3d transition series from Ca^{2+} to Zn^{2+}, the ions become softer as a consequence of the increasing number of d electrons.[41] Since π bonds are formed and back-donation occurs from the coordination of 2,2′-bipyridyl to Cu^{2+}, the d-electron content on Cu^{2+} decreases; that is it becomes more hard. Hence, through the combination of the borderline 2,2′-bipyridyl with the borderline Cu^{2+}, a harder species is created which is more favored to combine with O than with N ligands (the hardness increases in the series: $CH_3^- < NH_2^- < OH^- < F^-$ (*cf.* ref 41); this behavior is opposite to the "symbiotic" effect described by Jørgensen.[42]

The importance of ternary complexes in metal ion catalyzed reactions is well known. For example, the Cu^{2+}-catalyzed decomposition of H_2O_2 is strongly dependent on the kind of ligand bound to the metal ion.[43] Also, the rate of the metal ion catalyzed decarboxylation of acetonedicarboxylate, oxaloacetate, or dimethyloxaloacetate is increased by coordination of the metal ion to an aromatic ligand, *e.g.*, 2,2′-bipyridyl, compared with the aqueous metal ions,[44] while no enhancement is observed with aliphatic amines.[45] In addition, the hydrolysis of diisopropyl fluorophosphate is catalyzed through several Cu^{2+} complexes, among which the Cu^{2+}–2,2′-bipy 1:1 complex is especially effective; furthermore, the complexes of L-histidine, 1,10-phenanthroline, and imidazole are better catalysts than that of glycine.[46] Such observations and the described stability rules suggest that the difference in the reaction rate is closely connected with the stability of the ternary complexes formed during the reactions.

Acknowledgments.—We wish to thank Professor Dr. D. B. McCormick (Cornell University, Ithaca, N. Y.) for helpful comments. The measurements were performed with the skillful technical assistance of Miss R. Baumbusch, Miss G. Baum, and Mr. A. Tàlos. The computer, IBM 1620, was made available by the Rechenzentrum der Universität Basel. This investigation was supported by a research grant from the Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung.

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[45] J. V. Rund and K. G. Claus, *Inorg. Chem.*, **7**, 860 (1968).

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Racemization and Oxygen-18-Exchange Studies of Heterochelate Chromium(III) Complexes with the Ligands 2,2′-Bipyridine, 1,10-Phenanthroline, and Oxalate Ion. I. Racemization of the Bis(oxalato)2,2′-bipyridinechromate(III) and the Bis(oxalato)-1,10-phenanthrolinechromate(III) Anions

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The kinetics of racemization of the anions $Cr(ox)_2bipy^-$ and $Cr(ox)_2phen^-$ (ox = oxalate ion; bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline) fit the expression rate = $(k_1 + k_2[H^+] + k_3[H^+]^2)$[complex]. At 25° and unit ionic strength respective values are: $k_1 = 1.82 \times 10^{-4}$ sec^{-1}, $k_2 = 2.44 \times 10^{-4}$ M^{-1} sec^{-1}, $k_3 = 1.15 \times 10^{-4}$ M^{-2} sec^{-1}; $k_1 = 2.43 \times 10^{-4}$ sec^{-1}; $k_2 = 2.73 \times 10^{-4}$ M^{-1} sec^{-1}, $k_3 = 1.34 \times 10^{-4}$ M^{-2} sec^{-1}. Divalent metal ions catalyze the racemization reaction and give a rate expression similar to that for acid catalysis. Arrhenius parameters have been measured and previous work extended. An intramolecular racemization mechanism involving contributions from half-bonded oxalato ligands and from twist processes is suggested. Acid-catalyzed oxygen-18 exchange with solvent water follows the rate expression rate = $k'[H^+]$[complex], up to 1 M acid. All eight oxygen atoms of the oxalato ligands are exchanged at the same rate, and though the racemization results support a half-bonded oxalate mechanism for oxygen exchange, an interchange process cannot be eliminated. Divalent metal ions do not induce oxygen exchange. The danger in equating oxygen exchange and racemization rate data is discussed.

Introduction

Most studies on the racemization of metal complexes have been concerned with individual compounds rather than an interrelated series. The advantages of the last mentioned approach have been demonstrated previously in relation to nickel(II) complexes.[2] When a postulated mechanism includes factors common to more than one complex, then a more reliable interpretation may ensue. For this reason the series $Cr(ox)_2phen^-$, $Cr(ox)_2bipy^-$, $Cr(ox)(phen)_2^+$, and $Cr(ox)(bipy)_2^+$ (phen = 1,10-phenanthroline; bipy = 2,2′-bipyridine; ox = oxalate ion) has been prepared and characterized.[3]

[1] (a) Australian National University. (b) University of Queensland.

[2] J. A. Broomhead and F. P. Dwyer, *Australian J. Chem.*, **16**, 51 (1963).

[3] (a) J. A. Broomhead, M. Dwyer, and N. Kane-Maguire, *Inorg. Chem.*, **7**, 1388 (1968); (b) J. A. Broomhead, *Australian J. Chem.*, **15**, 228 (1962).

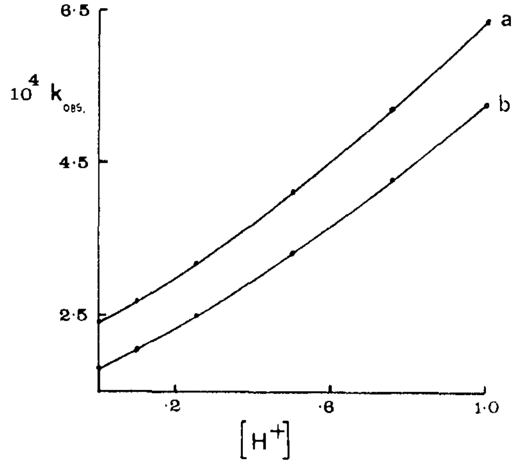

Figure 1.—Acid dependence of racemization rate constants for $Cr(ox)_2phen^-$ (a) and $Cr(ox)_2bipy^-$ (b) at 25° and unit ionic strength.

TABLE I

KINETIC DATA FOR THE RACEMIZATION OF $Cr(ox)_2bipy^-$ IN 1 *M* HCl

Temp, °C	10^4k_{obsd}, sec^{-1}	E_a, kcal mol^{-1}	Log *A* (*A* in sec^{-1})	ΔS, eu
25	5.29			
33	11.9	18.4	10.2	−13.8
40	23.5			

TABLE II

KINETIC DATA FOR THE RACEMIZATION OF $Cr(ox)_2(phen)^-$ IN 1 *M* HCl

Temp, °C	10^4k_{obsd}, sec^{-1}	E_a, kcal mol^{-1}	Log *A* (*A* in sec^{-1})	ΔS, eu
25	6.39			
33	14.3	18.3	10.2	−13.7
40	28.2			

In this paper we present results of racemization and ligand-exchange experiments for the anionic complexes for which some racemization studies were reported previously.[4] In subsequent papers the cationic complexes will be discussed and the overall behavior of chromium–oxalato complexes reviewed.

Experimental Section

Materials.—$K[Cr(ox)_2bipy]$ and $K[Cr(ox)_2phen]$ were prepared and resolved by methods already described.[3b] All other reagents used were of analytical grade quality. Oxygen-18-enriched (by 1.55%) water was supplied by Yedda Research and Development Co. Rehovoth, Israel.

Methods.—Racemization rates were determined by standard procedures using a Perkin-Elmer 141 automatic polarimeter and sodium or mercury lamp light sources. Initial rotations (10-cm tube) were usually about 1° and could be read to within ±0.002°. Temperature control was within ±0.1° and ionic strength was changed by addition of potassium chloride. Absorption spectral measurements were made using a Cary 14 spectrophotometer.

Oxygen-18-exchange experiments involved precipitation of the anions as their barium salts (using barium chloride) followed by thermal decomposition and isolation of the carbon dioxide liberated. Measurements of the $^{46}/_{44}$ ratios were made using a Nier-type isotope ratio mass spectrometer. Test exchange runs with nonenriched water gave normal values of the $^{46}/_{44}$ ratio. Complete mass spectra of typical samples were obtained with an Atlas CH-4 mass spectrometer and showed insignificant background impurities.

In an exchange run the oxygen-18 water containing hydrochloric acid was equilibrated for 30 min in a water bath thermostated to ±0.01°. Potassium chloride was added when required to maintain an ionic strength of 1. After equilibration a known amount of complex was added and dissolved by shaking. At appropriate times samples were removed into centrifuge tubes containing an ice-cold solution of barium chloride (80–120 mg of $BaCl_2$ in 0.3 ml of oxygen-18 water). Complete precipitation was obtained and the suspension was then centrifuged for 2 min. The supernatant liquid was removed and the precipitate washed twice with 8-ml volumes of absolute ethanol. Finally the tube and contents were dried at 70°. The centrifuge tube was then broken near the end so as to remove the complex and the whole was placed in a glass decomposition tube attached to a vacuum system which was then evacuated (10^{-4}–10^{-5} mm). The collection tube was outgassed with a hand torch and the decomposition tube was heated to 170° to remove water of crystallization which was pumped off. An acetone–Dry Ice cooled trap and a liquid nitrogen trap were next incorporated into the system. The temperature was then increased steadily over a 15-min period to 470° after which heating was discontinued. The system was isolated from the pump and by changing the cooling traps the carbon dioxide was transferred to the collection tube. This was removed and stored in a desiccator over Ascarite prior to measurement.

In the above procedure it is assumed that the oxygen of the CO_2 obtained is representative of both the carbonyl and carboxyl oxygens. Oxygen is, however, retained by the chromium as oxide and a full mass spectrum of the decomposition products showed that carbon monoxide was an important component. Separate condensation of the CO_2 and CO from the same sample of complex gave identical atom fractions of oxygen-18. The metallic oxide residue reduced by carbon also gave the same oxygen-18 composition as that above and this was equal to the atom fraction of oxygen-18 in the exchange solvent.

The atom fraction of the oxygen-18 in the solvent water was found by the method of Cohen and Urey.[5] R_∞ values (see later) were checked by the following experiment in which isotopically normal CO_2 (1 ml at NTP) was equilibrated for 48 hr with stock oxygen-18 water (9 ml) at 25°. The $^{46}/_{44}$ ratio of the CO_2 was then measured and corrected for both the isotopic fractionation effect and the small dilution effect present in an exchange run owing to the water content of the concentrated hydrochloric acid employed.

Absorption Spectral Studies.—The visible absorption spectra of $Cr(ox)_2bipy^-$ and $Cr(ox)_2phen^-$ have been followed for a longer time interval than that reported previously.[4] After 14 hr at 25° in 1 *M* HCl the intensities of the absorption maxima of these species decrease by 13% for $Cr(ox)_2phen^-$ and 16% for $Cr(ox)_2bipy^-$ while the shape of each spectrum was unchanged. These observations are consistent with partial or complete aquation of the oxalato ligands rather than the amine groups. Oxalato and aquo ligands possess similar field strengths and it is known that replacement of the strong-field amine ligands by the weaker oxalato group leads to marked shifts in the absorption maxima to longer wavelengths.[3a]

Racemization Studies.—Racemization rate constants (k_{obsd}) have been calculated from the slopes of the plots of time *vs.* log α (α = degrees rotation). The rate constants have an overall accuracy of ±2%. Kinetic parameters have been obtained using k_{obsd} and the Arrhenius equation, and entropies of activation have been calculated using the method of Glasstone, *et al.*[6]

The rates of racemization were found to follow a simple first-order rate law. In some cases more accurate values of the rate constants than reported previously[4] have been obtained. For comparison with oxygen-18 experiments, measurements have

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(4) J. A. Broomhead, *J. Inorg. Nucl. Chem.*, **27**, 2049 (1965).

(5) M. Cohen and H. C. Urey, *J. Am. Chem. Soc.*, **60**, 679 (1938).

(6) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp 195–199.

been made in the range 0–1 M in acid. Data at constant unit ionic strength are given in Figure 1. For 1 M HCl, activation energies and entropies together with the parent data are given in Tables I and II.

Divalent metal ions also showed a marked effect on the racemization rates. To minimize effects due to hydroxy complexes the pH of stock solutions of the various metal ions was adjusted to 2.2 by the addition of hydrochloric acid. The rate effects of the acid at this pH are virtually negligible.[4] Results for both complex anions are given in Table III.

TABLE III

METAL ION CATALYZED RACEMIZATION OF $Cr(ox)_2bipy^-$ AND $Cr(ox)_2phen^-$ AT 25° AND pH 2.2

Soln	Concn, M	10^4k_{obsd}, sec^{-1}	
		$Cr(ox)_2bipy^-$	$Cr(ox)_2phen^-$
H_2O	...	2.07[a]	2.32[a]
LiCl	1.0	2.99	3.63
$CoCl_2$[b]	0.083	3.66	4.41
$NiCl_2$[b]	0.083	4.73	5.54
$CuCl_2$[b]	0.021	...	3.68
$CuCl_2$[b]	0.042	...	5.23
$CuCl_2$[b]	0.083	7.41	8.74
$CuCl_2$[b]	0.166	...	16.9
$CuCl_2$[b]	0.333	...	38.3

[a] Reference 4. [b] Ionic strength (KCl) 1 M.

A comparison of rate constants for solutions continually exposed to the light beam with those of solutions kept in the dark between readings showed no photoinduced racemization phenomena.

Oxygen-18-Exchange Studies.—For oxygen-18-exchange runs rate constants have been calculated using a modified McKay equation.[7-9] This has the form $k_Et/2.303n = \log [(R_\infty - R_0)/(R_\infty - R_t)]$, where k_E is a pseudo-first-order rate constant containing a term first order in hydrogen ion, t is the reaction time in seconds, and n is the number of kinetically indistinguishable oxygen atoms in the complex (here eight). R_0, R_t, and R_∞ refer to the $^{46}/_{44}$ mass ratios of CO_2 from samples isolated at times zero, t, and infinity, respectively.

The first-order acid dependence of the oxygen-18 exchange for $Cr(ox)_2bipy^-$ and $Cr(ox)_2phen^-$ is shown in Figure 2. Temperature dependence results are shown in Figure 3.

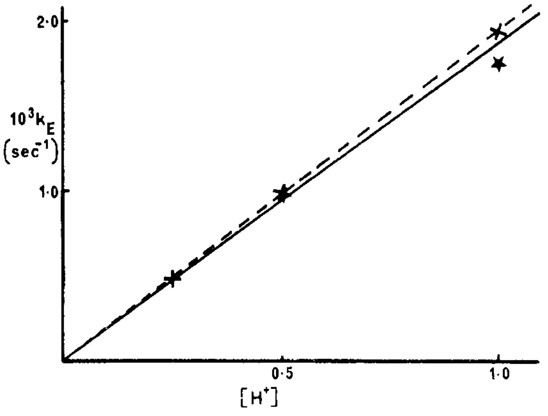

Figure 2.—Acid dependence of oxygen-18-exchange rate constants for $Cr(ox)_2phen^-$ (dotted line) and $Cr(ox)_2bipy^-$ (solid line) at 33° and unit ionic strength.

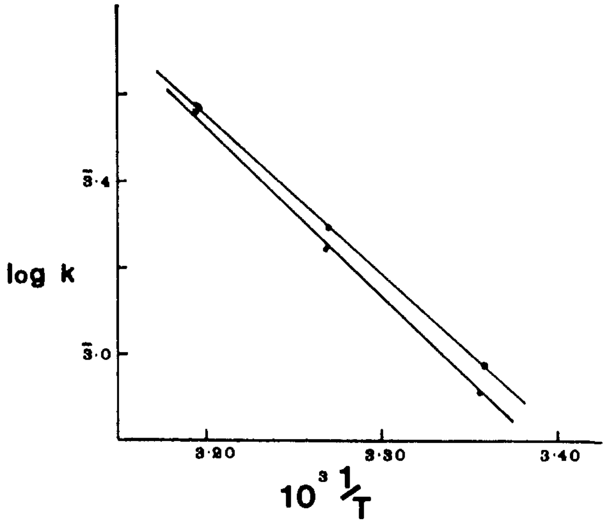

Figure 3.—Arrhenius plots for oxygen-18 exchange of $Cr(ox)_2phen^-$ (lower line) and $Cr(ox)_2bipy^-$ (upper line) in 1 M HCl.

Results and Discussion

The acid dependence curves shown in Figure 1 are consistent with a racemization rate law of the form $-d[\text{optically active complex}]/dt = k_{obsd}[\text{optically active complex}]$, where $k_{obsd} = k_1 + k_2[H^+] + k_3[H^+]^2$, k_{obsd} being the measured first-order rate constant for racemization, k_1 the rate constant for racemization in the absence of acid at unit ionic strength, and k_2 and k_3 the rate constants for pathways assuming mono- and diprotonated species, respectively (see later). Close agreement between k_{obsd} and calculated values of k_{obsd} for this rate expression is shown in Table IV. The near identity of the rate expressions and the closely similar rate data of Tables I and II, together with previous work on these complexes,[4] leave little doubt that they racemize in acid by similar mechanisms. It seems probable that the mechanisms involve partial dissociation of oxalate ligands. Ring opening could follow an initial rapid protonation of a carbonyl oxygen to give a trigonal-bipyramidal complex. Closure of this chelate ring can then proceed with equal probability of generating either enantiomer and the process is first order with respect to hydrogen ion. The second-order dependence on hydrogen ion is understood as a second protonation involving the remaining oxalate ligand. Racemization may follow readily with the subsequent opening of the two oxalate chelate rings facilitated by this protonation. Also some total dissociation of oxalate is to be expected and is consistent with the absorption spectral studies.

TABLE IV

CALCULATED AND OBSERVED ACID DEPENDENCE OF RACEMIZATION RATES FOR $Cr(ox)_2bipy^-$ AND $Cr(ox)_2phen^-$ AT 25° AND UNIT IONIC STRENGTH

[HCl], M	$Cr(ox)_2bipy^-$ [a]		$Cr(ox)_2phen^-$ [b]	
	10^4k_{obsd}, sec^{-1}	10^4k_{calcd}, sec^{-1}	10^4k_{obsd}, sec^{-1}	10^4k_{calcd}, sec^{-1}
0.10	2.06	2.07	2.71	2.71
0.25	2.51	2.50	3.21	3.19
0.50	3.33	3.33	4.13	4.13
0.75	4.30	4.30	5.23	5.23
1.00	5.29	5.41	6.39	6.50

[a] $k_1 = 1.82 \times 10^{-4}$ sec^{-1}; $k_2 = 2.44 \times 10^{-4}$ M^{-1} sec^{-1}; $k_3 = 1.15 \times 10^{-4}$ M^{-2} sec^{-1}. [b] $k_1 = 2.43 \times 10^{-4}$ sec^{-1}; $k_2 = 2.73 \times 10^{-4}$ M^{-1} sec^{-1}; $k_3 = 1.34 \times 10^{-4}$ M^{-2} sec^{-1}.

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(7) H. A. C. McKay, *Nature*, **142**, 997 (1938).

(8) H. A. C. McKay, *J. Am. Chem. Soc.*, **65**, 702 (1943).

(9) G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p 285.

These studies do not support loss of either phenanthroline or bipyridine in acid solution nor does the rate law found agree with the involvement of the phenanthroline base. Though the more flexible bipyridine molecule is capable of giving a half-bonded protonated stage, this seems very improbable for the rigid phenanthroline ligand. In the nickel(II) complexes of phenanthroline and bipyridine the presence of the bipyridine group is essential before acid-dependent dissociation ensues.[2]

From Table III the relative catalytic efficiency of the divalent metal ions is $Cu^{2+} > Ni^{2+} > Co^{2+}$. This is the same order as that of the formation constants of monooxalato complexes[10,11] and strongly suggests a parallel role for these ions similar to that of the hydrogen ion in promoting racemization by oxalate ring opening.

Table V

Calculated and Observed Copper(II) Ion Dependence of the Racemization of $Cr(ox)_2phen^-$ at 25° and Unit Ionic Strength

$[Cu^{2+}]$, M	10^4k_{calcd},[a] sec^{-1}	10^4k_{obsd}, sec^{-1}	$[Cu^{2+}]$, M	10^4k_{calcd},[a] sec^{-1}	10^4k_{obsd}, sec^{-1}
0.021	3.78	3.68	0.166	16.7	16.9
0.042	5.27	5.23	0.333	39.0	38.3
0.083	8.54	8.74			

[a] $k_1 = 2.43 \times 10^{-4}\ sec^{-1}$; $k_2 = 61.5 \times 10^{-4}\ M^{-1}\ sec^{-1}$; $k_3 = 145 \times 10^{-4}\ M^{-2}\ sec^{-1}$.

The data of Table III for $Cr(ox)_2phen^-$ are in good agreement with the rate law $-d[(+)Cr(ox)_2phen^-]/dt = k_{obsd}[(+)Cr(ox)_2phen^-]$, where $k_{obsd} = k_1 + k_2[Cu^{2+}] + k_3[Cu^{2+}]^2$. Here k_1 is the racemization rate constant in 1 M KCl, and k_2 and k_3 are rate constants associated with copper(II)–oxalato ligand interactions of the type already suggested for hydrogen ions. Calculated and observed first-order rate constants for this rate law are given in Table V. In addition chelate structures become possible which should contribute to chromium–oxygen bond weakening (Figure 4).

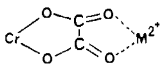

Figure 4.—Chelate bridging pathway for metal catalysis of racemization processes.

Bridging bichelate oxalate structures of this type have recently been described for Cu(II), Ni(II), and Zn(II).[12] The marked effect of metal ions is worth noting. Copper(II), for example, at a concentration of 0.064 M has the same effect on the racemization rate constant for $Cr(ox)_2phen^-$ as 1.0 M HCl under similar conditions. Temperature-dependence studies (Table VI) link the rate increases on the addition of copper(II) with a lowering of the activation energy (*cf.* ref 4). The greater effectiveness of copper(II) compared with the proton is also shown in the second- and third-order rate constants (k_2 and k_3 of Tables IV and V) which are orders of magnitude larger for the metal.

Table VI

Racemization of $(+)Cr(ox)_2phen^-$ in 0.042 M Copper(II) Chloride Solution at Unit Ionic Strength

Temp, °C	10^4k_{obsd}, sec^{-1}	E_a, kcal mol^{-1}	Log A (A in sec^{-1})	ΔS, eu
25	5.23			
33	11.2	17.1	9.3	−18.2
40	20.8			

Although the observations in acid solution support a contribution to racemization from half-bonded oxalate ligands, it is clear that there is a further pathway not accessible to acid or metal ion catalysis. This is measured by the rate constant k_1 and is evidently similar for both $Cr(ox)_2bipy^-$ and $Cr(ox)_2phen^-$. An intramolecular twist mechanism of the type suggested by Gehman[13] and further discussed by Brady[14] may possibly be contributing here.

The results of the acid-catalyzed oxygen-18 exchange with solvent water for $Cr(ox)_2bipy^-$ and $Cr(ox)_2phen^-$ (Table VII) show that both carbonyl and carboxyl oxygens exchange at the same rate. The exchange rates are strictly first order in acid (Figure 2). Negligible exchange occurs in the absence of acid. The exchange reaction is independent of the concentration of $Cr(ox)_2bipy^-$ and shows a slight dependence on the concentration of $Cr(ox)_2phen^-$ (Table VIII).

Table VII

Comparison of Calculated and Observed $^{46}/_{44}$ Mass Ratio Values (R) Assuming Complete Exchange at Infinite Time for 1 M Hydrochloric Acid Solutions at 33°

Complex	Reaction time, min	10^5R	
		Obsd	Calcd
$Cr(ox)_2bipy^-$	364[a]	1816	1825
$Cr(ox)_2phen^-$	374[a]	1804	1825

[a] Approximately 7 half-lives based on k_E.

Table VIII

Rate Data for the Exchange of Oxygen-18 between Solvent Water and Chromium–Oxalato Complexes at 33°

$[Cr(ox)_2phen^-]$, M	$[Cr(ox)_2bipy^-]$, M	$10^4k'$,[d] $M^{-1}\ sec^{-1}$	$[Cr(ox)_2phen^-]$, M	$[Cr(ox)_2bipy^-]$, M	$10^4k'$,[d] $M^{-1}\ sec^{-1}$
0.036[a]	. . .	17.4 ± 0.1	. . .	0.023[c]	19.2 ± 0.8
0.015[a]	. . .	19.8 ± 0.1	. . .	0.036[a]	19.4 ± 0.3
. . .	0.018[b]	19.0 ± 0.2			

[a] In 1 M HCl. [b] In 0.25 M HCl. [c] 0.5 M HCl. [d] $k_E = k'[H^+]$.

These observations are in agreement with the rate expression rate $= k_E[\text{complex}]$, where $k_E = k'[H^+]$. Here k' is the second-order exchange rate constant. A comparison of the data obtained in this work, together with related data on other anionic complexes and oxalic acid itself, appears in Table IX. It is remarkable that there is so little variation in these parameters which suggests that the exchange process occurs at a position removed from the effects of the metal atom.

A mechanism accommodating the above information involves rapid protonation of a carbonyl oxygen fol-

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[10] K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **4**, 1120 (1965).

[11] K. Yatsimirskii and V. P. Vasilev, "Instability Constants of Complex Compounds," Pergamon Press, Inc., New York, N. Y., 1960, pp 161–162.

[12] N. F. Curtis, *J. Chem. Soc., A*, 1584 (1968).

[13] W. Gehman, Thesis, The Pennsylvania State University, 1954.

[14] J. Brady, *Inorg. Chem.*, **8**, 1208 (1969).

lowed by the rate-determining attack of water on the carbonyl carbon and has been partly discussed in a previous communication[15] dealing with cationic chromium(III) and cobalt(III) complexes. It has also been suggested for oxygen exchange in $Pt(ox)_2^{2-}$.[16] A feature of this mechanism is that the necessary kinetic equivalence of both carbonyl and carboxyl oxygens is produced if rapid oxalate ring opening follows upon the initial protonation. Alternatively, the equivalence of all four oxygens can be obtained by the interchange of the carbonyl and carboxyl oxygens[17] through rotation about the C–C bond of the oxalato ligand as illustrated in Figure 5. Provided the interchange is fast compared to the rate of carbonyl oxygen exchange, then the two processes are kinetically indistinguishable.

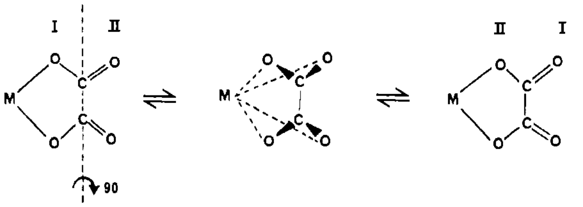

Figure 5.—Interchange mechanism for carboxyl (I) and carbonyl (II) oxygen atoms in the oxalato ligand.

A possible distinction between the ring-opening and interchange mechanisms is that the former could provide opportunity for racemization whereas the latter must lead to retention of configuration. A comparison of racemization (Tables I, II) and oxygen-exchange (Table IX) data in 1 M HCl reveals a close similarity between the rate parameters. However the rate expressions for the two reactions must also be considered. Oxygen exchange is first order in acid whereas racemization proceeds by paths which are zero, first, and second order in acid. Comparisons are then, at best, restricted to the paths showing first-order dependence on hydrogen ion. Undoubtedly the rate-controlling steps for oxygen exchange and racemization are different. For example, the observation that metal ions can accelerate the rate of racemization (Table III) is not paralleled by a similar effect on oxygen exchange. The results of experiments to check the effects of hexaaquocobalt(II) ions on the oxygen-exchange process are given in Table X and show a negligible influence for this metal. Unfortunately attempts to use copper(II) in the experiment were unsuccessful as the complexes could not then be readily precipitated.

TABLE IX

KINETIC PARAMETERS FOR OXYGEN-18 EXCHANGE IN 1 M HCl AT 25°

Exchanging species	10^4k_E, sec^{-1}	E_a, kcal mol^{-1}	Log A (A in sec^{-1})
$Cr(ox)_2phen^-$	8.20	18.4	10.4
$Cr(ox)_2bipy^-$	9.32	17.0	9.4
$Cr(ox)_2(H_2O)_2^-$ [a]	3.84	18.4	9.8
$Cr(ox)_3^{3-}$ [b]	12.8	18.0	10.6
$Rh(ox)_3^{3-}$ [c] (outer oxygens)	5.52	16.3	8.7
$Co(ox)_3^{3-}$ [b]	2.11	18.6	10.0
$H_2C_2O_4$	6.22	18.4	10.3

[a] J. Aggett, I. Mawston, A. L. Odell, and B. E. Smith, *J. Chem. Soc., A*, 1413 (1968). [b] C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *ibid.*, 4615 (1964). [c] L. Damrauer and R. M. Milburn, *J. Am. Chem. Soc.*, **90**, 3884 (1968).

TABLE X

OXYGEN-EXCHANGE RESULTS FOR CHROMIUM(III) COMPLEXES IN WATER AND IN 0.25 M COBALT(II) CHLORIDE SOLUTION AT 33°

$Cr(ox)_2phen^-$			$Cr(ox)_2bipy^-$		
Reaction time, hr	10^5R_t[a] H_2O	$CoCl_2$	Reaction time, hr	10^5R_t[a] H_2O	$CoCl_2$
2.5	421	...	2.9	421	...
10.1	421	...	10.5	421	...
24.2	420	...	24.5	421	...
17.5	...	438	17.5	...	438

[a] R_t = ${}^{46}/_{44}$ mass ratio. For isotopically normal CO_2 the measured ${}^{46}/_{44}$ ratio is 421 × 10^{-5}. The calculated R_∞ value is 2760 × 10^{-5}.

The enhanced rate of racemization in the presence of metals has already been discussed in terms of promoting the rate of Cr–O bond breaking. A similar role could well be played in the carbonyl oxygen-exchange process but it is of little consequence as the rate of Cr–O bond cleavage (or interchange) is already greater than the rate of carbonyl oxygen exchange. While it may seem reasonable that a metal should facilitate attack by a water molecule on the carbonyl carbon, a metal is clearly unable to complete the exchange process. The two reactions are shown in Figure 6. What may be regarded as a hydride transfer in A leads immediately to an alternative pathway for removal of H_3O^+ and hence to oxygen exchange whereas B has no such pathway.

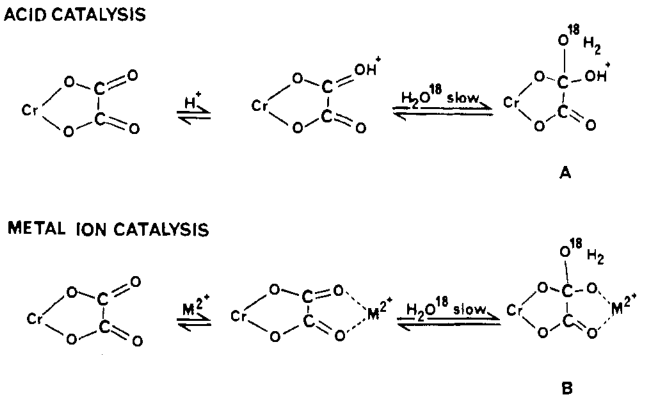

Figure 6.—Comparison of hydrogen ion and metal ion catalyzed pathways for carbonyl oxygen exchange.

It should be emphasized that though correlations may exist between exchange of oxygen in oxalato complexes and the racemization kinetics, the intimate mechanisms may well be different. The effects of metal ions on racemization do support the presence of half-bonded species and it is possible that oxygen exchange is by this path. However this work has shown

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[15] J. A. Broomhead, N. Kane-Maguire, I. Lauder, and P. Nimmo, *Chem. Commun.*, 747 (1968).

[16] J. E. Teggins and R. M. Milburn, *Inorg. Chem.*, **4**, 793 (1965).

[17] C. Andrade, Thesis, University of Chicago, Chicago, Ill., 1964.

that the rate expressions for oxygen exchange and for racemization of $Cr(ox)_2bipy^-$ and $Cr(ox)_2phen^-$ are different. When it is remembered that oxygen exchange can proceed entirely by an interchange mechanism and that this does *not* produce racemization, then the dangers in using the two sets of rate data become apparent. Even without an interchange mechanism the general exchange independence of changes in the central metal (Table IX) indicates that the rate-controlling step is probably attack of water on the carbonyl carbon. This is of no consequence in producing racemization.

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Synthesis and Characterization of N,N-Dialkyldithiocarbamate Complexes of Niobium(V) and Tantalum(V)

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N,N-Dialkyldithiocarbamate salts react with niobium and tantalum pentahalides in methanol to give compounds with the stoichiometry $MX(OCH_3)_2(S_2CNR_2)_2$. Compounds were prepared in which X was Cl, Br, and NCS and R was CH_3, C_2H_5, and $CH_2C_6H_5$. The compounds are air-stable crystalline materials. Solutions of the compounds in CH_3Cl, CCl_4, and *t*-butyl alcohol are stable; they decompose in primary alcohols. The compounds are nonelectrolytes and are monomeric. Ultraviolet, infrared, and proton magnetic resonance spectral data are presented.

Introduction

Few well-characterized crystalline complexes of niobium(V) and tantalum(V) are described in the literature.[1] Of those which are known many are unstable in solution or to the moisture in the atmosphere. The work reported in this paper describes some of our efforts to prepare relatively stable complexes of these elements.

N,N-Dialkyldithiocarbamate salts form complexes with a variety of metal ions. In these complexes the ligand typically coordinates as a bidentate ligand through the two sulfur atoms. Dithiocarbamate complexes of niobium ($Nb(S_2CN(CH_3)_2)_4$) and tantalum ($Ta(S_2CN(CH_3)_2)_5$) have been synthesized by the insertion of CS_2 into Nb–N bonds of dimethylamine complexes of niobium and tantalum.[2] Their properties have not been reported.

Experimental Section

Reagents.—Niobium and tantalum pentahalides were obtained from Alfa Inorganics Inc. Sodium diethyldithiocarbamate was obtained as a certified ACS reagent from Fisher Scientific Co. The dimethylammonium salt of dimethyldithiocarbamic acid and the zinc salt of dibenzyldithiocarbamic acid were obtained as "highest purity" grade reagents from Eastman Organic Chemicals. All solvents were ACS reagent grade and were dried over molecular sieves.

Physical Measurements.—Magnetic susceptibilities were measured at room temperature (25°) by the Gouy method. Conductivities were measured using a fill cell having a cell constant of about 0.4 cm^{-2} ml^{-1} and an Industrial Instruments Inc. Model RC1B conductivity bridge.

Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Infrared spectra were recorded in KBr wafers using a Perkin-Elmer Model 257 grating spectrophotometer. Integrated intensities were obtained using Ramsay's method of direct integration.[3] Acetonitrile solutions were used in intensity studies. Nmr spectra were recorded on a Varian T-60 spectrometer using $CDCl_3$ and CD_3CN as solvents. For detailed studies a Varian A-60A spectrometer was used.

Molecular weights were determined cryoscopically in sulfolane for the Nb–Cl derivatives. The sulfolane was purified and dried by distillation from powdered KOH under vacuum. Molecular weights were also determined using $CHCl_3$ solutions in a Mechrolab Inc. vapor pressure osmometer, Model 301A.

Methods of Analysis.—Niobium and tantalum were determined as M_2O_5 by igniting the compound in a porcelain crucible. Halide analyses were done by the Volhard method preceded by fusion of the sample with Na_2O_2 and NaOH. Carbon, hydrogen, sulfur, and nitrogen analyses were performed by Midwest Micro Lab Inc.

Preparation of Complexes. $NbCl(OCH_3)_2(dedtc)_2$.—A 5.5-g sample of $NbCl_5$ (0.02 mol) was weighed out in a 500-ml round-bottom flask in a drybox. Methanol (100 ml) was added. Vigorous evolution of HCl and a clear, colorless solution resulted. A solution of 9.00 g of $Na(dedtc)\cdot 3H_2O$ (0.04 mol) in 100 ml of methanol was prepared and added. A clear, dark wine red solution resulted. This solution bleaches over a period of 18–24 hr to a clear, light yellow solution containing large clusters of light yellow crystals. Recrystallization was accomplished by dissolving the compound in CCl_4, removing undissolved solid, and reducing the volume with a rotary evaporator until white crystals appeared. The compound was dried under vacuum.

$NbBr(OCH_3)_2(dedtc)_2$.—This compound was prepared in a manner similar to the chloro compound. The product is a white, crystalline compound.

$NbNCS(OCH_3)_2(dedtc)_2$.—A 5.5-g sample of $NbCl_5$ (0.02 mol) was dissolved in 100 ml of methanol. To this solution was added 8.1 g of NaSCN (0.10 mol). The solution turned yellow and a

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(1) F. Fairbrother, "The Chemistry of Niobium and Tantalum," Elsevier Publishing Co., New York, N. Y., 1967.

(2) D. C. Bradley and M. H. Gitlitz, *Chem. Commun.*, 289 (1965).

(3) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).