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Solvent Dependence of the EPR Spectra of Oxochromate(V) Complexes: Solution Structures and the Effects of Hydrogen Bonding between the Solvent and the Complex

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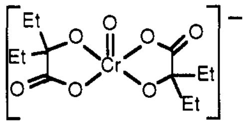
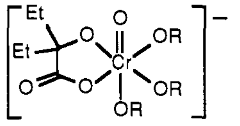
EPR spectra of bis(2-ethyl-2-hydroxybutanoato(2−))oxochromate(V), $[Cr(ehba)_2O]^-$ (I), in a range of solvents exhibit g_{iso} and A_{iso} values that are typical of five-coordinate Cr(V). This indicates that the distorted trigonal-bipyramidal structure observed in the solid state, in which the carboxylate groups occupy the axial sites, is retained in solution. However, there is EPR spectral evidence of a small amount of a second geometric isomer in certain solvents. In addition, EPR spectra of solutions of I in some solvents, such as ethanol and methanol, exhibit the signal of another Cr(V) complex in which one of the ehba ligands has been replaced by three solvent molecules to form (2-ethyl-2-hydroxybutanoato(2−))tris(solvento(1−))oxochromate(V) (II). The response due to this complex grows to become the major signal when the solution is placed over 3-Å molecular sieves. The shift in equilibrium between I and II over 3-Å molecular sieves arises from adsorption of ehba onto the zeolite and can be reversed by adding free H_2ehba to the solution. In the presence of chelating solvents, such as 1,2-diols and glycerol, the EPR signals assigned to Cr(V) products of the ligand-exchange reactions are also observed. The g_{iso} values of I are relatively insensitive to the nature of the solvent in which the Cr(V) complex is dissolved. The values of the ^{53}Cr hyperfine coupling constants are much more sensitive to the nature of the solvent, and a statistically significant correlation between these values and the hydrogen-bonding acidities of the solvent is observed. The decrease in ^{53}Cr A_{iso} values with increasing solvent hydrogen-bonding acidity is consistent with an increase in electron density of the unpaired electron on the metal as the ligands become weaker donors. The solvent dependence of the EPR properties of I has also led to a reinterpretation of the solvent dependences of the g_{iso} values of the Cr(V)/oxalato system in terms of the complexes bis(oxalato(2−))oxochromate(V) (III) and bis(oxalato(2−))(solvent)oxochromate(V) (IV).

Introduction

Recently, it has been shown that the Cr(V)/Cr(IV) redox potential of I is very sensitive to the nature of the solvent and shifts negative by over 1 V in going from a solvent that is a strong hydrogen-bonding acid (e.g. water) to a solvent that has little or no tendency to act as a hydrogen-bonding acid (e.g. dimethyl sulfoxide).[1-4] The major contribution to this phenomenon is due to hydrogen-bonding interactions between the solvent and the five oxygen donors of I. A smaller but significant contribution is due to the solvent dipoles interacting with the charge centers.[3,4]



I



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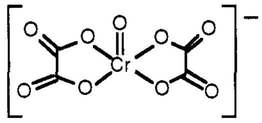
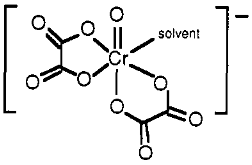


III



IV

EPR spectroscopy is commonly used to study Cr(V) transients in the oxidation of organic substrates by Cr(VI)[5] and is useful for determining electron density within these complexes. Recently, we have developed an empirical model for determining the solution structures of oxochromate(V) complexes from EPR spectra.[6] These results have shown that there is a correlation between the donor abilities of the ligands and EPR spectral parameters.[6] Since the formation of hydrogen bonds between the solvent and the donor atoms of the ligands will reduce the strength of the metal–ligand bonds, similar correlations between the hydrogen-bonding ability of the solvent and EPR spectral parameters might be expected. Apart from studies on the solvent dependence of the Cr(V)/oxalate system[7] (which we will show have been interpreted incorrectly), there have been few studies in this area. Reported here is the use of EPR spectroscopy as a probe of solvent/solute hydrogen bonding and for determining the solution structures of Cr(V) complexes.

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.[8] Crystallization of the product was induced by dropwise addition of hexane over a period of 10–15 min. Anal. Calcd for $C_{12}CrH_{22}NaO_8$: C, 39.03; Cr, 14.08; H, 6.00; N, 0.00. Found: C, 39.19; Cr, 13.6; H, 6.21; N, 0.00. The red-brown product is light sensitive, so it is necessary to keep the product in the dark in a desiccator. The partially protonated complex $[(Me_3PhN)_x(H)_y][Cr(ehba)_2O]$ $(x + y = 1)$ was prepared by solvent extraction of the chromium(V) complex into dichloromethane in the presence of trimethylphenylammonium chloride.[4] *Caution! These Cr(V) complexes are mutagenic, rapidly cleave DNA at micromolar concentrations, and are potential carcinogens.*[9] *Appropriate precautions should be taken to avoid skin contact and inhalation of Cr(V) dusts.*

Ethanol, methanol, glycerol, acetontrile, and acetone (all Ajax, AR grade), 2,2,2-trifluoroethanol and hexamethylphosphoramide (both Aldrich, LR grade), 2,4-pentanedione (EGA-Chemie, AR grade), dimethyl sulfoxide (Mallincrodt, AR grade), dichloromethane (May and Baker), 1,2-ethanediol and 1,2-propanediol (both Ajax, LR grade), and 1,3-propanediol (EGA-Chemie, 95–96%) were used as received. 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,

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Table I. Isotropic EPR Parameters of I at 20 ± 2 °C and Solvent Polarity, Hydrogen-Bonding Acidity, and Hydrogen-Bonding Basicity Parameters

solvent	α[a]	β[b]	π^*[c]	g_{iso}[d]	^{53}Cr A_{iso}/G[e]
2,2,2-trifluoroethanol	1.51	0.00	0.73	1.9782	18.6
water	1.17	0.18	1.09	1.9784	18.5
acetic acid	1.01		0.61	1.9784	18.5 (3)
methanol	0.93	0.62	0.60	1.9783	18.3[f]
1,2-ethanediol	0.90	0.52	0.92	1.9783	18.4 (3)
ethanol	0.83	0.77	0.54	1.9783	18.2[g]
1,3-propanediol				1.9785[h]	
dichloromethane	0.30	0.00	0.80	1.9785	18.0
2,4-pentanedione				1.9781	18.0
acetone	0.08	0.48	0.71	1.9780	17.9
acetonitrile	0.19	0.31	0.75	1.9776	17.8
hexamethylphosphoramide	0.00	1.05	0.87	1.9782	17.8
dimethyl sulfoxide	0.00	0.76	1.00	1.9775	17.7

[a] Hydrogen-bonding acidity parameter; refs 11, 12. [b] Hydrogen-bonding basicity parameter; refs 11, 12. [c] Solvent polarity parameter; refs 11, 12. [d] Error ±0.0002. [e] Error ±0.1 G, unless otherwise given in parentheses. [f] In the presence of molecular sieves, a second signal is observed, $g_{iso} = 1.9752$, $A_{iso} = 19.8 \pm 0.1$ G, due to (2-ethyl-2-hydroxybutanoato(2−))tris(methanolato(1−))oxochromate(V). [g] In the presence of molecular sieves, a second signal is observed, $g_{iso} = 1.9755$, $A_{iso} = \sim 20.0$ G, due to (2-ethyl-2-hydroxybutanoato(2−))tris(ethanolato(1−))oxochromate(V). [h] In the presence of molecular sieves, a second signal is observed, $g_{iso} = 1.9757$, tentatively assigned to the structure due to (2-ethyl-2-hydroxybutanoato(2−))(1,3-propanediolato-(2−)-*O,O'*)(1,3-propanediolato(1−)-*O*)oxochromate(V).

second-order corrections have been applied. The concentration of I used in these experiments was typically 2–3 mM.

Experiments performed over molecular sieves involved either shaking the appropriate solutions over the sieves for 1 h and then leaving the solution to stand an additional 1 h or peristaltically pumping the solutions around a closed loop, which included the cavity capillary and a 2-cm column of sieves. In the latter case, the progressive changes in the spectra were monitored.

Deprotonation of the partially protonated $[Cr(ehba)_2O]^-$ complex was achieved by the addition of small amounts of triethylamine (BDH, general purpose reagent) to the solution contained in the EPR cell. The overlapping peaks observed for the partially protonated complex were deconvoluted numerically by least-squares fitting of digitized spectra to individual Lorentzian derivatives with heights and widths being allowed to vary.

Statistical Analysis of Solvent Dependence of EPR Parameters. All correlations and statistical analyses were performed by using least-squares analyses of the experimental data. The programs STEPWISE and REGRESS in the statistics package MINITAB[10] were used for the multiple linear regressions. The STEPWISE program considers all of the solvent parameters and only retains those with an *F* statistic of 4 or greater (i.e. a *t* statistic of 2 or greater, where $t = F^{1/2}$).[10] The REGRESS program allows the number and type of solvent parameters to be chosen and obtains the best fit of all of the chosen parameters in a multiple linear regression.

Results

The solvent dependences of the isotropic EPR parameters are summarized in Table I, together with measures of the polarities (π^*), hydrogen-bonding acidities (α), and hydrogen-bonding basicities (β) of these solvents.[11,12] Typical EPR spectra are shown in Figure 1. When the EPR spectra of alcohol solutions of I are measured, a weak signal for a new Cr(V) complex is observed (Figure 1a). If this solution is placed over 3-Å molecular sieves, the second signal grows and becomes the major signal (Figure 1b); in addition, the Cr(V) signals decay much more rapidly. However, if excess H_2ehba is added to these solutions, only the signal due to I is observed and the solutions are much more stable (Figure 1c). The EPR parameters of the signal due to I do not change significantly over the 3-Å sieves or in the presence of excess H_2ehba. In solvents that can act as strong chelates, e.g. 1,2-diols and glycerol, ligand-exchange reactions occur and signals due to I, the mixed-ligand complex, V, and the fully exchanged complex,

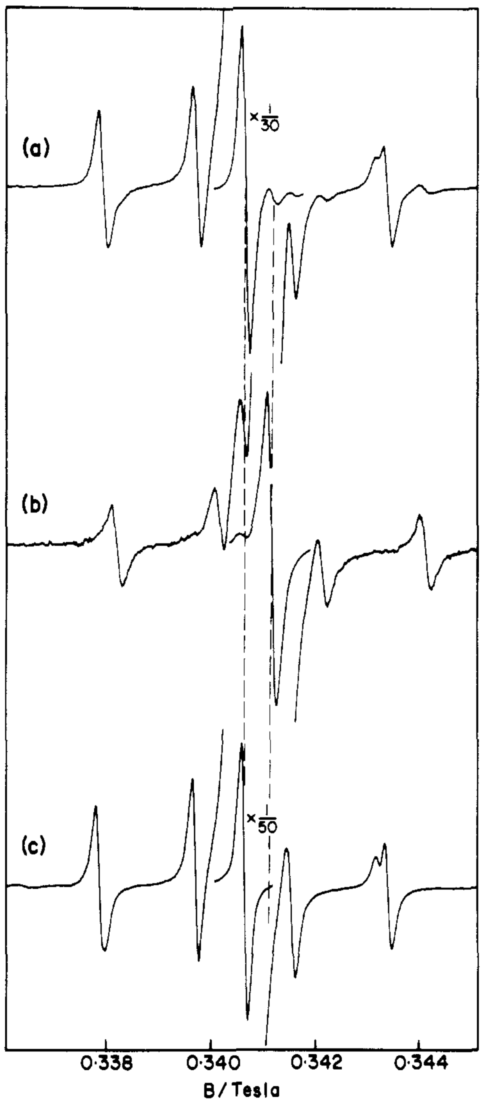
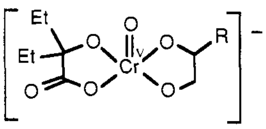
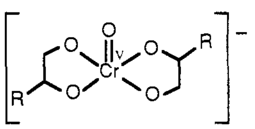


Figure 1. Typical EPR spectra of (a) I (2 mM) in methanol, (b) I (2 Mm) in methanol over 3-Å molecular sieves (the new signal that is observed at $g = 1.9752$ is due to II), and (c) I (4 mM) in methanol over 3-Å molecular sieves with excess H_2ehba (200 mM).



V



VI

VI, are observed.[13] In the cases of 1,2-propanediol and glycerol (1,2,3-propanetriol), the signals are too broad in the neat solvent to obtain accurate g_{iso} and A_{iso} values of the overlapping signals due to I, V, and VI. However, the values in 80% v/v aqueous solutions of these solvents gave g_{iso} and A_{iso} values that are similar to those observed in 1,2-ethanediol.

In solutions of the partially protonated complexes, two signals are observed from the splitting of the outer satellites of the ^{53}Cr hyperfine coupling pattern. Addition of the nonnucleophilic base triethylamine results in the collapse of the EPR spectrum so that only the signal with the lower value of A_{iso} remains. This behavior is illustrated in Figure 2 for a dichloromethane solution of the partially protonated complex. No superhyperfine coupling of the

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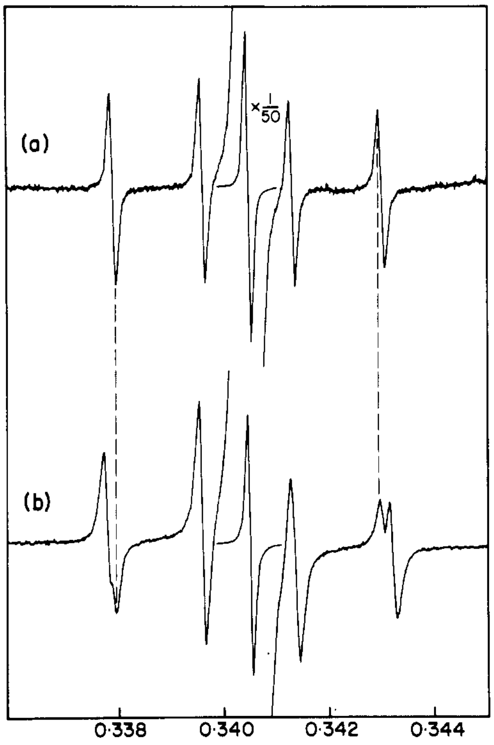

Figure 2. EPR spectrum of the partially protonated form of I in dichloromethane (a) after and (b) before the addition of a few drops of triethylamine.

proton to Cr(V) is observed in the signal due to the protonated complex, although the reason for this is uncertain without a more detailed analysis.

The addition of triethylamine (5% v/v) to the protic solvents results in the growth of the EPR signal which has the same EPR parameters as those observed in the presence of molecular sieves. This peak also grows with time relative to the signals due to I and becomes the main form of Cr(V) in some solvents. However, the relative intensities of the ^{53}Cr satellites (Figure 1) of the signal due to I do not change with time or with the addition of Et_3N or H_2ehba.

The g_{iso} values of I show a weak, but statistically significant, trend toward higher values as the hydrogen-bonding acidity of the solvent increases:

$$g_{iso} = 1.9779 + 0.00035\alpha \qquad (t = 2.05, R^2 = 0.318)$$

Since the uncertainty in the g_{iso} values is only a factor of 3 or 4 times less than the range in g_{iso} values, the weak correlation is not surprising.

A more definite trend is observed in the four-line isotropic coupling to ^{53}Cr (9.55% natural abundance, $I = {}^3/_2$), which increases with increasing hydrogen-bonding-acid strength (α) of the solvent in a strongly statistically significant manner. A plot of A_{iso} (for the major peaks of the ^{53}Cr satellites) versus α is given in Figure 3, and the A_{iso} values in 11 different solvents are related to α by the equation

$$A_{iso} = 17.8 + 0.599\alpha \qquad (t = 12.63, R^2 = 0.947)$$

The largest deviation between the calculated values of A_{iso} (from the above equation) and the experimental values (0.12 G) is within the experimental error of the measurements. No statistically significant correlations are observed with the other solvent parameters (π^*, β) in solution, and the addition of other solvent parameters to the regression involving α does not improve the correlation in a statistically significant fashion.

Discussion

The Structure of the Cr(V) Complexes as a Function of Solvent. The small variation in the g_{iso} values of I with solvent is not due to coordination of the solvent to a sixth coordination site, since

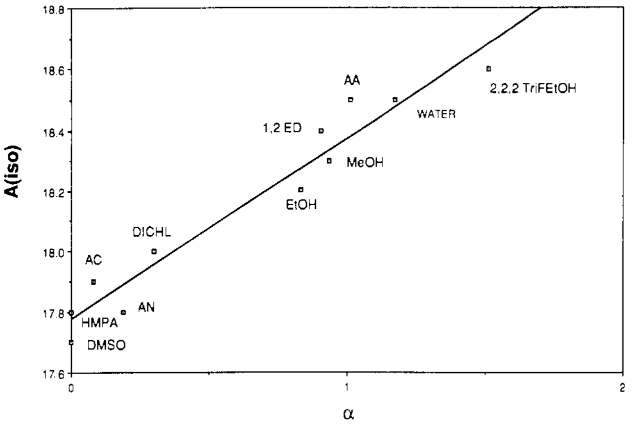

Figure 3. Plot of A_{iso} values of Ia versus the hydrogen-bonding acidity parameter, α.

the g_{iso} values are typical of five-coordinate oxochromate(V) complexes and are significantly larger than those observed for six-coordinate oxochromate(V) complexes.[6,14] The A_{iso} values are also typical of five-coordinate complexes. Five-coordination is also observed in the X-ray structure of I,[2] where two of the ethyl groups of the ehba ligands are within van der Waals contact, effectively blocking the sixth coordination site in a square-pyramidal description. The complex is so distorted from the square-pyramidal geometry by steric clashes that the structure is more accurately described as a distorted trigonal bipyramid in which the carboxylate groups occupy the axial positions.[2] The assignments of the solution structures are strengthened by a lack of a statistically significant correlation between the EPR parameters and the solvent parameters, β or D_N,[15,16] which are measures of the basic properties of the solvents. If a solvent molecule did coordinate to a potential sixth coordination site, then it is expected that the EPR parameters would be sensitive to the ability of the solvent to form a chemical bond with the Cr(V) center. The possibility of the observed solvent dependence being due to a rapid equilibrium between five- and six-coordinate forms of I, which changes as the solvent is varied, can also be discounted, since such changes in coordination numbers are slow on the EPR time scale.[14,17-19] In addition, if such a rapid equilibrium exists, then the position of the equilibrium, and hence the average A_{iso} parameters of such an equilibrium mixture, would be sensitive to β or D_N, which is not the case. Therefore, it is concluded that the distorted trigonal-bipyramidal structure of I that is found in the solid state[2] persists in solution, in all of the solvents that have been studied.

In solvents that are weak hydrogen-bonding acids, the outer ^{53}Cr satellites are split. This means that there are two complexes in solution with similar g_{iso} values but with different A_{iso} values. The splitting of these signals is due to partial protonation of one of the ehba ligands, since the addition of a nonnucleophilic base, triethylamine, results in the disappearance of the signal due to the protonated complex and only that due to I remains. The value of A_{iso} for the protonated complex is greater than that due to I, which is consistent with a decrease in the donor strength on the ehba ligand on protonation.[6] It is expected that protonation occurs

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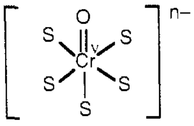
on the alcohol group of the ehba ligand because this is likely to be the most basic group in the complex. The fact that the central ^{53}Cr satellites exhibit only one peak may disguise a fast-exchange coalescence involving the protonation/deprotonation equilibrium. Even more accurate deconvolution studies than those performed here would be needed to distinguish between this possibility and the possibility of the overlapping peaks not being resolved. Alternatively, variable-temperature experiments may be useful in future studies.

Solvents that are also strong chelating ligands give rise to new signals that are due to the products of ligand-exchange reactions. In the case of the complexes with structure VI, the nature of the products of these reactions was established by comparison of the g_{iso} and A_{iso} (^{53}Cr and ^{1}H) values with those generated from the reaction of the neat solvent with Cr(VI).[5,13,14,17-19] The mixed-ligand complexes, V, were characterized from their g_{iso} and A_{iso} (^{53}Cr) values, which were intermediate between those of I and VI, and the multiplicity of the A_{iso} (^{1}H) coupling. More detailed characterizations of these reactions and their use in the isolation of new Cr(V) complexes will be reported elsewhere.[13]

The observation of a minor signal with a g_{iso} value distinctly different from that due to I when it is dissolved in methanol, ethanol, or 1,3-propanediol solution is also due to a ligand-exchange reaction. As is the case with chelating diols, this process is substantially enhanced when the solutions are placed over 3-Å molecular sieves and is due to the loss of ehba ligands from solution by adsorption onto the zeolites, thus driving the equilibrium toward II. This is established by examining the EPR spectrum under identical conditions in the presence of excess H$_2$ehba, whereby only the signal due to I is observed. The g_{iso} and A_{iso} values of the new complex are those expected for a six-coordinate complex,[6,14] and the calculated values of these parameters, from an empirical approach developed for oxochromate(V) complexes,[6] are consistent with the tris(solvento) structure, II. There is no evidence of an EPR signal that could be ascribed to the pentakis(solvento) complexes, VII, under these conditions. The experimental evidence available does not allow a determination of whether the solvent or ehba ligand occupies the position trans to the oxo group in the structure of II, which represents only one of the three possible geometric isomers. There may be more than one isomer of II present in solution, since the ^{53}Cr satellites are broader than those observed for I. The formation of the solvent complexes is also consistent with the more rapid decay of the Cr(V) complexes to form Cr(III) in the presence of the molecular sieves as opposed to the absence of the sieves, since the primary alcohol ligands are much more easily oxidized by Cr(V) than the tertiary alcohol groups of the ehba ligands. It is apparent that the removal of one ehba ligand relieves steric strain in the Cr(V) complex and enables the formation of six-coordinate complexes, II. The observation of these complexes only in solvents that are strong σ donors (high β or D_N) supports their assignment. Other factors will be important in determining their relative concentration in the presence of molecular sieves, such as the solvent dependence of the adsorption isotherm for ehba on the sieves.



where s=solvent or deprotonated solvent ligand.

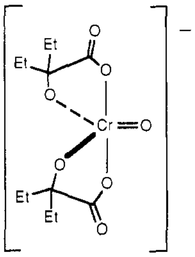
VII

Table II. Solvent Dependence of the EPR g_{iso} Values[7] and New Structural Assignments of the Oxochromate(V) Complexes Formed in the Reactions of Cr(VI) or Na$_3$CrO$_4$ with Oxalic Acid

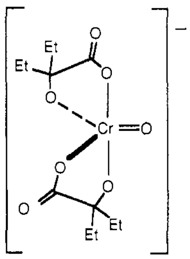
solvent	III	IV	VII or X
acetic acid[a]	1.9783 (2)		
nitrobenzene	1.9790 (3)		
acetonitrile	1.9781 (3)		
dioxane	1.9767 (4)		
methanol	1.9763 (4)		
N,*N*-dimethylformamide	1.9764 (3)	1.9711 (3)	
dimethyl sulfoxide	1.9759 (3)	1.9709 (3)	
N-methylacetamide	1.9767 (3)	1.9714 (3)	
concd perchloric acid	1.9764 (3)	1.9711 (3)	
water	1.9761 (6)	1.9702 (5) 1.9708 (6)[b]	
pyridine	1.975 (1)	1.972 (1)	
hexamethylphosphoramide	1.9754 (3)	1.9706 (5)	1.9688 (3)
formamide	1.975 (1)	1.970 (1)	1.965 (1)

[a] This work. [b] The sixth ligand is OH$^-$.

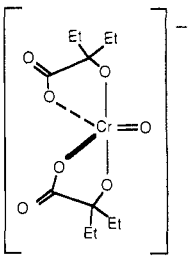
The observation that the outer ^{53}Cr satellites of the signal due to I in these solvents also split into two (Figure 1) is not due to the protonation/deprotonation equilibrium that is observed in dichloromethane, since the ratios of these satellites are unaffected by the addition of the nonnucleophilic base, triethylamine. The ratios of the ^{53}Cr satellites are also unaffected by the addition of acid and excess ligand, in the form of H$_2$ehba (Figure 1). Therefore, the splitting of the signals cannot be due to either a protonation/deprotonation equilibrium involving the ehba or oxo ligands or a change in the number of ehba ligands that are coordinated. Similarly, a change in coordination number from 5 to 6 is inconsistent with the identical g_{iso} values observed for these two complexes. The most likely explanation of this behavior is that there is more than one geometric isomer of I in solution. The major isomer (larger A_{iso} value) is assigned to the symmetric trigonal-bipyramidal structure that is observed in the solid state[2] in which the three most sterically demanding groups (the two tertiary alcoholate and the oxo groups) occupy the three equatorial sites, Ia. This enables the most sterically demanding groups to be as far away as possible. The tentative structural assignment for the other isomer is Ib, in which one carboxylate, one alcoholate, and the oxo group occupy the equatorial positions of the distorted trigonal bipyramid. This isomer will have less steric clashes than the isomer in which the two carboxylate groups and the oxo group occupy the equatorial positions, Ic, or other isomers in which the oxo group occupies an axial site. An alternative type of geometric isomerism would involve an equilibrium between a square-pyramidal and a trigonal-bipyramidal structure. However, since the square-pyramidal structure is less favored because of steric considerations, the first option is considered more likely in order to explain the presence of the putative geometric isomers. The fact that the ratio of these isomers changes with the solvent may be due to the minor isomer being stabilized more by hydrogen bonding, since it is most prominent in the strong hydrogen-bonding-acid solvents, such as water and the alcohols. An alternative explanation is that both isomers exist in all solutions, but the rate of interconversion of the isomers is slow compared to the EPR time scale in the strong hydrogen-bonding-acid solvents and fast for the weakly interacting solvents. Such an explanation is chemically reasonable because an intramolecular Berry twist would be expected to be slower when it requires a substantial rearrangement of hydrogen-bonded solvent molecules.



Ia



Ib



Ic

The nature of the isomers of I will be further investigated by the use of ^{13}C NMR spectroscopy. Preliminary NMR spectral results with I in solvents such as dimethyl sulfoxide and dichloromethane are consistent with the EPR results, which indicate that either only Ia exists in significant amounts in these solvents or two or more geometric isomers are interconverting rapidly on the NMR time scale at room temperature.[4,17]

The growth of the signal due to II with time in the presence of Et$_3$N is attributed to the base assisting in the deprotonation of the coordinated alcohol groups of the solvent, thereby making them better ligands and stabilizing II with respect to I.

Table III. Solvent Dependence of g_{iso} Values[7] and New Assignments of the Solution Structures of the Oxochromate(V) Complexes Formed in the Reaction of Oxalic Acid with Tetrachlorooxochromate(V)

solvent	III	IV	VII or X	XII	XI
nitrobenzene					1.9826 (4)
acetonitrile				1.9760 (5)	1.9822 (5)
dioxane	1.9777 (6)			1.9758 (6)	1.9814 (6)
methanol	1.976 (1)	1.9697 (8)			
N,*N*-dimethylformamide	1.9769 (6)	1.9711 (4)		1.9750 (6)	
dimethyl sulfoxide	1.9764 (6)	1.9704 (4)		1.9746 (6)	
N-methylacetamide		1.9706 (5)			
concd perchloric acid	1.9777 (4)	1.9714 (3)		1.9758 (5)	1.9820 (3)
water		1.972 (1)			
pyridine					
hexamethylphosphoramide	1.9752 (4)		1.9686 (4)	1.9738 (6)	
formamide	1.9767 (6)	1.9713 (6)			

The fact that the g_{iso} and A_{iso} values of I are unaffected by the addition of H_2ehba and no new EPR signals are observed in excess ligand shows that the often postulated complex containing three ehba ligands[20,21] does not exist in significant concentrations. It also throws doubt on the many kinetics papers of Bose, Gould, and co-workers that postulate the formation of six-coordinate complexes in the oxidation of organic substrates by I.[20,21] Our results indicate that the only six-coordinate oxochromate(V) complexes formed from I are those in which one of the ehba ligands has been lost. These results are also consistent with the large degree of steric interactions in the crystal structure of I,[2] which will inhibit the formation of six-coordinate complexes in which the solvent or any other ligand occupies the sixth coordination site. Detailed investigations of these aspects have been or will be described elsewhere.[13,14,17-19,22]

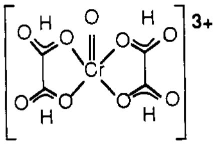
Correlations of the EPR Parameters of I with Solvent Parameters. If the five oxygen donor atoms of I are involved in strong hydrogen bonds with the solvent, they are less able to donate electron density to the Cr(V) center. Consequently, the single d electron, which occupies a nonbonding d orbital, will become more tightly bound to the Cr(V) center. This is consistent with the increase in the values of A_{iso} for Ia with increasing solvent/solute hydrogen bonding, which is clearly evident in Figure 3 and in the statistical significance of this correlation.

The relatively small effect of the solvent on the values of g_{iso} and A_{iso} as compared to those observed in the electrochemistry[1-4] is explained as follows. The EPR parameters only reflect the properties of the unpaired electron, which essentially resides in a nonbonding d orbital and is affected only slightly by changes in the donor strengths of the ligands. Such an analysis is supported by the small range of g_{iso} and A_{iso} values that are observed with a large range of ligands for a given coordination geometry.[5,6] By contrast, the electrochemical data represent the differences in total energies of the Cr(V) and Cr(IV) oxidation states. These energies are dominated by changes in the donor strengths of the ligands. Therefore, the electrochemical data are much more sensitive to the hydrogen-bonding interactions that will affect the strength of ligand binding to Cr(V) than are the EPR spectroscopic data. Nonetheless, the indirect effects of hydrogen bonding on the binding of the nonbonding d electron found from the EPR spectroscopic data do confirm the trends that are observed in the electrochemistry.[1-4]

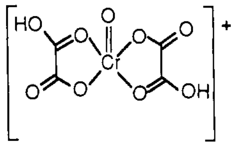
The importance of hydrogen bonding between solvents that are hydrogen-bonding acids and oxovanadate(IV) complexes has been established by ENDOR experiments,[23-25] where coupling of the V(IV) centers to the protons of uncoordinated solvent molecules are observed. Similar interactions are expected in the isoelectronic oxochromate(V) complexes, but to the authors' knowledge, such experiments have not been performed on oxochromate(V) complexes. Clearly, the ENDOR data that are available on the isoelectronic oxovanadate(IV) systems support our analysis that hydrogen bonding has an important influence in controlling the physical and chemical properties of oxochromate(V) complexes. Similar ENDOR studies are planned on the oxochromate complexes in the near future.

Solvent Dependence of the EPR Parameters of III and IV. The results reported here, along with the characterization of the five- and six-coordinate forms of bis(oxalato(2−))oxochromate(V), III and IV, respectively,[16-19] have also led to a reassessment of the solvent dependence of the EPR spectra from the reactions of Cr(VI), $Na_3Cr^VO_4$, or $[CrOCl_4]^-$ with oxalic acid.[7] The g_{iso} values and a reassignment of the structures to which they correspond are given in Table II (for Cr(VI) and $[CrO_4]^{2-}$) and Table III (for $[CrOCl_4]^-$). Unfortunately, the solvent dependences of the A_{iso} values were not reported in the paper by Russev et al.[7] However, the solvent dependence of I and the assignment of the structures of III and IV in water[14,17] enable structural assignments of the oxalato complexes in nonaqueous solvents.

In aqueous solutions, the complexes that give rise to signals with g values of 1.9761 (6) and 1.8708 (6) have been reassigned as III and IV, respectively.[14,17,18] In acetic acid containing acetic anhydride, the signal due to IV disappears completely, since there is no water to fill the vacant sixth coordination site.[14,17,18] Such behavior has been known for some time, but the oxalato complexes were incorrectly characterized as monochelate complexes.[26] The g_{iso} and A_{iso} values of the signal attributed to III are typical of five-coordinate oxochromate(V) complexes and not six-coordinate complexes.[6,14,17] In addition, the signal due to IV splits in two at higher pH values, consistent with a deprotonation of the aqua ligand;[14] i.e. the signal observed at $g = 1.9708$ (6) by Russev et al.[7] is due to complex IV with the sixth ligand being OH^-. By contrast, the signal due to III is unaffected by pH, which is consistent with the absence of acidic protons.[14] Finally, the positions of the g_{iso} values and the magnitude of the A_{iso} values are consistent with an empirical model for calculating these parameters.[6] Therefore, it is clear that the assignments given previously[7] (i.e. structure VIII for the signal at $g_{iso} = 1.9761$ (6), structure IX or III for the signal at $g_{iso} = 1.9708$ (6), and structure VII for the signal at $g_{iso} = 1.9702$ (6)) are incorrect. A further objection to structures VIII and IX is that protonations of the coordinated carboxylate groups are expected to be difficult, since protonation of $[Cr(ehba)_2O]^-$ at the much more basic alcoholate group only occurs in acidic solutions. Further, oxalate complexes



VIII



IX

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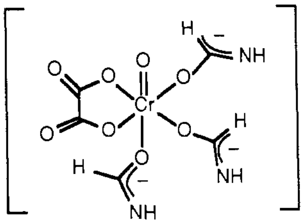
of metal ions in lower oxidation states, where the ligands will be more basic, e.g. *cis*-$[Cr(ox)_2(OH_2)_2]^-$, protonate only in acid concentrations of ≥0.001 M, and protonation results in ligand dissociation.[27-30]

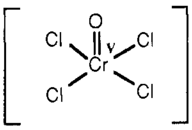
The reassignment of the structures of these complexes in water also enables the solvent dependence of the g_{iso} values to be understood. The first feature consistent with the structural assignments given in Table II is that complex IV is only observed in solvents which have moderate to high values of D_N or β,[7] where solvent coordination to a sixth site is most likely. Moreover, the proportion of IV with respect to III increases with increasing ability of the solvent to act as a ligand.[7] The g_{iso} values for structure III are relatively insensitive to solvent, like those of I, and are typical of those found for five-coordinate complexes.[6,14,17] The larger errors in the values of g_{iso} for III compared to I are probably the reason for a lack of a statistically significant correlation of this parameter with α. Similarly, the g_{iso} values of IV are typical of six-coordinate complexes over the range of the solvents.[6] The relative insensitivity of these values to the nature of the sixth ligand is explained by the other five donor atoms being the major factor in controlling the g_{iso} value, with only a minor contribution to the solvent, which is normally a weaker donor. The small effect that results from a large change in the donor ability of the sixth ligand is illustrated from the results in aqueous media where a change from OH_2 to OH^- as the sixth ligand only shifts the g_{iso} value by 0.0006 unit.[16] For g_{iso} values of IV, there are insufficient data points for which the appropriate solvent parameters are known to make meaningful correlations between these parameters.

Previously,[7] the third Cr(V) signals observed in H_2O (g_{iso} = 1.9702 (5)), hexamethylphosphoramide (HMPA, g_{iso} = 1.9688 (3)), and formamide (g_{iso} = 1.965) have been assigned to the pentakis(solvento)oxochromate(V) structure VII. It has been shown that the signal at g_{iso} = 1.9702 (5) in water is most likely due to IV. Formamide, like water, can readily deprotonate when coordinated, but the difference in g_{iso} values of 0.005 between IV and a potential deprotonated complex appears to be too large in comparison to the shifts observed on deprotonation of the aqua ligand in water. It is also unlikely that the bis chelates III and IV would exist in solution with VII without the monochelate complex X being present as a significant component of the Cr(V) complexes. The g_{iso} values reported[7] are consistent with either formulation, but structure X is assigned as being most likely for this complex by analogy with the chemistry of I. This also brings into question the assignment of structure VII as being due to the extra signal in HMPA. The stronger donor abilities of HMPA and formamide as compared with the other solvents are consistent with their abilities to produce significant amounts of the monochelate complexes. The g_{iso} values of VII and X would not be expected to be very different, and a more definitive assignment will be aided by an examination of the A_{iso} values.

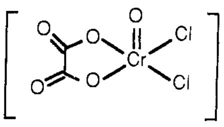


X

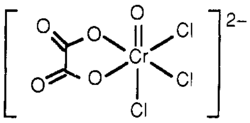
The reassignment of the structures of the Cr(V) complexes produced in the reaction of Cr(VI) or $[CrO_4]^{3-}$ with oxalic acid also rationalizes the chemistry of $[CrOCl_4]^-$ (XI) with oxalic acid in the same solvents;[7] i.e., some complexes are common to all three reactions (Tables II and III). The *g* values of the new complex assigned to structure XII are intermediate between those of III and XI (*g* = 1.988) and typical of those expected for the five-coordinate complex.[31,32] The assignment of structure XIII to the remaining *g* value is not as definitive and requires further study.



XI



XII



XIII

An important factor in the observation of six-coordinate complexes in the bis(oxalato) system is that there are more favorable steric interactions than is the case for I. However, this does not appear to be the only factor, since EPR spectroscopic evidence suggests that the bis(ethanediolato(2−))oxochromate(V) complex, VI, also remains five-coordinate in solvents that are strong donors. This complex can easily accommodate a six-coordinate structure, but apparently the donor strength of the chelate also plays a significant role in the control of the coordination number of the complex.

Conclusions

The analysis of the solvent effects on the EPR spectra of Cr(V) complexes (in particular, A_{iso} values due to ^{53}Cr hyperfine coupling) is a useful tool in delineating the structures of Cr(V) complexes in solution. The analysis described in this paper may enable the structures of other Cr(V) complexes in solution to be assigned.

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