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Ligand-Exchange Reactions of Chromium(V): Characterization of the Ligand-Exchange Equilibria of Bis(2-ethyl-2-hydroxybutanoato(2-))oxochromate(V) in Aqueous 1,2-Ethanediol and the Solution Structure of Bis(1,2-ethanediolato(2-))oxochromate(V)

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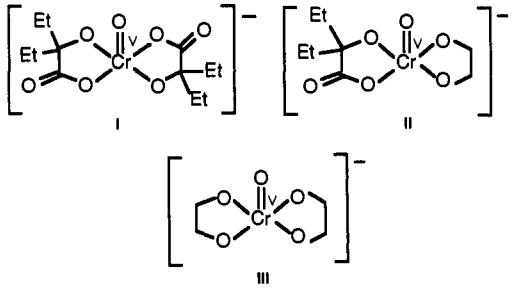
The complex bis(2-ethyl-2-hydroxybutanoato(2-))oxochromate(V), $[Cr(ehba)_2O]^-$ (I), undergoes a ligand-exchange reaction in aqueous solutions of 1,2-ethanediol to produce an equilibrium mixture of complex I and the complexes (1,2-ethanediolato(2-))(2-ethyl-2-hydroxybutanoato(2-))oxochromate(V), $[Cr(ed)(ehba)O]^-$ (II), and bis(1,2-ethanediolato(2-))oxochromate(V), $[Cr(ed)_2O]^-$ (III). The concentration ratios of these three complexes in solution were determined from the relative intensities of their EPR signals at g_{iso} = 1.9783 (2) (I), g_{iso} = 1.9791 (2) (II), and g_{iso} = 1.9803 (2) (III), respectively. The g values and the nine-line ^1H superhyperfine coupling (A_{iso} = 0.63 (3) G) observed for III and the five-line ^1H super hyperfine coupling observed for II (A_{iso} = 0.69 (6) G) identify the products of the ligand-exchange reaction but also caused serious overlap of the signals. In order to deconvolute these peaks for the determination of equilibrium constants, experiments were performed in aqueous 1,2-ethanediol-d_6. The equilibrium constant for the conversion of I to II, $(K_c)_1$, increases from 1.5 (5) × 10^{-5} in 2.0% v/v aqueous 1,2-ethanediol-d_6 to 2 × 10^{-4} in 20% v/v aqueous 1,2-ethanediol-d_6 but remains constant at ~2 × 10^{-4} over the range 20–95% v/v aqueous 1,2-ethanediol-d_6 solutions at 23 °C. The equilibrium constant for the conversion of II to III, $(K_c)_2$, increases slightly from 5 × 10^{-6} (20% v/v aqueous 1,2-ethanediol-d_6) to 1.5 × 10^{-5} (95% v/v aqueous 1,2-ethanediol-d_6) at 23 °C. If the reaction of I with neat 1,2-ethanediol is performed over 3-Å molecular sieves, the equilibrium is driven almost exclusively to the complex III, due to the absorption of the released 2-ethyl-2-hydroxybutanoate ligand on the surface of the zeolite. This method enables the facile preparation of essentially pure (99%) solutions of III or III-d_8, which are important as dynamically polarizable proton and deuteron targets, respectively. Complexes II and III undergo fluxional behavior that makes the protons of the 1,2-ethanediolato(2-) ligand chemically equivalent on the EPR time scale. Despite numerous EPR studies on III, its dynamic properties have not been recognized previously. On the balance of evidence, this equilibration is expected to occur via an intramolecular Berry twist, since it is too fast for a ring opening or an intermolecular process.

Introduction

Recently, there has been a considerable amount of interest in the chemistry[1-4] and biochemistry[5-7] of chromium(V). This interest arises from the observation of chromium(V) intermediates in the oxidation or organic substrates by Cr(VI),[1] from the use of Cr(V) complexes as selective oxidants,[2-4] and because of the implication of chromium(V) in the mechanism of Cr-induced cancers.[5-7] The bis(1,2-ethanediolato(2-))oxochromate(V) complex, III, was identified by EPR spectroscopy more than twenty



I II

III

years ago as the Cr(V) intermediate in the Cr(VI) oxidation of 1,2-ethanediol.[8] This Cr(V) complex, and related complexes, have been used as dynamically polarized proton and deuteron targets in high-energy experiments.[9-11] It has also been used extensively in investigations of the chemical properties of Cr(V).[1] Despite the variety of different studies that have been performed on this complex, it has never been isolated, and in fact, the only bis(diol) complex that has been isolated contains the relatively unreactive perfluoropinacol ligand.[12] However, the solution structure of III has been studied in detail by the use of EPR spectroscopy,[8-16] and the nine-line super hyperfine coupling of the protons to the Cr(V) center establishes the presence of two 1,2-ethanediolato(2-) ligands in the complex.

Recently, we have shown that the ligand-exchange reaction of I[17-19] in aqueous oxalic acid can be used to isolate bis(oxalato(2-))oxochromate(V) complexes that have only been seen previously as transient intermediates in the oxidation of organic substrates by Cr(VI).[20,21] On the basis of kinetic data, Krumpolc and Roček[22] first postulated that ligand exchange is the first step in the oxidation of 1,2-ethanediol by I. Similarly, the reaction of I in 1,2-ethanediol-d_6 has been used to produce a very effective polarized deuteron target, but the ligand-exchange chemistry that produced the deuteron target was not recognized.[11] Other workers

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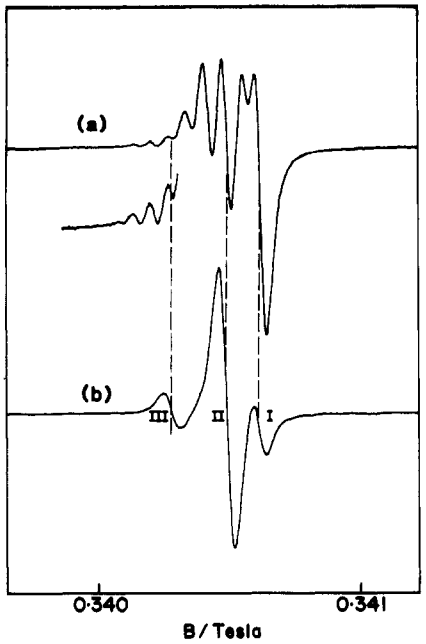

Figure 1. EPR spectra of complex I in 50% v/v aqueous 1,2-ethanediol: (a) aqueous 1,2-ethanediol at 19 °C (scale expansion below the main spectrum is a factor of 4); (b) 50% v/v aqueous 1,2-ethanediol-d_6 at 23 ● 1 °C.

have also used similar reactions to produce polarized deuteron and proton targets, but again the reactions have only been characterized to the extent that they produce several EPR signals by ligand-exchange reactions.[10] Reported here are the first detailed studies on the ligand-exchange chemistry of I in aqueous 1,2-ethanediol and 1,2-ethanediol-d_6, the characterization of the solution structures of the complexes that are produced, and the potential of this chemistry to be used in the synthesis of III for polarized proton and deuteron targets.

Experimental Section

Compounds and Reagents. $Na[Cr(ehba)_2O]\cdot H_2O$ was synthesized from 2-ethyl-2-hydroxybutanoic acid (Aldrich, 99%) and sodium dichromate (Merck) in acetone (Merck, AR grade) according to the literature method.[23] Crystallization of the product was induced by dropwise addition of hexane over a period of 10–15 min. The red-brown product is light sensitive so it is necessary to keep the product in the dark in a desiccator. *Caution! These Cr(V) complexes are mutagenic, rapidly cleave DNA at micromolar concentrations, and are potential carcinogens.*[5] *Appropriate precautions should be taken to avoid skin contact and inhalation of Cr(V) dust.*

Ethylene glycol (1,2-ethanediol, Ajax, LR grade) and 1,2-ethanediol-d_6 (Icon Services Inc., 99 atom % D) were used without further purification except for reactions over molecular sieves. The 3-Å molecular sieves (BDH, $^1/_{16}$-in. pellets) were activated by heating for 6 h at 180–200 °C under vacuum (0.05–0.10 mmHg). Drying the solvents over these molecular sieves had no significant effect on the EPR parameters.

EPR Spectroscopy. EPR spectra were recorded on a JEOL JES-PE ESR spectrometer operating at ~9.4 GHz. Sample temperatures were controlled by a temperature-monitored flow of dry nitrogen gas through the cavity. Magnetic fields were measured by a proton magnetic resonance gaussmeter and corrected for the offset from the sample position. The frequency was measured with a wavemeter indirectly calibrated via the resonance of DPPH (g = 2.0036). In the analysis of the spectra, second-order corrections have been applied. The spectra were examined for modulation broadening, and the modulation amplitude was chosen so as to eliminate any broadening.

All spectra were recorded within 4 min of mixing and were relatively stable over a period of 1 h. Experiments performed over molecular sieves involved either shaking the appropriate solutions over the sieves for 1 h and then leaving the solution to stand for a further 1 h or peristaltically pumping the solutions around a closed loop that included the cavity capillary and a 2-cm column of sieves. In the latter case, the progressive changes in the spectra were monitored.

In the case of spectra in aqueous 1,2-ethanediol, the overlapping peaks were deconvoluted by hand, by graphically examining the ratios of the various signals as a function of the concentration of 1,2-ethanediol. This was aided by the known spectra of I and III and the results in 1,2-ethanediol-d_6. More accurate concentrations were obtained in 1,2-ethanediol-d_6, where the lack of serious overlap has allowed the concentrations of the various species to be determined directly from the peak heights (equivalent to peak areas in this case, since the widths and shapes were identical).

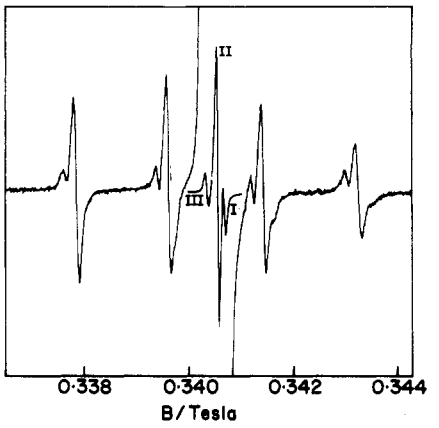

Figure 2. EPR spectrum of I in 50% v/v aqueous 1,2-ethanediol-d_6 showing the ^{53}Cr hyperfine coupling of the various complexes in solution. The central ($^{50,52,54}Cr$) spectrum was run at a gain of 10 and a modulation amplitude of 0.25 G, while the ^{53}Cr hfs spectrum was run at a gain of 250 and a modulation amplitude of 3.2 G.

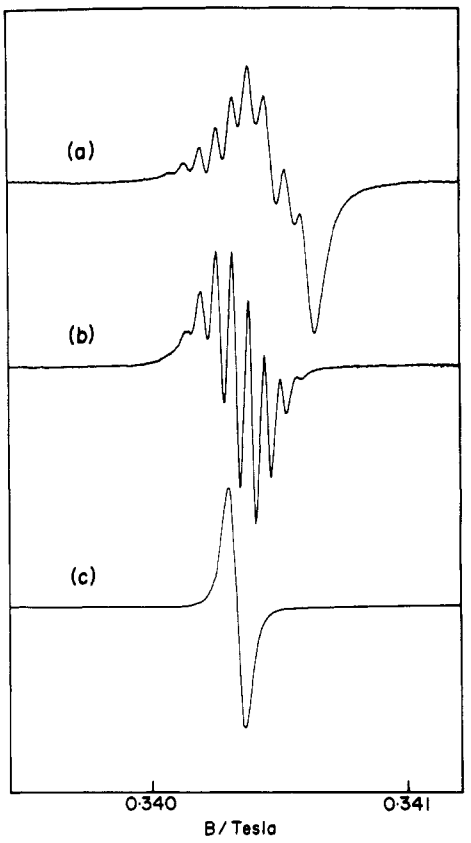

Figure 3. EPR spectra of I (0.54 mM) in 100% 1,2-ethanediol: (a) initial spectrum showing significant amounts of I and II; (b) spectrum after circulating solution over 3-Å molecular sieves for 2 h (note loss of signals due to I and II); (c) spectrum in 100% 1,2-ethanediol-d_6 after circulating solution over 3-Å molecular sieves for 2 h, showing only the signal due to III.

Results

EPR Spectroscopy. EPR spectra of I in aqueous solutions of 1,2-ethanediol were recorded within 4 min of dissolution and

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Table I. Isotropic Spin Hamiltonian Parameters for the Cr(V) Species in the System Cr/ehba/ed in Aqueous 1,2-Ethanediol and Aqueous 1,2-Ethanediol-d_6 at 23 ± 1 °C

assigned struct	g_{iso}[a]	A_{iso}-(^{53}Cr)/G[a]	A_{iso}-(^{1}H)/G[a]	ref
$[Cr(ehba)_2O]^-$[b]	1.9783 (2)	18.4 (3)		this work
	1.9784 (2)	18.5 (1)		26[e]
$[Cr(ehba)(ed)O]^-$	1.9790 (2)	c	0.69 (6)	this work
$[Cr(ed)_2O]^-$	1.9800 (2)	17.8 (3)	0.63 (3)	this work
	1.9801	17.9	0.62	15[f]
$[Cr(ehba)(ed\text{-}d_4)O]^-$	1.9791 (2)	17.9 (3)	d	this work
$[Cr(ed\text{-}d_4)_2O]^-$	1.9803 (2)	17.9 (3)	d	this work
	1.9802		d	36

[a] There are no significant variations in the values of g_{iso} and A_{iso} over the entire range of solvent mixtures. [b] The EPR parameters are the same for I in aqueous solutions of both 1,2-ethanediol and 1,2-ethanediol-d_6. [c] The ^{53}Cr hyperfine coupling for this peak is not resolved due to the serious overlaps caused by ^{1}H superhyperfine splitting of these resonances. [d] The ^{2}H superhyperfine coupling is too small compared to the line width to observe. [e] Values in water. [f] Values in reagent grade 1,2-ethanediol. The complex was generated from the reaction of $K_2Cr_2O_7$ with 1,2-ethanediol ($A_{iso}(^{17}O)$ = 1.31 G).

resulted in complex EPR spectra that contained several overlapping signals. All of these EPR signals were relatively stable over the short periods of time required to record the spectra.[24,25] As the concentration of 1,2-ethanediol was increased, the single peak due to I (ignoring ^{53}Cr satellites) decreased in intensity with concomitant increases in intensities of the overlapping multiplets at higher g values (Figures 1–3). By examination of these signals over the range of concentrations, the EPR spectra were resolved into three separate signals with relative intensities that change according to the ratio of the solvent mixture. Apart from that of I (g_{iso} = 1.9783 (2)), one of these signals exhibits the well-known[8,13–16] nine-line ^{1}H superhyperfine coupling of the bis(1,2-ethanediolato(2−))oxochromate(V) complex, III. Its g_{iso} and A_{iso}(^{53}Cr and ^{1}H) values agree well with those reported in the literature for the generation of III from the reaction of Cr(VI) with 1,2-ethanediol. The central feature in the EPR spectrum is assigned to II (see Discussion) and possesses a five-line ^{1}H superhyperfine coupling pattern. The value of A_{iso}(^{1}H) for II is 0.69 (6) G, which is the same within experimental error as that observed for III. The g_{iso} value of II is intermediate between those of the signals assigned to I and III. As the concentration of 1,2-ethanediol is increased, the signal due to II increases with respect to that due to I and the signal due to III increases with respect to that due to II. The EPR parameters of these complexes are summarized in Table I along with literature values for I[26] and III.[15]

Because of the serious overlap of the peaks and the resultant difficulties in obtaining concentration ratios of the species I–III in solution, experiments were performed in aqueous 1,2-ethanediol-d_6. These results confirm the presence of only three species in solution (apart from the possibility of accidental coincidences), and the g_{iso} and A_{iso}(^{53}Cr) values do not change in a significant manner in going from the nondeuterated to deuterated 1,2-ethanediol (Table I), consistent with the above analysis. The ^{1}H superhyperfine coupling is now lost, and all three signals have the same peak shape and the same widths within experimental error (i.e. peak-to-peak separations, Figures 1–3). In addition, the ^{53}Cr hyperfine coupling of complex II is resolved (Figure 2). The values of the EPR parameters of any given complex showed no significant dependence on the ratio of the two solvents over the entire range from pure water to pure 1,2-ethanediol. Within experimental error, the values of these parameters were also independent of whether the spectra were recorded in H_2O/1,2-ethanediol, H_2O/1,2-ethanediol-d_6, or D_2O/1,2-ethanediol-d_6.

Table II. Equilibrium Constants for the Ligand-Exchange Reactions of I (0.5$_4$ mM) in Aqueous 1,2-Ethanediol-d_6 at 23 ± 1 °C

$[edH_2]^a$	[I][b]	[II][b]	[III][b]	$[edbaH_2]^{b,c}$	$10^4(K_c)_1$[d]	$10^5(K_c)_2$[e]
0.357	0.49	0.051	~0	0.051	0.15 (5)	
0.893	0.43	0.11	~0	0.11	0.30 (8)	
1.79	0.34	0.21	~0	0.21	0.7 (2)	
3.57	0.17	0.36	0.015	0.39	2.3 (6)	0.5 (1)
3.57[f]	0.14	0.38	0.012	0.40	3.0 (8)	0.4 (1)
8.93	0.11	0.38	0.050	0.48	1.9 (5)	0.7 (2)
14.29	0.069	0.35	0.12	0.59	2.1 (5)	1.4 (4)
16.97	0.062	0.34	0.14	0.62	2.0 (5)	1.5 (4)

[a] Molar concentration calculated from the percent 1,2-ethanediol-d_6. [b] Concentrations (mM) calculated from the relative peak heights of the three signals in the EPR spectra. [c] Amount of ehba released in the formation of II and III. [d] $(K_c)_1$ = {[II][ehbaH$_2$]}/{[I][edH$_2$]}. [e] $(K_c)_2$ = {[III][ehbaH$_2$]}/{[II][edH$_2$]}. [f] D_2O/1,2-ethanediol-d_6.

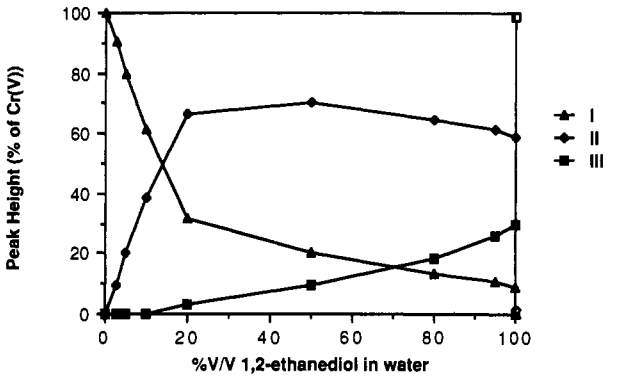

Figure 4. Equilibrium concentrations of the three Cr(V) complexes in 0.54 mM solutions of I in aqueous 1,2-ethanediol-d_6 at 23 ● 1 °C as a function of % v/v 1,2-ethanediol-d_6. The points indicated by open symbols at 100% 1,2-ethanediol-d_6 are obtained from solutions in the presence of 3-Å molecular sieves, whereas the other points on the curve at 100% 1,2-ethanediol-d_6 represent the extrapolated values in the absence of the sieves.

The chemical deconvolution of the overlapping peaks in 1,2-ethanediol-d_6 enables more accurate determinations of the concentrations of I and the deuterated analogues of II and III (II-d_4 and III-d_8, respectively) from the relative peak heights of the three signals (assuming that these are the only three chromium species in solution[24]). The data obtained from 0.5$_4$ mM solutions of I at 23 ± 1 °C in solvent mixtures ranging from 2% v/v 1,2-ethanediol-d_6/water to 95% v/v 1,2-ethanediol-d_6 are summarized in Table II, and the percentage of each component in the solution mixture is plotted as a function of % v/v 1,2-ethanediol-d_6/water in Figure 4. As the % v/v of 1,2-ethanediol-d_6 increases, the proportion of I with respect to II-d_4 and III-d_8 decreases in the same manner that was described for the overlapping signals in 1,2-ethanediol. The concentration of II-d_4 increases rapidly until the % v/v of 1,2-ethanediol-d_6 reaches ~20%. At this point, the mixed-ligand complex constitutes approximately 66% of the total concentration of chromium(V). At higher concentrations of 1,2-ethanediol-d_6, the percentage concentration of II-d_4 in the reaction mixture increases slowly until a maximum is reached at approximately 50% v/v solutions where the concentration of II-d_4 constitutes approximately 70% of the total Cr(V) concentration. Even at 95% 1,2-ethanediol-d_6, II-d_4 remains as the major Cr(V) complex in solution (~63%). Under these conditions a significant amount of I remains (~11%), but III-d_8 exists in higher concentrations (~26%) than I.

When solutions of I in neat 1,2-ethanediol or 1,2-ethanediol-d_6 are dried over 3-Å molecular sieves, the signals due to I and II

(24) The stabilities of the Cr(V) complexes that were generated by this method have been confirmed by UV/vis spectroscopy. The half-lives for decomposition of the Cr(V) complexes are typically ≥1 under the conditions that have been employed in these experiments, even in solutions that contain the highest concentrations of water.[25] Therefore, the amounts of Cr(VI) and Cr(III) generated from the disproportionation of Cr(V), and/or Cr(III) produced from the ligand-assisted reduction of Cr(V), are insignificant within the accuracy of the determination of the concentrations, i.e. less than 5% decomposition has occurred at the time of measurement.

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(or II-d_4) virtually disappear and the nine-line signal due to III (or the singlet due to III-d_8) constitutes ≥99% of the total intensity of the EPR signal (Figure 3). The signals due to I and II almost disappear after ~1 h, and the reaction is complete after 2 h as the solution is cycled through the column of sieves, leaving only III in solution. Once all of the Cr(V) complexes have been converted to III, the signal remains stable for at least 3 h (i.e., no loss in signal intensity).

From the equilibrium concentrations, the equilibrium constants for the two equations

$$\mathrm{I} + \mathrm{H_2ed} \rightleftharpoons \mathrm{II} + \mathrm{H_2ehba} \quad (K_c)_1 \qquad (1)$$

$$\mathrm{II} + \mathrm{H_2ed} \rightleftharpoons \mathrm{III} + \mathrm{H_2ehba} \quad (K_c)_2 \qquad (2)$$

were calculated on the assumption that the concentration of H_2ehba released can be calculated from the concentrations of II-d_4 and III-d_8 in solution.[27] At 23 °C, the values of $(K_c)_1$ vary from 0.2×10^{-4} in 2.0% v/v 1,2-ethanediol-d_6/water to 2.0×10^{-4} in 95% v/v 1,2-ethanediol-d_6/water, while the values of $(K_c)_2$ vary from 0.5×10^{-5} in 20% v/v 1,2-ethanediol-d_6/water to 1.5×10^{-5} in 95% v/v 1,2-ethanediol-d_6/water. The values obtained over the range of solvent conditions are contained in Table II. These values are in semiquantitative agreement with those calculated by deconvolution of the spectra that were obtained in 1,2-ethanediol, although the latter were necessarily much less accurate because of the deconvolution that was required. The results also showed no significant variations in the equilibrium constants obtained in D_2O/1,2-ethanediol-d_6 solutions compared to H_2O/1,2-ethanediol-d_6 solutions of the same composition.

Synthesis. Many attempts were made at preparing III by the reaction of neat 1,2-ethanediol with I over 3-Å molecular sieves. Using the ligand-exchange chemistry in the presence of molecular sieves, we have shown that essentially pure solutions of III can be obtained. However, even under conditions where the desired complex is the sole (>99%) Cr(V) complex in solution, these experiments have not been successful in isolating the pure complex. The isolation has been hampered by several factors, including the very high solubility of the complex in the 1,2-ethanediol solvent that is required for the synthesis, the tendency for the complex to oxidize the ligand during the isolation procedures, the difficulty in removing the solvent, the fact that equilibria are pushed toward the left in more concentrated solutions because of an increase in the concentration of free ehba, and the apparently much lower solubility of II in comparison to III.[25] This has resulted in the isolation of samples that have significant, but variable, amounts of Cr(III) (UV/vis spectroscopy), Cr(V) dimers, and/or II (EPR, IR, and microanalysis). Experiments are continuing in this area, but the synthetic procedures are difficult.

Discussion

Solution Structures and Fluxional Behavior. The nine-line central feature (^{50}Cr, ^{52}Cr, and ^{54}Cr isotopes) in the EPR spectrum of $[Cr(ed)_2O]^-$ is due to the superhyperfine coupling with the eight CH_2 protons of the chelating 1,2-ethanediolato(2−) ligands and has been noted by several other workers.[8,13-16] It has also been shown, from the ion-exchange behavior of this complex,[14] that it is anionic and, therefore, all of the alcohol groups must be deprotonated. Previously, the superhyperfine structure has been interpreted as being consistent with a square-pyramidal structure containing eight equivalent protons. However, in the square-pyramidal structure (which is thought to be the stable structure in solid glasses from an analysis of the g anisotropy of the EPR spectrum at low temperatures),[13] the protons are not equivalent but there are two sets of four equivalent protons. One set of protons sits above the plane of the 1,2-ethanediolato(2−) ligands and is close to the oxo group, whereas the second set of protons lies below this plane. These two sets of protons have quite different chemical and magnetic environments and would not be expected to couple to the same extent with the unpaired electron, which is contained in a nonbonding d orbital of the Cr(V) center. Therefore, the EPR spectra imply that $[Cr(ed)_2O]^-$ does not exist as a static (on the EPR time scale) square-pyramidal structure in aqueous 1,2-ethanediol under ambient conditions. Such a static structure on the EPR time scale (10^{-6} s) would result in ^{1}H superhyperfine coupling that would give rise to a quintet of quintets in the most general case.[28] Similarly, a static trigonal-bipyramidal structure, like that observed for the parent complex, $[Cr(ehba)_2O]^-$,[29] has four different chemical environments for the protons and would result in a complex coupling pattern (triplet of triplets of triplets of triplets, in the most general case) due to the ^{1}H superhyperfine coupling. The equivalence of the four oxygens (as shown by the ^{17}O superhyperfine coupling pattern in the ^{17}O-labeled complex[15]) is also inconsistent with such a structure, although the ^{17}O coupling pattern does not distinguish between a static square-pyramidal structure or a fluxional structure. Therefore, it is not possible for the eight protons of III to be chemically equivalent for a five-coordinate complex or, indeed, a six-coordinate complex in which a solvent molecule occupies a position that is either cis or trans to the oxo group. Moreover, the g_{iso} and A_{iso} values are not consistent with a six-coordinate geometry;[18,19,26,30] hence, the EPR spectral results need to be rationalized in the context of a five-coordinate geometry.

The likely explanation for the spectroscopic results is that the complex is undergoing a rapid set of Berry twists or pseudorotations on the EPR time scale (Scheme I). A series of such twists would be required before all proton positions have been exchanged. Therefore, the rate of these twists must be much faster than the time scale of the EPR experiment at ambient temperatures (~23 °C), which is approximately 1 μs.

The intramolecular process for equilibration of the protons is favored over an intermolecular process, since ligand-exchange reactions are slow on the EPR time scale, as evidenced by the observation of distinct signals for complexes I–III. Similar observations have been made in other ligand-exchange reactions of oxochromate(V) complexes and also with regards to the change in coordination numbers from five-coordinate to six-coordinate.[18,19] In the bis(oxalato(2−))oxochromate system, an equilibrium does exist between a five-coordinate and a six-coordinate complex in which the solvent occupies the sixth coordination site.[18,19,26] However, the fact that distinct signals are observed for these two complexes establishes that the half-lives for bond formation reactions in five-coordinate complexes and bond breaking reactions in the six-coordinate complexes are greater than 1 μs. Electrochemical experiments have established that this process has a half-life that is ≤1 ms.[18,19] Therefore, such processes in the oxalato systems have rate constants of the order 10^3–10^4 s^{-1} at ambient conditions. Analogous processes in the reactions under study would be expected to have comparable rate constants, since similar steric factors apply. While a mechanism that involves a rapid equilibrium between III and a small amount of a six-coordinate complex would provide fluxional behavior that is sufficient to make all of the protons equivalent, the rate would appear to be far too

(27) Since the Cr(V) complexes are stable within the time scale required for the EPR measurements,[24] and the ligand-exchange equilibria occur over the millisecond time scale,[18,19,25] this assumption is valid. The limiting factor in the calculations of the equilibrium constants is the accuracy to which the initial concentration of I is known. This arose because, in order to minimize decomposition, each solution had to be made up individually immediately before the spectra were run, rather than being made up more accurately by using stock solutions. Consequently this necessitated the measurement of small volumes of 1,2-ethanediol-d_6 and submilligram quantities of I, which results in fairly large errors (~20%) in the initial concentration of I.

(28) It is possible to observe a nine-line EPR spectrum for III with the correct intensities (1:8:28:56:70:56:28:8:1) in a structure that contains inequivalent protons, provided that $(A_{iso})_{cis}$ is only slightly different from $(A_{iso})_{trans}$. However, such a situation is unlikely, especially given our arguments about the quite different environments of the cis and trans protons, plus supporting evidence for a rapid Berry twist in related species, and the expectation that Berry twists should be rapid in these types of complexes. There are also other special cases that will give rise to different multiplicities other than a quintet of quintets or a nonet, but since these are not observed, they are not relevant to the discussion.

(29) Hambley, T. W.; Judd, R. J.; Lay, P. A. *J. Chem. Soc., Dalton Trans.* **1989**, 2205–2210.

(30) Bramley, R.; Ji, J.-Y.; Lay, P. A. To be published.

low to explain the observed behavior, which must have a rate constant of $>10^7$ s^{-1}. This also precludes a mechanism that involves exchange between the chelating ligand and the solvent.

It is likely that only an intramolecular mechanism can explain the fluxionality of complex III. These mechanisms fall into two classes, either a twist mechanism or a mechanism that involves ring opening of one of the chelate rings. The latter is considered unlikely for several reasons. First, breaking of a relatively strong Cr–O bond is expected to result in a significant activation enthalpy, which is inconsistent with the very low potential barrier that is required to obtain a rate constant that is greater than 10^7 s^{-1}. Second, a ring-opening reaction would result in an intermediate or transition state that was four-coordinate. This is unlikely to occur, because where equilibria that involve changes in coordination number exist, they are between five- and six-coordinate complexes. Therefore, a substitution reaction (of which a ring-opening and -closing reaction is a special case) is much more likely to occur via an associative rather than dissociative mechanism. An associative mechanism involving solvent should result in a process that is slow compared to the fluxional change. Thus, a twist mechanism remains as the most plausible explanation for the equilibration of the protons of the EPR time scale. The Berry twist mechanism is the most likely, because it is known to have a low activation barrier, and there are many five-coordinate complexes that exhibit similar fluxional behavior.[31] Indeed there are several other examples of five-coordinate complexes containing two bidentate ligands that undergo a rapid series of Berry pseudorotations in order to rapidly equilibrate inequivalent protons or chelate rings.[31]

The structure of the mixed-ligand complex, II, is characterized unambiguously by a number of independent facts. (i) Its concentration increases with respect to I and decreases with respect to III as the concentration of 1,2-ethanediol in water increases. This shows that II has one 1,2-ethanediolato ligand per Cr(V). (ii) Its g_{iso} value is intermediate between those of I and III, which establishes that its donor atoms are three alcoholate oxygens and one carboxylate oxygen.[30,32] (iii) The well-known structures, I and III, which are in equilibrium with II, both have two chelating ligands. This points to the intermediate complex also having two chelating ligands. (iv) The five-line ^1H superhyperfine coupling pattern observed for II is consistent with the presence of a single chelating 1,2-ethanediolato(2–) ligand.[33] (v) The fact that the value of $A_{iso}(^1H)$ is the same within experimental error as that for III indicates that the 1,2-ethanediolato(2–) ligand in II most probably has a geometric relationship to the Cr(V) center similar to that of the ligands in III. (vi) The values of g_{iso} and $A_{iso}(^{53}Cr)$ are inconsistent with a six-coordinate structure in which water occupies a sixth coordination site, since such a structure would result in smaller g_{iso} and larger A_{iso} values than those observed.[18,19,30] (vii) Coordination of water in a sixth coordination site is also inconsistent with the increase in the concentration of II as the concentration of water is decreased.

The five-coordinate bis-chelate complex, II, that is established from the above facts is almost certainly fluxional in solution, since either a square-pyramidal or a trigonal-bipyramidal structure would result in all of the protons of the 1,2-ethanediolato(2–) ligand being inequivalent. In the absence of fluxional behavior, this would result in a complex coupling pattern with a maximum of sixteen lines (a doublet of doublets of doublets of doublets) due to the ^1H superhyperfine coupling, rather than the five-line spectrum that is observed.[34] Again, the equilibration of the four protons on the EPR time scale indicates that the Berry twists must be fast in relation to the EPR time scale, despite one of the ed ligands of III being replaced by a much bulkier ehba ligand. It is interesting to note, in this regard, that the parent complex I appears to undergo slow Berry twists on the EPR time scale at room temperature, since there is strong evidence that two geometric isomers are present in alcohol solvents.[26] It is likely that the rate of intramolecular interconversion may be very much dependent on the steric bulk of the ligands.[35] While variable-temperature EPR spectroscopy may help to resolve these issues, it will be difficult because of the limited temperature range that is available before such solvent mixtures freeze. Moreover, it will be difficult to distinguish between the effects of broadening of the signals due to viscosity changes and those due to slowing the time scale of the Berry twist down to the time scale of the EPR experiment. Likewise, spectra in frozen solutions will not resolve the issue of the rate of the Berry twists, because the ^1H superhyperfine coupling is obliterated by the broad signals that are observed in these phases at liquid-nitrogen temperatures.[13,15]

There is no evidence of an equilibrium between III and a six-coordinate complex in which a monodentate edH_2 or edH ligand binds in the sixth coordination site. This is somewhat surprising, since the bis(oxalato(2–))oxochromate(V) complex, $[Cr(ox)_2O]^-$, is in equilibrium with a six-coordinate complex, bis(oxalato(2–))(solvent)oxochromate(V), $[Cr(ox)_2(solvent)O]^-$, in solvents that are good σ donors, such as water, alcohols, etc.[17–19,26] Distinct EPR signals for these two complexes are observed, which along with electrochemical data establishes the rate constant for such reactions is between 10^3 and 10^5 s^{-1}, under ambient conditions.[18,19] There is no evidence of a corresponding equilibrium in the system under study, since a six-coordinate complex would result in a second signal that would have A_{iso} and g_{iso} values distinctly different from those observed for the five-

(31) Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119–235.

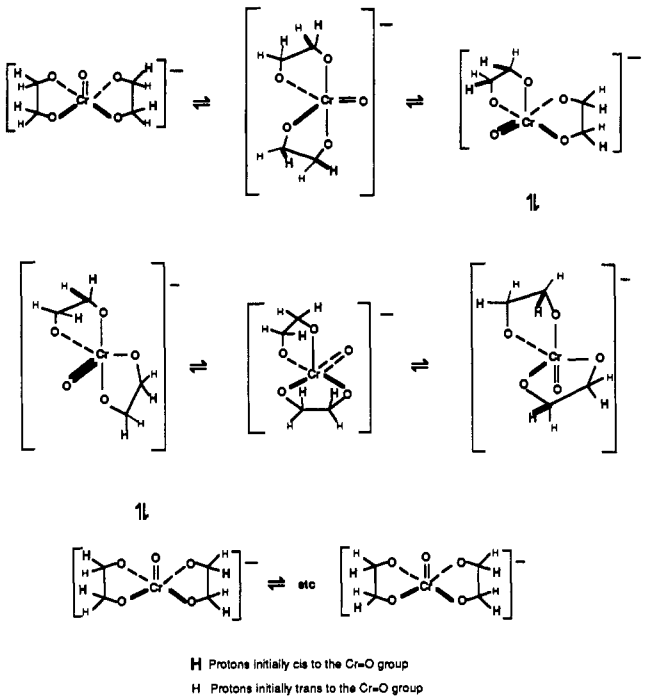
(32) One reviewer suggested that these two results are also consistent with a structure that had one chelating ehba ligand, one monodentate ehba ligand bound via an alcoholate group, and one monodentate edH ligand. Apart from such a structure being unlikely in terms of unfavorable entropic factors, a monodentate ehba ligand would not compete effectively for a coordination site in the presence of very large excesses of water and 1,2-ethanediol ligands in such a labile system. Moreover, the three-line hyperfine coupling pattern that would arise from such a complex is inconsistent with the observed five-line pattern. Therefore, such a structure is both chemically unreasonable and inconsistent with the experimental observations.

(33) A second reviewer has suggested the possibility of structures we consider to be even less likely for II than that mentioned in note 32. Such structures would have two monodentate edH^- ligands with one chelating ehba or two monodentate ehba ligands. While such structures could explain the five-line superhyperfine coupling patterns, they suffer from the same objections raised in note 32. In addition, if complex II did have such a structure, the ratio of its concentration with respect to III would not vary with varying concentrations of 1,2-ethanediol, since both complexes would have two 1,2-ethanediolato ligands per complex. Again, such a structure is both chemically unreasonable and inconsistent with all of the experimental observations.

(34) A quintet with the correct ratios of 1:4:6:4:1 would also be obtained in a static structure if each of the four inequivalent protons had virtually the same values of A_{iso}. This explanation is exceedingly unlikely. Not only do the cis and trans protons on the chelate ring have quite different chemical environments but the two cis protons will be in quite different environments and the two trans protons will be in quite different environments. For instance, in a square-pyramidal structure, one CH_2 group will be trans to a carboxylate and one trans to an alcoholate group. This is also likely to result in different M–O bond lengths to the different halves of the ed chelate. In a trigonal-pyramidal structure, one these Cr–O bonds will be axial and the other equatorial. This will, by necessity, result in quite different coupling patterns for the two inequivalent trans protons and the two inequivalent cis protons. It is likely that the steric requirements of the ehba ligand will result in a least some distortion of this complex away from a square-pyramidal geometry.[29]

(35) Possible evidence in support of this hypotheses is that oxochromate(V) complexes with 1,2-propanediolato(2–) do not exhibit well-resolved ^1H superhyperfine coupling but show only broad signals at room temperature in the neat solvent. The broad signals could be explained in terms of the equilibrium of the protons being on a time scale similar to the EPR time scale. However, under some conditions where the 1,2-ethanediolato(2–) complexes show well-resolved ^1H superhyperfine coupling and the 1,2-propanediolato(2–) complexes do not, the glycerol (1,2,3-propanetriolato(2–)) complexes also show ^1H superhyperfine coupling. Since the 1,2-propanediolato(2–) and 1,2,3-propanetriolato(2–) complexes differ only by replacing a methyl group by an hydroxymethyl group, similar steric factors are expected to apply to these two complexes. This anomaly may be explained by the fact that the 1,2-propanediolato(2–) ligand is chiral and can lead to more isomers when complexed to Cr(V) than can the achiral 1,2,3-propanetriolato(2–) ligand. Hence, the ^1H superhyperfine coupling of the complexes containing the former ligand may be obscured by overlapping signals from several geometric isomers: Bramley, R.; Ji, J.-Y. Unpublished results. In order to resolve this ambiguity, it is planned to perform experiments in the future with *S*-1,2-propanediol.

Scheme I. Berry Twist Mechanism for the Equilibration of the Protons in III



coordinate complex. A rapid equilibrium on the EPR time scale between a five-coordinate and a six-coordinate form of III can also be discounted. Such an equilibrium would be expected to be slow on an EPR time scale and would result in a significant dependence of A_{iso} and g_{iso} values on the concentration of 1,2-ethanediol in the aqueous solutions.

The reason for the lack of significant concentrations of a six-coordinate form of III in these solutions, despite steric considerations similar to those that pertain to the equilibria with oxalate as the ligand, probably arises from the different abilities of these chelates to act as donors. Deprotonated diols are much better σ and π donors than dicarboxylates, and hence, the ed ligand will donate more electron density to the Cr(V) center than the ox ligand. Therefore, the Cr(V) center in $[Cr(ox)_2O]^-$ is much more electrophilic and more able to attract a nucleophile to form a six-coordinate complex than is $[Cr(ed)_2O]^-$.

The lack of a significant variation in the values of g_{iso}, $A_{iso}(^{53}Cr)$, and $A_{iso}(^{1}H)$ for all of the Cr(V) complexes over the range of solvent mixtures from 1% v/v aqueous 1,2-ethanediol to 100% 1,2-ethanediol is consistent with detailed studies on the solvent dependence of the EPR parameters of I.[26] It has been shown that g_{iso} values are relatively insensitive to the nature of the solvent, but A_{iso} values can show a significant variation with solvent. The small variation in $A_{iso}(^{53}Cr)$ of I correlates, in a strongly statistically significant manner, with the hydrogen-bonding acidity of the solvent.[26] This has been interpreted as being due to the influence of solvent–solute hydrogen bonding involving the five oxygen donor atoms of I. Since water and 1,2-ethanediol are both strong hydrogen-bonding acids, I is expected and observed to have similar values of A_{iso} in these two solvents.[26] Therefore, it is not surprising that the values of both this parameter and the other EPR parameters show little variation (within experimental error) over the entire range of solvent mixtures.

Ligand-Exchange Equilibria and Synthetic Implications. The nature of the ligand-exchange chemistry has been established from the identification of the EPR signals of I and III from their characteristic EPR parameters. Complex II has not been reported previously, but its structure was assigned unambiguously in the previous sections. This is important because the EPR signal of a second Cr(V) complex (apart from III) has been observed when Cr(VI) oxidizes 1,2-ethanediol-d_4 or -d_6.[36] This signal has the same g value as that observed for II, but the results presented here establish that the species that gives rise to the extra signal in the Cr(VI) oxidation of 1,2-ethanediol is not a major contributor to the intensity of the signal due to II. If it were, then it would be prominent in solutions in which only III is in solution (i.e. solutions of I in neat 1,2-ethanediol over molecular sieves). Therefore, if it is present at all, its concentration is so small as to have no significant effect on the equilibrium constants that have been reported here.

The time that it takes to record the spectra after the dissociation of the Cr(V) complex into the water/1,2-ethanediol mixture (~4 min) is sufficient to allow the ligand-exchange reactions (milliseconds time scale[18,19,25]) to reach equilibrium values, but is not long enough to bring about significant decomposition of the Cr(V) complexes in solution ($t_{1/2} \geq 1$ h[24]). The only other problem that could complicate the analysis of the equilibrium constants is the presence of exchange-coupled Cr(V) dimers,[37,38] which would be EPR silent at room temperature. Cr(V) dimers have been observed in other systems, but there is no evidence for such dimers under the experimental conditions that were employed here (i.e. in the presence of a large excess of ligand[38] and at low total concentrations of Cr(V)).

The strength of the bonding of the ehba ligands to the Cr(V) center of I in aqueous 1,2-ethanediol is quite remarkable. Given that ed contains two alcoholate donor groups, it is expected to be stronger as both a σ and π donor to Cr(V) than the ehba ligand, which contains an alcoholate and a carboxylate donor. However, the equilibrium data show that, in aqueous 1,2-ethanediol, the complexes containing ehba ligands are more thermodynamically stable than their congeners in which one ehba ligand is replaced by an ed ligand. There are several competing factors that influence the values of the equilibrium constants apart from the inherent strength of binding of the ligands to Cr(V). These include the following. (i) The doubly deprotonated ligand, ed, is a much stronger base than the doubly deprotonated ehba ligand (at least for the first protonation, which involves an RO^- group for ed but an RCO_2^- group for ehba). This means that both of the ligand-exchange equilibria will be pushed toward the reactants, rather than the products; i.e., the pK_{a1} and pK_{a2} values of the ligands are important factors in determining the values of $(K_c)_1$ and $(K_c)_2$. (ii) There are solvent effects on the stability of the Cr(V) complexes. Complex III is expected to be a stronger hydrogen-bonding base than complex I both on steric grounds and because of it having more basic oxygen donors. This will tend to push the equilibria to the right. (iii) The relative solvation of the free ligands (ehba and ed) will also affect the equilibrium constants, $(K_c)_1$ and $(K_c)_2$, but it is difficult to predict what influence that this will have on the values of these constants. This arises because ehba is a stronger hydrogen-bonding acid (because of the presence of a carboxylic acid group) than is 1,2-ethanediol, but the latter is a stronger hydrogen-bonding base. While these opposing factors make it difficult to estimate whether ehba or 1,2-ethanediol will be more strongly solvated, these solvation contributions are unlikely to be the reason for the values of these equilibrium constants being much less than one.

The reasons that factor i is most important in pushing the equilibria toward the reactants are obvious from the pK_{a1} values of the two ligands. In order to illustrate this, the five competing equilibria that are present in the equilibrium represented by eq 1 are given in eqs 3–7. Therefore, the equilibrium constant for $(K_c)_1$ is given by eq 8. Since the equilibria represented by

(36) Mitewa, M.; Bontchev, P. R.; Kabassanov, K.; Malinovski, A. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 793–798. Our results support the notion in this reference that the second signal that is observed in the reaction of $[CrO_4]^{2-}$ with 1,2-ethanediol-d_4 or -d_6 arises from an intermediate in which one 1,2-ethanediolato(2−) ligand is bound to a dioxochromium(V) center. It is evident that such an intermediate is not observed in the ligand-exchange reactions of I in the neat solvent over molecular sieves.

(37) Heberhold, M.; Kremnitz, W.; Razavi, A.; Thewalt, U. *Angew. Chem.* **1985**, *97*, 603–604.

(38) Nishino, H.; Kochi, J. K. *Inorg. Chim. Acta* **1990**, *174*, 93–102.

$$I(aq) + {}^{-}OCH_2CH_2O^{-}(aq) \rightleftarrows II(aq) + {}^{-}OC(Et)_2CO_2^{-}(aq) \quad (K_c)_3 \quad (3)$$

$$HOCH_2CH_2OH(aq) + H_2O(l) \rightleftarrows H_3O^{+}(aq) + HOCH_2CH_2O^{-}(aq) \quad K_{a1}(edH_2) \quad (4)$$

$$HOCH_2CH_2O^{-}(aq) + H_2O(l) \rightleftarrows H_3O^{+}(aq) + {}^{-}OCH_2CH_2O^{-}(aq) \quad K_{a2}(edH_2) \quad (5)$$

$${}^{-}O(Et)_2CO_2^{-}(aq) + H_3O^{+}(aq) \rightleftarrows H_2O(l) + HO(Et)_2CO_2^{-}(aq) \quad 1/K_{a2}(ehbaH_2) \quad (6)$$

$$HO(Et)_2CO_2^{-}(aq) + H_3O^{+}(aq) \rightleftarrows H_2O(l) + HO(Et)_2CO_2H(aq) \quad 1/K_{a1}(ehbaH_2) \quad (7)$$

$$(K_c)_1 = \frac{(K_c)_3 \cdot K_{a1}(edH_2) \cdot K_{a2}(edH_2)}{K_{a1}(ehbaH_2) \cdot K_{a2}(ehbaH_2)} \quad (8)$$

$K_{a2}(edH_2)$ and $K_{a2}(ehbaH_2)$ both involve the deprotonation of an alcohol group, they are expected to be similar. This means that the major factors influencing the values of $(K_c)_1$ are the values of $(K_c)_3$ and the ratio $K_{a1}(edH_2)/K_{a1}(ehbaH_2)$. The value of pK_{a1} for $ehbaH_2$ is 3.40,[39] whereas that for edH_2 is 14.8.[40] Therefore, the ratio of the K_{a1} values is of the order of $10^{-11.4}$ and the values of $(K_c)_3$ are of the order of 10^6–10^7. Similarly, the values of $(K_c)_4$ for the eq 9 are of the order of 10^5–10^6. This detailed analysis

$$II(aq) + {}^{-}OCH_2CH_2O^{-}(aq) \rightleftarrows III(aq) + {}^{-}OC(Et)_2CO_2^{-}(aq) \quad (K_c)_4 \quad (9)$$

of the equilibrium data establishes that the ed ligand is in indeed a much better donor ligand than the ehba ligand. This analysis is also supported by the spectroscopic results. The facts that the values of g_{iso} increase in the order I < II < III and A_{iso} values decrease in the order I > II ≈ III both indicate that the ed ligand is a stronger donor to Cr(V) than the ehba ligand in aqueous 1,2-ethanediol.[30] Solvent effects may also be important in determining the values of $(K_c)_3$ and $(K_c)_4$. Factor ii will tend to increase the values of $(K_c)_3$ and $(K_c)_4$, since there is a dependence of EPR parameters of I on the hydrogen-bonding acidity of the solvent[26] and water/1,2-ethanediol solvents are strong hydrogen-bonding acids.[41] In addition, the variation in the Cr(V/IV) redox couples of I by ~1 V (100 kJ mol^{-1}) over a range of solvents[42] illustrates the importance of hydrogen bonding in stabilizing these types of complexes in solution. There will be an opposing factor to this, since the more basic ed ligand will be stabilized more by hydrogen bonding than the ehba ligand. Therefore, it is difficult to estimate how much the values of $(K_c)_3$ and $(K_c)_4$ represent the intrinsic strengths of the different donor ligands as opposed to hydrogen-bonding effects on the four ions that are involved in a particular equilibrium.

The importance of factor i in influencing the thermodynamic stability of oxochromate(V) complexes toward ligand-exchange reactions is also highlighted in the ligand-exchange chemistry of I with oxalic acid (oxH_2) in 50% v/v acetic acid.[17-19] On the basis of chemical considerations and EPR parameters,[30] the order of the donor strength of the three ligands is expected to be ox < ehba < ed. However, the values of the equilibrium constants for the ligand-exchange reactions of I with oxalic acid are much larger than the corresponding values of the reaction of I with edH_2 (eqs 1 and 2). With use of an analysis similar to that outlined in eqs 3–8, the value of the ratio $[K_{a1}(oxH_2) \cdot K_{a2}(oxH_2)]/[K_{a1}(ehbaH_2) \cdot K_{a2}(ehbaH_2)]$ will be of the order of 10^{15},[43] which is the driving force for the displacement of the ehba ligands by ox ligands in the reaction between I and oxalic acid.[18,19] In general, the pK_a values of the ligands have a very important role in influencing the position of these types of ligand-exchange equilibria.

The variation in the values of the equilibrium constants with the composition of the solution mixture is not large and varies by little more than 1 order of magnitude over the entire range of solvent mixtures. The lower values obtained in solutions containing a high water content may arise from the smaller water molecule being able to hydrogen bond more readily with the sterically hindered complex, I, than for the same interaction between 1,2-ethanediol and I. This will tend to push the equilibria to the right in solutions containing a high water content. Specific solvation of this type is well-known in solvent mixtures.[44] However, the acid/base equilibria shown in eqs 4–7 will also depend on the concentration of water and will be an important factor in influencing the position of the equilibria as a function of the solvent concentration.

The observation that molecular sieves push the ligand-exchange equilibria toward the right is not only true for equilibria involving chelating diolates, such as ed, but also is true for the displacement of ehba ligands by monodentate alcohols.[26] This is believed to occur by the adsorption of the ehba ligand onto the surface of the zeolite, and the effects of the zeolite on the ligand-exchange equilibria can be reversed by the addition of $ehbaH_2$.[26] It was expected that this factor may be important in providing a synthetic route to the isolation of III. While this complex can be generated in essentially quantitative yields in solution (Figure 3), a method for its isolation from solution in a pure form has been elusive. Its isolation has been hindered by a number of factors, including the oxidation of the ligand to 2-hydroxyethanone (glycolaldehyde) with concomitant reduction to Cr(III) during the relatively long periods required for isolation,[14,22] the high solubility of III, and the effects of driving the equilibria back toward I and II as solutions are concentrated. It is also possible that dimerization reactions may occur at higher concentrations of Cr(V),[38] but this requires further investigation. Various methods aimed at overcoming these problems are being pursued, but the isolation of a pure form of this complex from solution remains a difficult task.

Even if III continues to elude isolation in the solid state, the ligand-exchange chemistry allows the facile preparation of solutions of this complex in essentially quantitative yields. This will enable the physical properties and solution chemistry of III to be studied free from contamination by Cr(VI) and Cr(III) (a consequence of the previous preparative method that involves the oxidation of 1,2-ethanediol by Cr(VI)).[8-16] Moreover, for the important use of solutions of III and III-d_8 as dynamically polarized proton and deuteron targets, respectively, it is essential that these solutions only contain small amounts of Cr(III) in order to maximize their effectiveness as targets.[10,11] This new synthetic method for the synthesis of solutions of III is also applicable to the preparation of other Cr(V) complexes with diol,[35] triol,[35] and other ligands[18,19] and, therefore, is likely to be of general use in the preparation of dynamically polarized targets based on Cr(V).

Conclusions

Previously unrecognized fluxional behavior in $[Cr(ed)_2O]^{-}$ and related complexes has been established for the first time. These processes, which render all of the protons equivalent on the EPR time scale, are thought to occur via a series of rapid Berry twists.

The use of ligand-exchange chemistry with $[Cr(ehba)_2O]^{-}$ as the starting material, has allowed the generation of $[Cr(ed)_2O]^{-}$ in quantitative yields in neat 1,2-ethanediol solutions that are placed over 3-Å molecular sieves. This synthetic procedure appears to be quite general and should enable many Cr(V) complexes to be generated in quantitative yields, free from the complications due to the presence of Cr(VI) and Cr(III) in solutions where Cr(V)

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complexes are generated from the oxidation of excess ligand by Cr(VI). However, the isolation of these complexes as pure solids still remains a difficult problem.

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Factors Influencing the Nitrogen vs Oxygen Bonding Mode of Amides Bound to Pentaamminecobalt(III) and the Kinetics and Mechanism of Rearrangement

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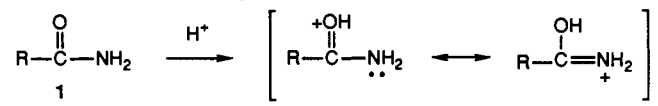
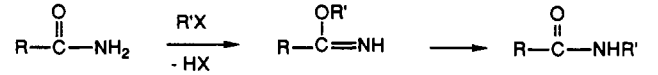
The preparation, characterization, properties, and rearrangements of a series of pentaamminecobalt(III) complexes of amides, $RCONH_2$, are described (R = H, CH_3, CF_3, CH_2Cl, CH_2F, $CH{=}CH_2$, C_6H_5, C_6H_4-4-F, C_6H_4-2-NO_2). Some of the nitrogen-bonded amide complexes were synthesized by base-catalyzed hydration of $[(NH_3)_5CoN{\equiv}CR]^{3+}$; others, including those inaccessible by this route, were synthesized by linkage isomerization of the oxygen-bonded amide complexes, $[(NH_3)_5CoOC(NH_2)R]^{3+}$, in coordinating but aprotic solvents containing noncoordinating base. The N-bonded amide products were isolated pure in both basic and acidic forms, $[(NH_3)_5CoNHCOR]^{2+}$ and $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$. The former are thermodynamically stable, while the latter (pK'_a <4), although kinetically robust, are thermodynamically unstable with respect to the corresponding O-bonded linkage isomer and rearrange slowly in solution ($t_{1/2}$ hours, 25 °C). The isomer equilibrium for amides as O- or N-bonding *neutral* ligands lies at least 100:1 to the side of the O-bonded isomer in sulfolane, in which neither ligand deprotonation nor solvolysis of either isomer could be detected. In coordinating solvents, $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ also solvolyzes, at a rate comparable to that for competing N to O isomerization. For Me_2SO these reactions have been identified by ^1H NMR measurements. The results require the isomer interconversion to be intramolecular. All the N-bonded amide complexes $[(NH_3)_5CoNHCOR]^{2+}$ protonate at oxygen (in Me_2SO-d_6), producing $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$; the sole exception is the case R = CF_3, which does not detectably protonate. The rate of N to O isomerization in sulfolane is dependent on the substituent R, but the rates span a range of only a factor of about 20. When the substituent can donate an electron pair (R = NH_2, $NHCH_3$, $N(CH_3)_2$, NHC_6H_5, OC_2H_5, OH), N to O isomerization is several orders of magnitude faster ($t_{1/2}$ seconds). The rate distinction between these two classes of isomerizing compounds is attributed to the different positions of the tautomeric equilibrium between N- and O-protonated forms of $[(NH_3)_5CoNHCOR]^{2+}$ and the differences in reactivity between the tautomers. The solution structures for these tautomers in Me_2SO are established by the ^1H NMR spectra. The O to N linkage isomerization was not observed in neutral aqueous solution because competing hydrolysis is faster. However the reaction can be forced in aprotic solvents in the presence of a noncoordinating base, and the propensity for this reaction is related to the ability of the O-coordinated neutral amide to dissociate a proton from the remote nitrogen (pK'_a ca. 11, H_2O, formamide-*O*, and acetamide-*O*). The mechanism is discussed and analogies are drawn with the Chapman rearrangement, which involves O to N migration of substituents on organic amides and imino esters. Factors that influence the interconversion of linkage isomers, including the site of protonation, isomer acidity, solvent, temperature, and amide substituents, are discussed and compared with related linkage isomeric complexes of pentaamminecobalt(III).

Introduction

Carboxylic acid amides **1** are very weak bases and also poor nucleophiles for electrophilic reagents. The oxygen is both more



basic and more nucleophilic than the nitrogen atom.[1] However, while good electrophiles *initially* alkylate the O-terminus of amides, these compounds often rearrange upon heating to the N-substituted products:[2]



This result indicates that the carbonyl oxygen is the preferred nucleophile whereas the N-alkylated amide is the thermodynamically more stable compound. This (Chapman[3]) rearrangement is carried out typically at about 180 °C, or as low as 100 °C in the presence of excess alkylating agent. The mechanism is intramolecular for *O*-aryl imidates although at least partly intermolecular for *O*-alkyl compounds.[4]

Amides are ambidentate ligands for metal ions,[5a] and by analogy with the above, one might expect kinetically controlled syntheses to lead to the O-metalated complex, while the N-bonded form would be favored under equilibrium conditions. Amides, for which formamide and acetamide have been the prototypes,[5a,12,13] have a tendency to coordinate via oxygen to "hard" metal complexes[5] but via nitrogen to "soft" metals,[6] consistent with the greater basicity of the amide oxygen. Thus the "hard" labile complex[7] $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ reacts with **1** in poorly coordinating solvents (acetone, sulfolane), yielding exclusively[8] the

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