[Cu(phen)$_2$(CN)]NO$_3$, 42741-08-2; [Cu(phen)$_2$(CN)]PF$_6$, 61723-53-3.

Supplementary Material Available: Tables I–III showing calculated and observed magnetic susceptibility data (4 pages). Ordering information is given on any current masthead page.

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Volumes of Activation for Intramolecular Racemization Mechanisms. High-Pressure Racemization of Bipyridyl, Phenanthroline, and Oxalato Complexes of Chromium(III) in Solution

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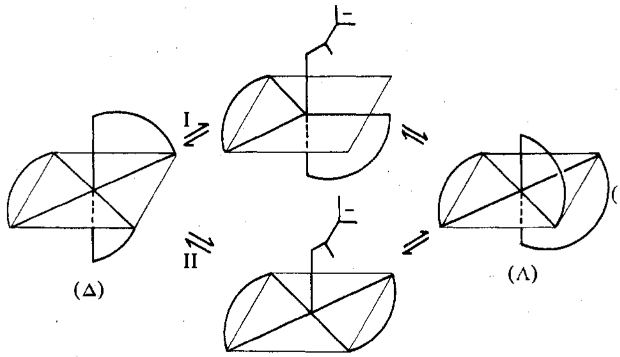
The effect of high pressure on the rates of racemization of metal complexes in solution has been evaluated for the first time. The racemization of Cr(phen)$_3^{3+}$ exhibits a volume of activation, $\Delta V^\ddagger = +3.3 \pm 0.2$ cm^3 mol^{-1}, which is shown to be consistent with an intramolecular twist mechanism. The racemization of Cr(C$_2$O$_4$)$_3^{3-}$ exhibits $\Delta V^\ddagger = -16.3 \pm 0.4$ cm^3 mol^{-1}, consistent with racemization through one-ended dissociation of an oxalato ligand. Cr(phen)(C$_2$O$_4$)$_2^-$ and Cr(bpy)(C$_2$O$_4$)$_2^-$ exhibit $\Delta V^\ddagger = -12.3 \pm 0.3$ and $\Delta V^\ddagger = -12.0 \pm 0.3$ cm^3 mol^{-1}, respectively, and these racemizations are assigned a one-ended dissociation mechanism. Cr(phen)$_2$(C$_2$O$_4$)$^+$, Cr(bpy)$_2$(C$_2$O$_4$)$^+$, and Cr(bpy)$_3^{3+}$ exhibit $\Delta V^\ddagger = -1.5 \pm 0.2, -1.0 \pm 0.1$, and $+3.4 \pm 0.3$ cm^3 mol^{-1}, respectively, and these are all assigned intramolecular twist mechanism. Enthalpies and entropies of activation were evaluated for all of these systems; $\Delta H^\ddagger$ values are least for Cr(C$_2$O$_4$)$_3^{3-}$ and greatest for Cr(phen)$_3^{3+}$ and Cr(bpy)$_3^{3+}$ while $\Delta S^\ddagger$ values, all large and negative, show the reverse trend.

Introduction

Both intermolecular and intramolecular mechanisms have been proposed for racemization and isomerization in six-coordinate octahedral chelate complexes, and recent studies to elucidate these mechanisms have been the subject of a recent extensive review.[1] The intermolecular mechanism, involving complete loss of one chelate ligand, may be detected by isotopic exchange studies and by comparison of dissociation or aquation rates with those for isomerization or racemization. However, the elucidation of intramolecular mechanisms is more difficult even though extensive information has accumulated from exchange studies and from measured enthalpies and entropies of activation. A new approach which we are now proposing is to study the effect of high pressure upon the rates of racemization in solution to evaluate the volume of activation, $\Delta V^\ddagger$, for the racemization process. Each of the possible intramolecular mechanisms may then be considered in terms of the difference in volume of the transition state for the racemization and the corresponding ground state. This approach has been fruitful in elucidating details of inorganic substitution and redox reactions[2,3] and similar interpretative approaches should apply to racemization processes.

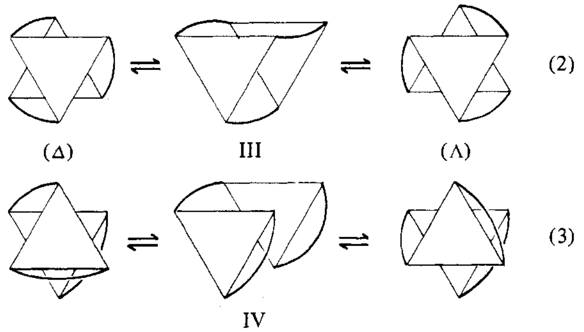
Two essentially different types of intramolecular mechanism have been proposed for complexes of bidentate ligands and are differentiated by whether racemization occurs with or without bond rupture. The bond-rupture mechanism was first proposed by Werner[4] and involves a *one-ended dissociation* of a bidentate ligand from the central metal ion. This dissociative process is accompanied by rearrangement of the remaining groups to a five-coordinate transition state which would have either the limiting trigonal-bipyramidal (I) or the square-pyramidal (II) structure. This rearrangement must involve motion or twisting of at least one of the intact chelate rings. Reattachment of the dangling ligand and reversion to an octahedral configuration may occur at the identical site to that

Scheme I



(1)

Scheme II



for dissociation, in which case the optical isomer is regenerated, or alternately at the other possible site whereby the opposite isomer is generated. The mechanism can be represented in Scheme I where the dangling ligand carries a formal charge, as in oxalate.

The transition state, and any related intermediate, in eq 1 remains five-coordinate and arguments have been developed[2] that the intrinsic volume of such a truly five-coordinate species will be equivalent to that of its six-coordinate precursor except for the additional volume swept out in solution by the dangling ligand. Furthermore the mechanism, in its simplest form, assumes only changes in bond angles within the complex without changes in bond length. The volume of activation should then be equal to the volume change generated by one-ended release of the bidentate ligand. For a neutral ligand, $\Delta V^{\ddagger}$ would be expected to be positive. For a charged species, as with the oxalato ligand employed in this study, the solvent surrounding the newly implanted charge will suffer electrostriction of a magnitude exceeding any volume increase due to the intrinsic volume of the ligand. Consequently, one-ended dissociation of a charged ligand should yield a negative volume of activation. A detailed analysis of this case has been incorporated subsequently in the Discussion.

The mechanism by which racemization can occur without bond rupture being necessary is usually referred to as a *twist* mechanism. By twisting the ligands from the octahedral configuration, an inactive trigonal-prismatic transition state and intermediate can be generated. The complex may return from this transition state to the original isomeric form or twist an identical amount in the opposite sense to produce the opposite isomer. The first twisting mechanism was proposed by Ray and Dutt[5] with further modified twists being reported by Bailar[6] and Springer and Sievers.[7] Subsequently authors, either implicitly (Fay and Piper,[8] Springer and Sievers[7]) or explicitly (Brady[9]), have pointed out that there is essentially only one type of twisting mechanism, which when carried out about the various threefold axes of the octahedron may give rise to two possible nearly trigonal-prismatic transition states, one with approximately D_{3h} symmetry (III) and the other with nearly C_{2v} (IV) symmetry. Racemization through a twist mechanism may therefore be represented in terms of a "Bailar" twist process as shown in Scheme II. Springer and Sievers recognized that the Ray–Dutt twist is a special case of the Bailar twist. The Ray–Dutt twist is a rigid-ring process in which donor–metal–donor bond angles and chelate internal ring angles remain constant throughout. The Bailar twist involves a flexing of rings such that changes can occur in all of the internal chelate ring angles.

The intramolecular twist mechanism is assumed to occur to a first approximation without any bond lengthening or ligand dissociation, regardless of the nature of the ligands involved. Since the twist mechanism is confined to changes in bond angles, then the formation of either of the trigonal-prismatic transition states from an octahedral ground state should involve a negligible volume change. A pressure-independent rate of racemization, with $\Delta V^{\ddagger}$ approximately zero, would therefore be expected.

In order to test these mechanistic expectations, we selected for high-pressure studies the rates of racemizations of $Cr(ox)_3{}^{3-}$ and of $Cr(phen)_3{}^{3+}$.[10] Early studies by Long[11] with tris(oxalate) complexes of metal ions indicated that no exchange of free $^{11}C_2O_4{}^{2-}$ with $Cr(ox)_3{}^{3-}$ and $Co(ox)_3{}^{3-}$ occurred, although such exchange did occur with certain other metal ions. This observation excludes the possibility of a dissociative intermolecular mechanism for the racemization of $Cr(ox)_3{}^{3-}$. There is now extensive exchange and kinetic evidence, which is reviewed in the Discussion, that racemization of $Cr(ox)_3{}^{3-}$ involves a one-ended dissociation of an oxalato ligand in an intramolecular mechanism at least for the acid-catalyzed path. On the other hand, the large rigid flat phenanthroline ligands in $Cr(phen)_3{}^{3+}$ impose considerable steric constraints on one-ended phen dissociation. A twist mechanism has already been proposed for $Fe(phen)_3{}^{2+}$ complexes[12,13] and a twist mechanism is very likely. Our earlier high-pressure studies[14] in the aquation of a number of phen complexes of iron(II) also provide a useful check on the value of $\Delta V^{\ddagger}$ for phen dissociation since for these complexes $\Delta V^{\ddagger} = 12–18$ cm^3 mol^{-1}. For our calibration systems, we therefore expected a negative $\Delta V^{\ddagger}$ value for the racemization of $Cr(ox)_3{}^{3-}$ and a near-zero value for racemization of $Cr(phen)_3{}^{3+}$.

The two calibration systems were supplemented with the other members of the series $Cr(ox)_3{}^{3-}$, $Cr(ox)_2(phen)^-$, $Cr(ox)_2(bpy)^-$, $Cr(ox)(phen)_2{}^+$, $Cr(ox)(bpy)_2{}^+$, $Cr(bpy)_3{}^{3+}$, and $Cr(phen)_3{}^{3+}$ for this study. Within this series, it was of interest to inquire as to whether a change in racemization mechanism occurred between the two extremes of $Cr(ox)_3{}^{3-}$ and $Cr(phen)_3{}^{3+}$ depending on the number of phen ligands and bpy ligands. The latter ligands, in a one-ended dissociative mode, could undergo twisting motions which are denied to the phen ligand.

All members of this series were prepared and resolved and their rates of racemization measured over a range of high pressure to evaluate volumes of activation. The reaction conditions were chosen to avoid the operation of an acid-catalyzed path which occurs for bpy and oxalato complexes; this path would have introduced an additional uncertainty in observed values of $\Delta V^{\ddagger}$ due to an unknown volume contribution from an acid preequilibrium. Since reliable data were not available for the uncatalyzed racemization paths, enthalpies and entropies of activation for each complex were also determined. At the time of completion of the experimental work, all data for the $Cr(phen)_3{}^{3+}$ and $Cr(bpy)_3{}^{3+}$ complexes were unreported. A recent temperature study[15] of the $Cr(phen)_3{}^{3+}$ systems agrees well with the data reported here.

Experimental Section

The **preparations** of the racemic chromium(III) complexes $[Cr(phen)_3](ClO_4)_3$,[16] $[Cr(bpy)_3](ClO_4)_3$,[16] $[Cr(ox)(phen)_2]Cl$,[17] $[Cr(ox)(bpy)_2]Cl$,[17] $K[Cr(ox)_2(phen)]$,[18] $K[Cr(ox)_2(bpy)]$,[18] and $K_3[Cr(ox)_3]$[19] were performed as previously reported.

The **resolution** of each complex was performed successfully using reported techniques. The resolved complex (−)-$[Cr(phen)_3](ClO_4)_3$ was obtained using silver antimonyl (+)-tartrate as resolving agent,[20] (−)-$[Cr(bpy)_3](ClO_4)_3$ by resolution with (−)-$K_3[Cr(ox)_3]$,[21] (+)-$K[Cr(ox)_2(phen)]$ and (+)-$K[Cr(ox)_2(bpy)]$ by resolution with (+)-$[Co(ox)(en)_2]Cl$,[18] (+)-$[Cr(ox)(phen)_2](ClO_4)$ and (+)-$[Cr(ox)(bpy)_2](PF_6)$ by resolution with (+)-$K[Cr(ox)_2(phen)]$[17] and (−)-$K_3[Cr(ox)_3]$ by resolution with (−)-$[Co(ox)(en)_2]Cl$.[22] A recently reported method for the resolution of racemic $[Co(ox)(en)_2]Cl$ was used successfully.[23]

High-pressure racemization kinetics were conducted in a high-pressure sampling vessel immersed in an oil bath thermostated to the appropriate temperature. All reactions were performed in 0.05 M aqueous hydrochloric acid solution with complex concentrations in the range 10^{-4} to 10^{-3} M. Aliquots of the reaction solution were

Table I. Rates of Racemization of Chromium(III) Complexes at Various High Pressures in 0.05 M HCl

Complex	Temp, °C	Pressure, kbars	$10^4 k_{obsd}$, s^{-1}
$Cr(ox)_3^{3-}$	15.0	0.001	5.43
		0.345	6.87
		0.690	8.70
		1.035	11.3
		1.380	14.3
$Cr(ox)_2(phen)^-$	25.0	0.001	2.58
		0.345	3.04
		0.690	3.66
		1.035	4.34
		1.380	5.20
$Cr(ox)_2(bpy)^-$	25.0	0.001	1.91
		0.345	2.27
		0.690	2.65
		1.035	3.13
		1.380	3.72
$Cr(ox)(phen)_2^+$	45.0	0.001	2.23
		0.690	2.32
		1.380	2.41
		2.070	2.54
$Cr(ox)(bpy)_2^+$	45.0	0.001	2.20
		0.690	2.26
		1.380	2.32
		2.070	2.39
$Cr(phen)_3^{3+}$	75.0	0.001	0.667
		0.690	0.613
		1.380	0.565
		2.070	0.522
$Cr(bpy)_3^{3+}$	75.0	0.001	0.834
		0.690	0.767
		1.380	0.696
		2.070	0.646

collected from the pressure vessel via a bleed valve at appropriate time intervals, and the rotation was measured rapidly at the Na D line on an adjacent Perkin-Elmer 241MC polarimeter fitted with a 1-dm path length thermostated microcell. Reactions were performed at intervals over the pressure range 0.001 (room pressure) to 2.069 kbars.[24] Rate coefficients for racemization (k_{obsd}) were evaluated from plots of log (rotation) against time over several half-lives, and reported k_{obsd} values are the average of at least two independent runs at each pressure. The reproducibility of k_{obsd} was always better than ±4%.

The **racemization kinetics** at different temperatures were measured for each complex at room pressure over a temperature range of 20 °C. The reaction solution was maintained at the appropriate temperature in the thermostated polarimeter cell throughout the reaction, or alternatively samples were drawn at appropriate time intervals from a reaction vessel maintained at the required temperature in a thermostated oil bath and the rotations measured rapidly as before. Rate coefficients were calculated as described above.

Results

High-Pressure Racemization. The rate of racemization in aqueous 0.05 M hydrochloric acid solution showed a marked acceleration upon the application of high pressure in the case of the $Cr(ox)_3^{3-}$, $Cr(ox)_2(phen)^-$, and $Cr(ox)_2(bpy)^-$ complexes. In contrast, only a small acceleration or retardation of the rate of racemization on the application of pressure was observed with the complexes $Cr(phen)_3^{3+}$, $Cr(bpy)_3^{3+}$, $Cr(ox)(phen)_2^+$, and $Cr(ox)(bpy)_2^+$.

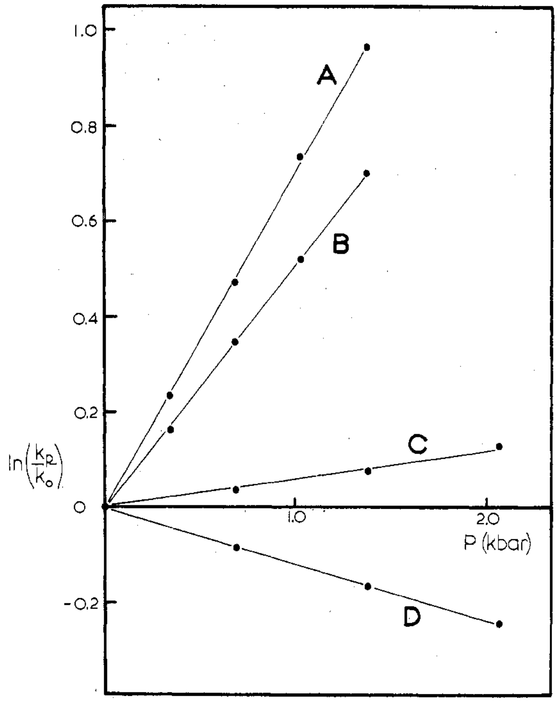


Figure 1. Pressure variation of rate coefficients for racemization of (A) $Cr(ox)_3^{3-}$, (B) $Cr(ox)_2(phen)^-$, (C) $Cr(ox)(phen)_2^+$, and (D) $Cr(phen)_3^{3+}$ in aqueous 0.05 M hydrochloric acid.

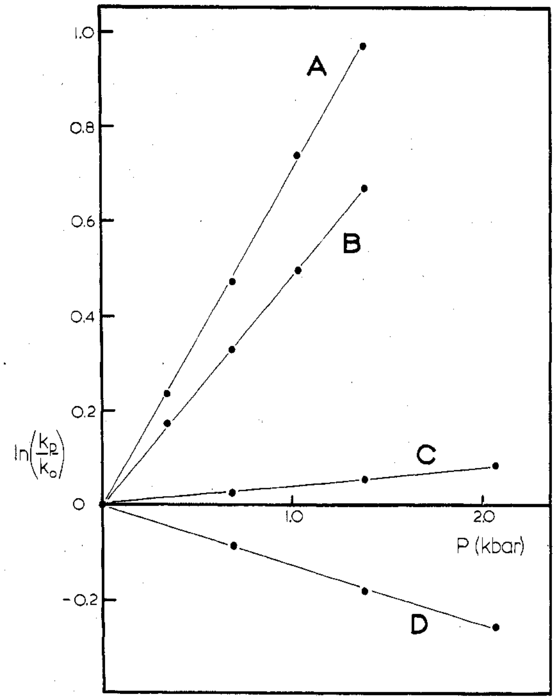


Figure 2. Pressure variation of rate coefficients for racemization of (A) $Cr(ox)_3^{3-}$, (B) $Cr(ox)_2(bpy)^-$, (C) $Cr(ox)(bpy)_2^+$, and (D) $Cr(bpy)_3^{3+}$ in aqueous 0.05 M hydrochloric acid.

Table I summarizes mean values of the rate coefficients determined at different pressures. The data for all seven complexes are accommodated adequately by the simple relationship between the pressure variation of the rate coefficient and the volume of activation ($\Delta V^{\ddagger}$), namely

$$(\partial \ln k/\partial P)_T = -\Delta V^{\ddagger}/RT \qquad (4)$$

so that no apparent pressure dependence of the volume of activation itself is observed over the pressure range used in this study. This is shown in Figure 1 for the oxalate–phenanthroline complexes and in Figure 2 for the oxalate–bipyridyl complexes, where in each case ln (k_P/k_O) is a linear function of the applied pressure at least up to 1.4 kbars. The volumes of activation for racemization were deduced using eq 4 and values of $\Delta V^{\ddagger}$, together with their standard deviations calculated by a normal least-squares routine, are included in Table II. Since these statistically estimated standard deviations are quite low, estimates of the maximum allowable error are also given.

Variable-Temperature Racemization. The rate of racemization at room pressure in aqueous 0.05 M hydrochloric acid solution was measured for each complex at five different

Table II. Volumes of Activation for Racemization of Chromium(III) Complexes

Complex	$\Delta V^{\ddagger}$, cm^3 mol^{-1}		Complex	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	
$Cr(ox)_3^{3-}$	-16.3 ± 0.2[a]	(± 0.4)[b]	$Cr(ox)(bpy)_2^+$	-1.0 ± 0.05	(± 0.1)
$Cr(ox)_2(phen)^-$	-12.3 ± 0.15	(± 0.3)	$Cr(phen)_3^{3+}$	$+3.3 \pm 0.05$	(± 0.2)
$Cr(ox)_2(bpy)^-$	-12.0 ± 0.15	(± 0.3)	$Cr(bpy)_3^{3+}$	$+3.4 \pm 0.1$	(± 0.3)
$Cr(ox)(phen)_2^+$	-1.5 ± 0.1	(± 0.2)			

[a] ± values are standard deviations estimated by least squares. [b] Parenthesized values are graphically estimated uncertainties as deduced from maximum and minimum slopes of $(\ln k_P)/(\ln k_O)$ vs. P.

Table III. Rates of Racemization of Chromium(III) Complexes at Room Pressure and Various Temperatures in 0.05 M HCl

Complex	Temp, °C	$10^4 k_{obsd}$, s^{-1}	Temp, °C	$10^4 k_{obsd}$, s^{-1}
$Cr(ox)_3^{3-}$	6.0	2.39	19.8	9.43
	10.5	3.76	25.1	16.1
	15.0	5.43		
$Cr(ox)_2(phen)^-$	14.8	0.896	30.4	4.34
	20.1	1.55	35.1	7.22
	25.0	2.58		
$Cr(ox)_2(bpy)^-$	14.8	0.712	30.4	3.33
	20.2	1.20	35.1	5.31
	25.0	1.91		
$Cr(ox)(phen)_2^+$	35.1	0.855	49.9	3.79
	40.2	1.42	55.7	6.34
	45.0	2.23		
$Cr(ox)(bpy)_2^+$	35.1	0.840	49.9	3.62
	40.2	1.42	55.7	6.11
	45.0	2.20		
$Cr(phen)_3^{3+}$	65.0	0.267	80.0	1.10
	70.1	0.413	85.0	1.82
	75.0	0.667		
$Cr(bpy)_3^{3+}$	65.0	0.331	80.0	1.29
	70.1	0.487	85.0	2.07
	75.0	0.834		

Table IV. Enthalpy and Entropy of Activation Data for Racemization of the Chromium(III) Complexes

Complex	Medium	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	Ref
$Cr(ox)_3^{3-}$	0.05 M aq HCl	66.5 ± 3.6	-76 ± 4	*a*
	H_2O	65.3	-99	25
	0.98 M aq HCl	73.1	-62	26
$Cr(ox)_2(phen)^-$	0.05 M aq HCl	72.9 ± 2.2	-69 ± 2	*a*
	H_2O	74.7	-71	27
	1.0 M aq HCl	76.0	-57	28
$Cr(ox)_2(bpy)^-$	0.05 M aq HCl	70.7 ± 2.8	-79 ± 3	*a*
	H_2O	67.8	-100	27
	1.0 M aq HCl	76.4	-58	28
$Cr(ox)(phen)_2^+$	0.05 M aq HCl	79.9 ± 2.3	-64 ± 2	*a*
	1.0 M aq HCl	84.7	-57	29
$Cr(ox)(bpy)_2^+$	0.05 M aq HCl	78.5 ± 1.8	-68 ± 2	*a*
	1.0 M aq KCl	85.6	-53	29
	1.0 M aq HCl	81.4	-61	29
$Cr(phen)_3^{3+}$	0.05 M aq HCl	94.3 ± 4.2	-56 ± 3	*a*
	H_2O	98.2	-46	15
$Cr(bpy)_3^{3+}$	0.05 M aq HCl	90.8 ± 4.0	-63 ± 3	*a*

[a] This work.

Table V. Rates of Racemization of Chromium(III) Complexes at Room Pressure, at 25 °C, and in 0.05 M HCl

Complex	$10^4 k_{obsd}$, s^{-1}	E_a, kJ mol^{-1}
$Cr(ox)_3^{3-}$	16	68.9
$Cr(ox)_2(phen)^-$	2.6	75.4
$Cr(ox)_2(bpy)^-$	1.9	73.1
$Cr(ox)(phen)_2^+$	0.28	82.5
$Cr(ox)(bpy)_2^+$	0.29	81.2
$Cr(phen)_3^{3+}$	0.0025[a]	93.0
$Cr(bpy)_3^{3+}$	0.0036[a]	93.7

[a] Obtained by extrapolation of results at higher temperature.

temperatures over a temperature range of approximately 20 °C. The mean values of the rate coefficients determined at different temperatures are summarized in Table III.

The activation energy (E_a) and enthalpy of activation ($\Delta H^{\ddagger}$) for racemization of each complex were deduced from plots of log k vs. $1/T$, and the entropy of activation ($\Delta S^{\ddagger}$) was calculated subsequently from E_a and the racemization rate in the usual manner. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, together with standard deviations calculated by a standard least-squares routine, are collected in Table IV. Data from previous studies are included in this table for comparative purposes.

For each complex, the rate of racemization at a fixed temperature was found to be essentially independent of acid concentration in the range 0.01–0.05 M H^+, consistent with an acid-independent racemization pathway under the selected conditions. The rates of racemization and energy of activation of the complexes at room pressure and 25 °C are reported in Table V. The observed rate diminishes markedly throughout the series from $Cr(ox)_3^{3-}$ to $Cr(phen)_3^{3+}$, by the order of 10^{-4}. This general decrease is reflected in an increasing energy of activation with decreasing rate of racemization.

Discussion

Racemization of $Cr(phen)_3^{3+}$ and $Cr(bpy)_3^{3+}$. Like that of other $M(phen)_3$ complexes,[30] the structure of $Cr(phen)_3^{3+}$ in aqueous solution may be visualized[31] as a three-bladed propeller, the blades of the propeller being the planar phen ligands. Within this structure there are three V-shaped pockets large enough to accommodate two water molecules each, and proton NMR line width studies[32] of the $Cr(phen)_3^{2+}$ cation suggest that this water penetrates some 200 pm into the phen pockets. The Cr^{III}–N bond distance is 206 pm[33] and the N(1)–N(10) separation in the phen ligand is 265 pm, giving a bite of 1.29 with a N(1)–Cr–N(10) bond angle of 79.4°. This bite[34] and bond angle are close to the requirements[1,6] of a trigonal-prismatic intermediate with a theoretical bond angle of 81° 48′. These structural characteristics suggest that an intramolecular twist mechanism of the rigid chelate twist variety is likely to be the preferred mechanism for racemization. The thickness of the phen ring (380 pm) is so great as to make one-ended dissociation very improbable and the comparable process of aquation of $Fe(phen)_3^{2+}$ is associated[14] with $\Delta V^{\ddagger} = +15.4$ cm^3 mol^{-1}. In this case, this volume change is considered to be generated by lengthening of both Fe–N bonds to the phen ligand by some 61 pm.

The observed value for the racemization of $Cr(phen)_3^{3+}$, $\Delta V^{\ddagger} = +3.4$ cm^3 mol^{-1}, is close to zero as anticipated for the first approximation description of an intramolecular twist mechanism. The small positive deviation from zero could be attributed either to a small expansion in Cr–N bond distances on forming the trigonal-prismatic transition state or to secondary effects upon the water in the V-shaped pockets of $Cr(phen)_3^{3+}$. The latter explanation is preferred since there is well-documented evidence[32] that the corresponding intramolecular process for $Fe(phen)_3^{2+}$ is markedly affected by the viscosity of the solvent. It seems plausible that motion of the rigid phen chelates to form the transition state will tend to squeeze out water trapped in the V-shaped pockets, thereby making a slight positive contribution to the observed value of $\Delta V^{\ddagger}$.

The kinetic behavior of the $Cr(bpy)_3^{3+}$ cation is remarkably close in its values of rate, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and especially $\Delta V^{\ddagger}$ (see

Table VI. Measured Activation Parameters for Racemization of Chromium(III) Complexes

Complex	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
$Cr(ox)_3^{3-}$	−16.3	66.5	−76
$Cr(ox)_2(phen)^-$	−12.3	72.9	−69
$Cr(ox)_2(bpy)^-$	−12.0	70.7	−79
$Cr(ox)(phen)_2^+$	−1.5	79.9	−64
$Cr(ox)(bpy)_2^+$	−1.0	78.5	−69
$Cr(phen)_3^{3+}$	+3.3	94.3	−56
$Cr(bpy)_3^{3+}$	+3.4	90.8	−63
Av std dev	±0.3	±3.0	±2.7

Table VI) to those of $Cr(phen)_3^{3+}$. This suggests that there is no contribution from a possible dissociation and twisting of the bpy ligand in the uncatalyzed racemization pathway. The mechanism for racemization of $Cr(bpy)_3^{3+}$ based especially on the small positive ΔV^* seems to be also an intramolecular twist with an accompanying positive volume contribution from water trapped in the clefts between the rotating bpy ligands.

The proposed intramolecular twist mechanism for $Cr(phen)_3^{3+}$ and $Cr(bpy)_3^{3+}$ cations is characterized by very low rates of racemization at 25 °C (Table IV) and relatively high enthalpies of activation. Large ΔH^* values would be expected for d^3 complexes with the phen and bpy ligands of high ligand field strength. Although the entropies of activation are less negative than those for other complexes in the series (Table VI), there is no abrupt change in ΔS^* values which might be construed as indicating a change in mechanism within the series. The negative ΔS^* value is comparable to those observed for racemization of tris(tropolonato)[35] and tris(dithiocarbamato)[36] complexes but the values do not provide unequivocal evidence for the presumed intramolecular twist mechanisms in these systems.

Racemization of $Cr(ox)_3^{3-}$. The oxalato ligand in chromium(III) complexes exhibits a Cr–O bond distance of 192 pm[37] and an O–O separation of 254 pm giving a bite of 1.32 and a O–Cr–O bond angle of 83°. This bite is larger than that of the phen ligand and the bond angle somewhat greater than that for a trigonal-prismatic transition state, 81° 48′. Nevertheless the oxalato ligand is expected to be flexible and adaptable to a Bailar twist so that an intramolecular twist mechanism cannot be excluded on the basis of its structural characteristics.

The best evidence for the alternative one-ended dissociation mechanism comes from kinetic studies[38–40] of racemization and oxygen exchange of the oxalato ligand with solvent $^{18}OH_2$. All 12 oxygen atoms in $Cr(ox)_3^{3-}$ exchange at equivalent rates,[39] but at 25 °C in 1 M $HClO_4$, the rate of racemization is 11 times faster than the total rate of oxygen exchange.[40] This suggests that if racemization proceeds by ring opening, then the ring-opening and -closing process is faster than the oxygen exchange, even though both processes have similar activation energies. This observation also eliminates the possibility of a solvent water molecule occupying the vacated site in a five-coordinate intermediate since this should lead to oxygen exchange for each ring opening but it could occur[28] via an interchange mechanism by rotation about the C–C bond of the oxalato ligand which remains bonded at all times to the chromium center. This exchange pathway does not provide a pathway for racemization.

Racemization and oxygen exchange are both subject to acid catalysis but, as distinct from the oxygen exchange, the rate of racemization increases[41] at a rate much greater than the stoichiometric acidity. The rate of racemization is also accelerated by metal ions[25,26] as distinct from oxygen exchange. Both the proton and metal ions are presumed to promote bond fission of the oxalato ligand to yield a one-ended oxalato intermediate. The rate of racemization is also decreased by organic solvents[42–45] although specific solvation effects obscure any clear rate dependence on the dielectric constant of the medium. In acetone–water solvents,[46] the rate of racemization decreases as the dielectric constant and protic nature of the medium decrease, consistent with destabilization of the carboxylate anion generated by one-ended dissociation. We suggest that this body of evidence justifies our view that racemization of $Cr(ox)_3^{3-}$ can be regarded as a suitable prototype for a one-ended dissociative mechanism.

An estimate of ΔV^* for one-ended dissociation of an oxalato ligand can be made as follows. The dissociation could implant in the solvent a carboxylate group of unit charge some 400–560 pm from the chromium(III) center, depending on the degrees of rotation which occur about the O–C and C–C bonds of the oxalate (Scheme I). Thus the carboxylate anion may be viewed as a charge independent of the parent anion and exercising its own electrostrictive effect upon the solvent water. This volume change can be taken to be ΔV° for the ionization of carboxylic acids

$$R\text{–}COOH + H_2O \rightarrow RCOO^- + H^+(aq) \qquad (5)$$

(where by convention $\bar{V}(H^+) = 0$). For nine phenyl-substituted acetic acids, the average value is $\Delta V^{\circ} = -12.0$ cm^3 mol^{-1}; for propionic acids it is −12.9, and for butyric acids it is −14.2 cm^3 mol^{-1}.[47] The value[48] for oxalic acid (−9.0 cm^3 mol^{-1}) is subject to a concentration correction of −1 to −2 cm^3 mol^{-1}. Assuming a mean value of $\Delta V^{\circ} = -12.5$ cm^3 mol^{-1} for reaction 5 and $V^{\circ}(H^+) = -1.5$ cm^3 mol^{-1},[49] then the generation of the carboxylate anion in water contributes an electrostrictive volume effect at the carboxylate site of −11.0 cm^3 mol^{-1}.

An additional factor must be the volume increase accompanying the release of the atoms of the oxalato ligand into the solvent. In the initially chelated oxalato ligand, both C═O groups are already in contact with the solvent which would be expected to adjust continuously to the C═O motion as the oxalato group is dissociated. The only net volume change should be that due to the release of the O atom originally coordinated to the chromium center. An O atom, radius 74 pm, would contribute a volume change of +1.0 cm^3 mol^{-1} on release into the solvent. The sum total of the two effects due to release of an oxalate group into the solvent would be expected to be $\Delta V^{\circ} \simeq -11.0 + 1.0 = -10$ cm^3 mol^{-1}.

A third volume factor to be considered is that the release of an essentially independent CO_2^- ion into the solvent reduces the formal charge of the remaining five-coordinate parent ion from 3− to 2−. The simple Born treatment of ions in a uniform dielectric would predict[2] a change in electrostriction proportional to Z^2/r for ions of charge Z and radius r. Since both chromium species would have comparable radii of about 400 pm, the Born treatment would predict a reduced electrostrictive effect in the five-coordinate intermediate and thus a substantial volume increase. However, there is strong evidence that this approach breaks down for large complex ions. For the hydrolysis reaction

$$Cr(OH_2)_6^{3+} + H_2O \rightleftarrows Cr(OH_2)_5OH^{2+} + H^+(aq) \qquad (6)$$

$\Delta Z^2 = -4$ and the Born treatment predicts $\Delta V^{\circ} = +25$ cm^3 mol^{-1} while the Couture and Laidler[50] empirical relations for partial molar volumes predict $\Delta V^{\circ} = +20$ cm^3 mol^{-1}. However, the experimentally determined value is $\Delta V^{\circ} = -3.8 \pm 0.7$ cm^3 mol^{-1}. For the analogous acidity constants of $Co(NH_3)_5OH_2^{3+}$, $\Delta V^{\circ} = -2.2 \pm 0.6$ cm^3 mol^{-1}, for $Fe(OH_2)_6^{3+}$, $\Delta V^{\circ} = -1.2 \pm 0.2$ cm^3 mol^{-1}, and for $Tl^{3+}(aq)$ $\Delta V^{\circ} = -3.2 \pm 0.9$ cm^3 mol^{-1}.[52] It appears that the electrostrictive effect of large complex ions is determined not by their formal charge but by the specific interaction of the peripheral atoms of the complex with the solvent. This effect is shown in the hydrodynamic properties[53] of $Fe(phen)_3^{2+}$, $Fe(bpy)_3^{2+}$, and $(Co(en)_2(OH)_2)_3Co^{6+}$ in water. On the basis of this evidence, we therefore suggest to a first approximation that there is no volume change when the formal charge of the chromium ion is reduced from 3− to 2−.

This analysis is one-ended dissociation of $Cr(ox)_3^{3-}$ therefore leads to an expected value $\Delta V^{\ddagger} \simeq -10$ cm^3 mol^{-1} compared to the observed value $\Delta V^{\ddagger} = -16.3$ cm^3 mol^{-1}. The more negative value of $\Delta V^{\ddagger}$ observed might arise from bond contraction as the five-coordinate intermediate is formed but this would be subject to a large energy barrier. A more likely contribution is from additional solvent water interaction in the transition state. Although the oxygen-exchange evidence clearly shows that the sixth coordination site is not occupied by solvent water, nevertheless the more open transition state could accommodate a more contracted secondary hydration sphere with a negative volume contribution. This secondary mechanistic process would be consistent with the sensitivity of the racemization reaction to the nature of the solvent and to the large negative entropy of activation which is observed.

Racemization of $Cr(phen)(ox)_2^-$ and $Cr(bpy)(ox)_2^-$. In the absence of acid catalysis, the $Cr(phen)(ox)_2^-$ and $Cr(bpy)(ox)_2^-$ anions racemize at virtually the same rate at 25 °C (Table V) and exhibit virtually identical volumes of activation and very similar values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table VI). Likewise in acid media, both anions exchange their eight oxygen atoms with solvent water at virtually identical rates.[39]

The observed values of $\Delta V^{\ddagger}$ (−12.3 and −12.0 cm^3 mol^{-1}) for racemization of these two anions are very close to the predicted value (10 cm^3 mol^{-1}) for one-ended dissociation of an oxalato ligand. Uncertainties concerning electrostrictive volume contributions arising from changes in charge of the parent chromium complex are proportionally less for these 1− anions compared to the $Cr(ox)_3^{3-}$ anion. The secondary volume contribution from closer approach of the secondary hydration sphere in the five-coordinate intermediate, which was invoked for the $Cr(ox)_3^{3-}$ anion, may be much less for these anions because of the steric influence of the bulky phen and bpy ligands. We therefore conclude on the basis of the $\Delta V^{\ddagger}$ values that racemization of $Cr(phen)(ox)_2^-$ and $Cr(bpy)(ox)_2^-$ proceeds by one-ended dissociation of one oxalato ligand with flexing of the second, intact, oxalato ligand to generate a five-coordinate transition state (I or II in Scheme I).

The slightly higher $\Delta H^{\ddagger}$ values for these two anions compared to that for $Cr(ox)_3^{3-}$ (Table VI) would be consistent with a larger enthalpy barrier for generating I or II in the presence of phen or bpy ligands of higher ligand field strength than oxalate.

Racemization of $Cr(phen)_2(ox)^+$ and $Cr(bpy)_2(ox)^+$. The $Cr(phen)_2(ox)^+$ and $Cr(bpy)_2(ox)^+$ cations racemize at the same rate at 25 °C (Table V) and exhibit virtually identical values of $\Delta V^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ (Table VI). Both cations exchange their four oxygen atoms with solvent water at identical rates.[39] The values of $\Delta V^{\ddagger}$ fall abruptly from the large negative values for $Cr(phen)(ox)_2^-$ and $Cr(bpy)(ox)_2^-$ anions, for which one-ended oxalate dissociation has been proposed for their racemization. The near-zero values of $\Delta V^{\ddagger}$ suggest that the two cations racemize instead by an intramolecular twist mechanism for which our first-order approximation suggested $\Delta V \simeq 0$.

An intramolecular twist mechanism may be viewed in terms of motion of one rigid phen, or bpy, ring and one flexible oxalate ring (eq 2 or 3) in Scheme II. This is accompanied by a significant increase in $\Delta H^{\ddagger}$ as would be expected for motion of ligands of high ligand field strength. The small positive volume contribution from squeezing out of water molecules in the clefts of $Cr(phen)_3^{3+}$ and $Cr(bpy)_3^{3+}$ does not need to be invoked in these systems which have more open structures with fewer water molecules trapped in such clefts.

It is significant that the act of replacing one of two oxalato ligands in $Cr(phen)(ox)_2^-$ and $Cr(bpy)(ox)_2^-$ to yield $Cr(phen)_2(ox)^+$ and $Cr(bpy)_2(ox)^+$ seems to be accompanied by a drastic change in racemization mechanism. Although the oxalato ligand in $Cr(phen)_2(ox)^+$ and $Cr(bpy)_2(ox)^+$ is presumably undergoing independent one-ended dissociation, the rigid phen and bpy ligands appear not to be able to twist to generate a five-coordinate intermediate (I or II) of sufficiently low energy for this pathway to be effective in racemization. For the bis(oxalato) complexes, twisting of the second oxalato ligand entails a lower energy requirement, and one-ended dissociation with an accompanying twist is an effective pathway for racemization.

Conclusion

The effects of high pressure upon the rates of racemization of $Cr(ox)_3^{3-}$ and $Cr(phen)_3^{3+}$, selected as prototypes for one-ended dissociation and twist mechanisms, respectively, are distinctively different. This has permitted the assignment of one-ended dissociative mechanisms for the racemization of $Cr(phen)(ox)_2^-$ and $Cr(bpy)(ox)_2^-$ (for which $\Delta V^{\ddagger}$ is large and negative) and twist mechanisms for the racemization of $Cr(phen)_2(ox)^+$, $Cr(bpy)_2(ox)^+$, and $Cr(bpy)_3^{3+}$ (for which $\Delta V^{\ddagger}$ is close to zero). The approach seems worthy of development and we are currently undertaking high-pressure racemization studies of metal complexes in both protic and aprotic solvents.

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Registry No. $Cr(ox)_3^{3-}$, 15054-01-0; $Cr(ox)_2(phen)^-$, 21748-33-4; $Cr(ox)_2(bpy)^-$, 21748-32-3; $Cr(ox)(phen)_2^+$, 32626-76-9; $Cr(ox)(bpy)_2^+$, 32629-19-9; $Cr(phen)_3^{3+}$, 41587-82-0; $Cr(bpy)_3^{3+}$, 15276-15-0.

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Notes

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Structure of Tris(*N,N*-dimethylthiocarbamato)iron(III), $Fe(SOCN(CH_3)_2)_3$

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Extensive studies of tris-chelate complexes of a variety of metals have yielded reasonably firm mechanistic information on the nature of their rearrangement reactions.[1] Such information is based on ground-state geometries, as determined by diffraction methods, and on kinetic parameters. All tris chelates of the type $M(AA)_3$ appear to show at least D_3 idealized symmetry.[2] The twist angle, φ, which is the projection of the bite angle, α, onto a plane perpendicular to the C_3 symmetry axis, may be used for a partial description of geometry. The trigonal prism (symmetry D_{3h}) has the ligand triangles eclipsed and thus has φ of 0°, while the trigonal antiprism (and possible octahedron of symmetry O_h) has the ligand triangles staggered and thus has φ of 60°.

The β-diketonates and the dithiocarbamates are the most studied of these tris chelates. These two types show interesting structural and mechanistic differences. The β-diketonates have φ near 60° and rearrange by bond-rupture pathways; the dithiocarbamates have φ near 38° and rearrange via a trigonal-twist pathway.[1] Yet there is at present no totally satisfying understanding of the influence of solid state geometry on dynamics.[1] Thus additional studies, both mechanistic and structural, especially on new tris-chelate systems, are needed.

Generally the chemical and structural properties of the (mono)thiocarbamate–metal complexes differ markedly from those of the corresponding dithiocarbamates.[3] It is significant, then, that very recently[4] Nakajima et al. described the preparation of tris(thiocarbamato)iron(III) complexes. These complexes are apparently the first, simple tris(thiocarbamate) complexes to be prepared. With the expectation that such complexes will be of interest mechanistically and that interpretation of kinetic data will require knowledge of ground-state structures, the present note establishes the ground-state geometry of one such complex, tris(*N,N*-dimethylthiocarbamato)iron(III).

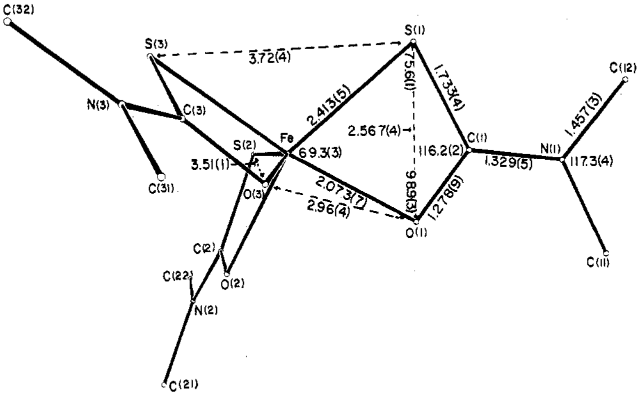

Figure 1. A sketch of the $Fe(SOCN(CH_3)_2)_3$ molecule showing the labeling scheme and principal, average bond distances and angles.

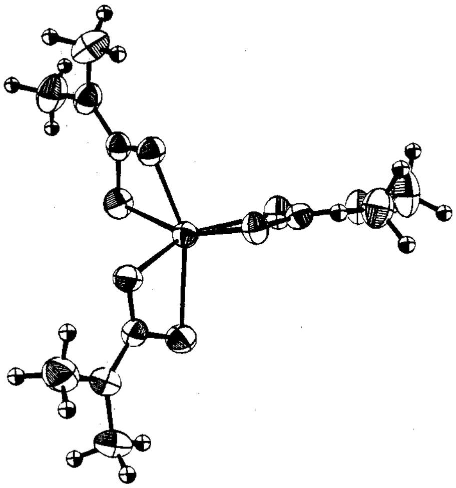

Figure 2. A drawing of the $Fe(SOCN(CH_3)_2)_3$ molecule displaying vibrational ellipsoids at their 50% level, except for hydrogen atoms which have been drawn artificially small. In the drawing the O(1)–O(2)–O(3) triangle is closer to the viewer than is the S(1)–S(2)–S(3) triangle.

Experimental Section

Suitable crystals of tris(*N,N*-dimethylthiocarbamato)iron(III), $Fe(SOCN(CH_3)_2)_3$, were kindly supplied by Professor Toshio Tanaka. The crystal structure determination followed experimental and calculational procedures standard in this laboratory.[5] The dark-violet, air-sensitive crystals belong to the triclinic system with a = 9.329 (3), b = 11.571 (4), c = 8.880 (2) Å, α = 102.92 (2), β = 116.13 (2), γ = 95.17 (2)°, V = 811.2 Å^3 (λ(Mo Kα_1) = 0.70930 Å), ρ_c = 1.507 g/cm^3 for two molecules of $C_9H_{18}FeN_3O_3S_3$ per cell, ρ_o = 1.49(1) g/cm^3. A total of 3923 unique reflections were collected by diffractometer methods out to 55° in 2θ (Mo Kα); of these 3279 have $F_o^2 > 3\sigma(F_o^2)$ and were used in subsequent calculations. These data were corrected for absorption effects; transmission factors ranged from 0.565 to 0.740 for a crystal of calculated volume 0.139 mm^3 and a linear absorption coefficient of 13.0 cm^{-1}. The structure was solved by Patterson methods and refined by full-matrix, least-squares techniques. Space group C_i^1-$P\bar{1}$ was assumed; this assumption is justified by the eventual location in a difference Fourier map of all hydrogen atoms on the methyl carbon atoms. These hydrogen atoms were placed in idealized positions (C–H = 0.95 Å) and added as fixed contributions in the final cycle of refinement. This cycle of 172