1} free ligand is 32.7 l mol^{-1} s^{-1}, indicating that $t_{\frac{1}{2}}$ of anation at this ligand concentration is shorter than that of ^{18}O exchange of (I) under comparable conditions of acidity and temperature.

The effect of added free ligand on the rate constants for exchange of co-ordinated oxygen with solvent water (Table 5) confirms that $t_{\frac{1}{2}}$ of the anation–aquation equilibrium is smaller than that for the ^{18}O exchange reaction. Increasing c_{H_2mida} caused k_{ex} of (I) to decrease. At $c_{H_2mida} = 0.40$ mol l^{-1}, the rate constants of oxygen exchange of H_2mida with $H_2{}^{18}O$ in the absence and presence (0.05 mol l^{-1}) of $[Cr(mida)_2]^-$ at pH 2.15 and 100.0 °C were 3.28 and 9.78 s^{-1} respectively (Tables 2 and 5). It is expected from the relative values of k_1 for (I) and free ligand, evaluated from Tables 1 and 2, that slower exchange of oxygen in the free ligand should be accelerated in the presence of complex since the anation–aquation equilibrium is established more rapidly than either exchange reaction.

TABLE 5

Effect of free-ligand concentration on the exchange rates for 0.05 mol l^{-1} *trans*-$[Cr(mida)_2]^-$ and $H_2{}^{18}O$ at 100.0 °C and pH 2.15

c_{H_2mida}/mol l^{-1}	0.00	0.10	0.20	0.30	0.40	0.40
$10^5k_{ex}/s^{-1}$	72.1	39.8	30.5	22.8	17.1	9.78 *

* For exchange of H_2mida and $H_2{}^{18}O$ in the same kinetic run.

We measured the rate of exchange of complexed and of free ligand in the same kinetic run. Table 5 shows that the respective rate constants in a solution containing $c_{H_2mida} = 0.40$ mol l^{-1} and $c_{[Cr(mida)_2]^-} = 0.05$ mol l^{-1} were 17.1 and 9.78 s^{-1}. Gourley and Milburn[12] suggested that relative rates should be compared only after correction of observed rates (k_{ex}) in terms of g-atoms of ligand exchanged per mol, *i.e.* effectively only values of $t_{\frac{1}{2}}$ should be compared. When this procedure was adopted the respective values of the rate constants were 2.40×10^{-5} and 2.13×10^{-5} (g-atom)$^{-1}$ mol s^{-1}, *i.e.* equal within experimental error. [Correction of the ratio of 39.1 : 1 for exchange of co-ordinated and free ligand oxygen in isolated systems (see above) by the Milburn factor reduced the ratio to 19.6 : 1.] The reduction of this ratio to *ca.* 1 : 1 in a system containing a large excess of free ligand in the presence of a small amount of complex indicates that exchange proceeds mainly through a species where the ligand is attached to a highly polar metal centre. Because of the relatively rapid anation–aquation equilibrium, this result is to be expected. But although the aquation–anation equilibrium between $[Cr(C_2O_4)_3]^{3-}$ and $[Cr(C_2O_4)_2(OH_2)_2]^-$ is slow, the rates of oxalate ^{18}O exchange of these two complexes with water are similar to those of the free oxalate ion with water. We previously commented (see above) that the large differences in rate constants of exchange of oxygen in co-ordinated and free ligands in the present system is an indication of metal-ion catalysis.

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

[12] S. G. Gourley and R. M. Milburn, *Inorg. Chem.*, 1972, **11**, 2262.

It is not likely that this acceleration is due to a charge difference of −1 for the complex and zero for the free ligand, since it has been shown[12] that a change in charge from −3 for $[Cr(C_2O_4)_3]^{3-}$ to +1 for $[Cr(C_2O_4)(OH_2)_4]^+$ changes the rate by a factor of $\leqslant 4$. Table 6 summarises some literature data on ^{18}O exchange of oxalato-ligands in Cr^{III} oxalato-complexes of two differing charge types. In both cases aqua-complexes exhibit slower exchange than those containing basic ligands. The present system differs from those in Table 6 because the basic N donor is on the same ligand as the exchanging O atom.

TABLE 6

Comparison of rate constants of exchange of oxalate oxygen between aquaoxalato- or (basic ligand)-oxalato-complexes of chromium(III) and solvent water at $c_{H^+} = 1.0$ mol l^{-1}, *I ca.* 1 mol l^{-1}, and 25 °C

Complex	$10^4 k_{ex}$ [a]/ (g-atom)$^{-1}$ mol s^{-1}	*R* [b]	Ref.
$[Cr(OH_2)_2(C_2O_4)_2]^-$ [c]	0.48		9
$[Cr(phen)(C_2O_4)_2]^-$ [c]	1.03	2.15	*d*
$[Cr(bipy)(C_2O_4)_2]^-$ [c]	1.17	2.44	*d*
$[Cr(OH_2)_4(C_2O_4)]^+$ [e]	0.25		12
$[Cr(phen)_2(C_2O_4)]^+$ [e]	0.68	2.71	*f*
$[Cr(bipy)_2(C_2O_4)]^+$ [e]	0.69	2.75	*f*
$[Cr(en)_2(C_2O_4)]^+$ [e]	0.69	2.76	*f*

phen = 1,10-Phenanthroline, bipy = 2,2′-bipyridine, and en = ethylenediamine.

[a] Originally published values of k_{ex} divided by number of kinetically equivalent exchangeable O atoms per molecule. [b] Ratio of the rate of ^{18}O exchange of the aquaoxalato-complex to that of the (basic ligand)oxalato-complex with same overall charge. [c] Eight exchangeable O atoms. [d] J. A. Broomhead, N. Kane-Maguire, and I. Lauder. *Inorg. Chem.*, 1970, **9**, 1243. [e] Four exchangeable O atoms. [f] J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, 1971, **10**, 955.

This suggests that the correct explanation may well be a deceleration of exchange of the free ligand due to zwitterion formation. The difference of 10^8 in the two dissociation constants of H_2mida reflects this postulate.[13] Lack of solvation in a bulky tertiary ammonium ion has been established[14] and this would contribute to the decrease in ^{18}O exchange rate of the free mida ligand compared with a free oxalato- or co-ordinated mida ligand.

EXPERIMENTAL

Materials.—Sodium *trans(fac)*-bis(*N*-methyliminodiacetato)chromate(III), $Na[Cr(mida)_2]$, was prepared according to the literature[4] (Found: C, 33.0; H, 4.05; Cr, 14.0; N, 7.60. Calc. for $C_{10}H_{14}Cr_2N_2NaO_8$: C, 32.9; H, 3.85; Cr, 14.2; N, 7.65%). Triaqua(*N*-methyliminodiacetato)-chromium(III) perchlorate, $[Cr(mida)(OH_2)_3][ClO_4]$, was prepared according to ref. 4, but was eluted from the column with 0.15 mol l^{-1} sodium perchlorate at 1—2 drops per min. The middle fraction was 0.0146 mol l^{-1} in complex and had $\lambda_{max.}$ = 392 and 552 nm with $\varepsilon_{max.}$ = 48.4 and 59.0 l mol^{-1} cm^{-1} respectively (*cf.* $\varepsilon_{max.}$ 48 and 60 l mol^{-1} cm^{-1}).[4] *N*-Methyliminodiacetic acid, H_2mida, m.p. 216—217 °C (lit.,[15] 215 °C) was prepared according to the literature (Found: C, 41.0; H, 5.95; N, 9.60. Calc. for $C_5H_9NO_4$: C, 40.8; H, 6.20; N, 9.50%). Other reagents were AnalaR or were purified before use. Acid solutions were standardised against sodium hydroxide which had been previously standardised with dry AnalaR hydrazine sulphate.

Apparatus.—pH Measurements were made on a Radiometer (Copenhagen) 4 pH meter. These were unaffected by small added concentrations of perchlorate ions. Visible spectra were measured on Cary 14 or Shimadzu QV 50 spectrophotometers. Oxygen-18 analyses were carried out using an A.E.I. MS 3 mass spectrometer.

Measurement of Reaction Rates.—All reactions were carried out in oil-baths maintained to ±0.1 °C by using a Gallenkamp contact thermometer, Klaxon stirrer, and heating element.

Kinetics of Oxygen Exchange.—Weighed samples of $Na[Cr(mida)_2]$, (I), were dissolved in water containing 1.66 atom % abundance ^{18}O and the pH adjusted at room temperature by adding conc. HCl with a microjet to a rapidly stirred solution. This avoided precipitation of $HCr(mida)_2$. After establishment of aquation equilibrium (see above) and attainment of constant pH (a few minutes at low pH to *ca.* 1 h at the highest pH used), aliquot portions (*ca.* 2 cm^3) sealed in ampoules were placed in a constant-temperature bath. Samples were removed at intervals, cooled rapidly, and $K[Cr(mida)_2]$ precipitated from the reaction mixture by addition of KCl (*ca.* 0.2 g). The precipitate was filtered off, washed with ice-cold water and then 95% alcohol, and dried *in vacuo*. The salt was then pyrolysed by gentle heating *in vacuo* to give carbon dioxide which was analysed for 44 : 46 mass ratio. The precipitated $K[Cr(mida)_2]$ was not contaminated by either free ligand or aquated complex, even in the presence of a large excess of free ligand (Found: C, 31.5; H, 3.65. Calc. for $C_{10}H_{14}CrKN_2O_8$: C, 31.5; H, 3.70%). The aquated complex is very soluble and hygroscopic. Hence all exchange data refer only to the eight oxygen atoms of the original substrate, $[Cr(mida)_2]^-$.

Weighed samples of H_2mida were dissolved in $H_2{}^{18}O$ and the pH was adjusted by addition of conc. $HClO_4$ or NaOH (*ca.* 2 mol l^{-1}, dissolved in $H_2{}^{18}O$). Samples were removed from the thermostat baths at intervals and brought to pH *ca.* 8 (barely colourless to phenolphthalein) by addition of NaOH. A few drops of silver(I) nitrate were added, and after standing the solutions in the dark room for some time and then scratching the sides of the ampoule with a glass rod the fine white precipitate of silver(I) *N*-methyliminodiacetate was filtered off and treated as described for the complex salt above.

The initial abundances of ^{18}O in $Na[Cr(mida)_2]$ and H_2mida were measured on zero-time samples of $K[Cr(mida)_2]$ and Ag_2(mida), and excess abundances were calculated relative to these values. For the fast reactions, infinite-time values for complete exchange were measured after *ca.* 8—10 half-lives. In some cases the infinite-time abundance was measured on a sample of carbon dioxide which had been in equilibrium with a portion of the exchange solution for 48 h at room temperature. The CO_2

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[13] M. T. Beck, *J. Inorg. Nuclear Chem.*, 1960, **12**, 353; *Acta Chim. Hung. Trans.*, 1960, **22**, 159; D. R. Lloyd and R. Prince, *J. Chem. Soc.*, 1963, 3645; V. L. Hughes and A. E. Martell, *J. Amer. Chem. Soc.*, 1956, **78**, 1319.

[14] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' Wiley, New York, 1957, p. 392.

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

obtained from direct pyrolysis gave identical ^{18}O 44 : 46 ratios before (and after) gas-chromatographic separation:[16] $K[Cr(mida)_2]$ 0.197 (0.197); $Ag_2(mida)$, 0.200 (0.200)% ^{18}O. This indicates that foreign gaseous material did not interfere with the mass-spectrometric analysis.

Plots of $-\log(1 - F)$ against time [$F = (a_t - a_0)/(a_\infty - a_0)$, a = % ^{18}O] were linear for more than 90% total exchange. The pseudo-first-order rate constants of exchange, k_{ex}, were calculated by using a modified[17] McKay[18] equation, (2), where n = number of exchanging oxygen

$$k_{ex} = 0.693n/t_{\frac{1}{2}} \qquad (2)$$

atoms in the system, *i.e.* $n = 4$ for H_2mida and $n = 8$ for $Na[Cr(mida)_2]$. The uncertainties in estimation of k_{ex} are *ca.* ±2%.

The effect on the oxygen exchange of $[Cr(mida)_2]^-$ with (*a*) varying complex and (*b*) varying free-ligand concentration at constant pH was also studied and the initial experimental procedure varied slightly for these two sets of experiments.

(a) *Varying complex concentration.* After initial adjustment of the solutions with complex concentrations of 0.025, 0.050, and 0.075 mol l^{-1} respectively to pH 2.20 ± 0.01 at room temperature the bulk solutions were thermostatted at 100 °C for 40 min, and after rapid cooling to room temperature gave new pH values of 2.73, 2.88, and 2.97. The latter two samples were readjusted to pH 2.73, reheated for 30 min, and after a further adjustment to pH 2.73 and 30 min heating the pH of the three solutions were 2.74, 2.78, and 2.83 respectively.

(b) *Varying free-ligand concentration.* Constant pH 2.15 was obtained after 30 min thermostatting of the bulk solutions (c_{H_2mida} = 0.1 to 0.4 mol l^{-1}) at 100 °C.

Measurement of rate of oxygen exchange of free and complexed ligand in the same kinetic run. In a solution containing $c_{H_2mida} = 0.40$ and $c_{[Cr(mida)_2]^-} = 0.05$ mol l^{-1} the rate constants of ^{18}O exchange of both complexed and free-ligand oxygen atoms were measured. Each aliquot portion was treated first with $K[NO_3]$ to precipitate $K[Cr(mida)_2]$, and from the filtrate $Ag_2(mida)$ was precipitated by addition of $Ag[NO_3]$.

Kinetics of the Aquation Reaction at 100 °C.—Weighed samples of $Na[Cr(mida)_2]$ were dissolved in deionised water and the pH adjusted as described above. Samples, sealed in ampoules, were placed in a constant-temperature bath, and after attainment of thermal equilibrium (1 min) were removed at 30—60 s intervals and immediately frozen. The pH of each aliquot portion was noted after thawing and spectral changes in the range 350—580 nm were measured. Rate constants were calculated from plots of $\log_{10}(A_\infty - A_t)$ against t at 560 nm (A_t and A_∞ are absorbances at time t and ∞ respectively). Differences in spectra between the complex and its aquated products also occurred at 405 and 480 nm, but at 480 nm the values of A increased rapidly initially and then decreased steadily. This has been interpreted[8] in terms of formation of an intermediate, (III), prior to $[Cr(mida)(OH_2)_3]^+$.

Kinetics of Anation Reaction at 100 °C.—The required volume of $[Cr(mida)(OH_2)_3][ClO_4]$ solution was added to a solution containing a weighed amount of H_2mida. pH Changes were followed throughout the run. Samples, sealed in ampoules, were removed at 2 min intervals from the thermostat bath and the rate constant was calculated from the change in absorbance at 560 nm. At 480 nm the absorbance continued to increase for six half-lives before gradually decreasing.

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