

EPR and ^1H ENDOR Study of the Solution Equilibria of Bis(2-ethyl-2-hydroxybutanoato(2-))oxochromate(V) and Bis(2-hydroxy-2-methylbutanoato(2-))oxochromate(V)

Mario Branca,^{1a} Alessandro Dessi,^{1b} Giovanni Micera,^{*,1a} and Daniele Sanna^{1a}

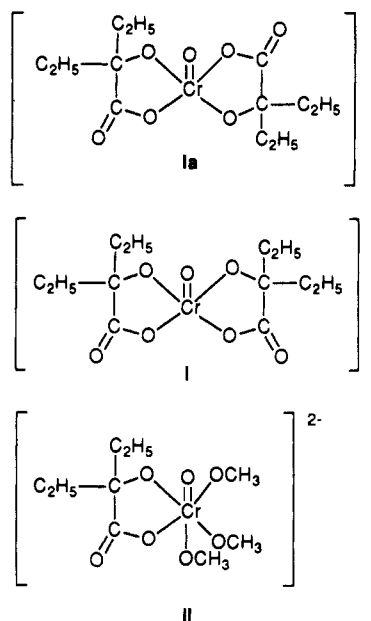
Department of Chemistry, University of Sassari, and Istituto per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, CNR, Via Vienna 2, 07100 Sassari, Italy

Received June 26, 1992

The behavior of the bischelated oxochromium(V) complex of 2-ethyl-2-hydroxybutanoate(2-) and its 2-hydroxy-2-methylbutanoate(2-) analogue has been reexamined by EPR and ^1H ENDOR spectroscopy in a range of solvents. It has been confirmed that the complexes rearrange in solution to yield two species which are in equilibrium, the kinetics of the process being dependent on the nature of the solvent. The results rule out that such a rearrangement is due to an acid-base process involving the alcoholic group of one of the ligands and suggest that the two species are the cis and trans isomeric forms of the bischelated complex, both exhibiting a distorted five-coordinate geometry.

Introduction

α -Hydroxy carboxylic acids can stabilize the rather unusual Cr(V) oxidation state even in aqueous solution.²⁻⁹ The first compounds of this type, the chelated Cr(V) complex *trans*-bis(2-ethyl-2-hydroxybutanoato(2-))oxochromate(V), here abbreviated as $[\text{CrO}(\text{ehba})_2]^-$ (I), and its analogue with the 2-hydroxy-



2-methylbutanoato ligand (hmba), were reported by Krumpolc and Rocek.³ As shown by X-ray analysis, in these complexes the metal ion binds the alcoholate and carboxylate groups of two ligands, the resulting stereochemistry at chromium(V) being

intermediate between the square pyramid and the trigonal bipyramid.^{3,4}

Further studies suggested that in aqueous solution, upon addition of excess ligand, the ehba complex equilibrates to form a mixture of $[\text{CrO}(\text{ehba})_2]^-$ and $[\text{CrO}(\text{ehba})_2(\text{Hehba})]^{2-}$, the latter form involving a third ligand molecule deprotonated only at the carboxyl group and apically bound to the metal ion.^{5,6} However, other papers rejected this interpretation.⁷⁻⁹

Recently, a paper described the behavior of the ehba complex in a variety of solvents as a function of the solution composition, namely ligand excess, added base, etc., as studied by isotropic EPR spectroscopy.⁸ It was found that two species were always in equilibrium. In nonprotic solvents, the ratio between the two species was affected by the addition of base and a protonation equilibrium was invoked. Therefore, one of the species was assigned as the parent bischelated complex (I) and the other one as the corresponding species protonated at the alcoholic group of a ligand molecule (Ia). On the other hand, the same findings in protic solvents were interpreted as being suggestive of an equilibrium between different five-coordinate stereochemistries for I. Being interested in this field, we have also investigated the chemistry of these complex systems in solution using EPR and ^1H ENDOR spectroscopy and report here additional data that could be of help in the assignment of the complexed species.

Experimental Section

$\text{Na}[\text{CrO}(\text{ehba})_2]\cdot\text{H}_2\text{O}$ and $\text{Na}[\text{CrO}(\text{hmba})_2]$ were synthesized from 2-ethyl-2-hydroxybutanoic and 2-hydroxy-2-methylbutanoic acids (Aldrich) and sodium dichromate in acetone according to literature methods.² ^{53}Cr -enriched $\text{K}_2\text{Cr}_2\text{O}_7$ was prepared from a CrO_3 sample (Icon) with the following isotopic composition: ^{53}Cr , 98.23%; ^{52}Cr , 1.77%. EPR spectra were recorded on a Varian E9 or a Bruker 220D instruments operating at the X-band frequency. ^1H ENDOR measurements were carried out with a Bruker ENDOR accessory, as described previously,^{10,11} using the following instrumental settings: microwave frequency power, 60 mW; radio-frequency power, 100 W at 14 MHz; FM modulation depth, 100 kHz.

Results

The isotropic EPR spectra of $\text{Na}[\text{CrO}(\text{ehba})_2]\cdot\text{H}_2\text{O}$ recorded at room temperature in methanol or ethanol solution were in good agreement with the results reported by Bramley et al.⁸ Two

- (1) (a) University of Sassari. (b) CNR.
- (2) Krumpolc, M.; DeBoer, B. G.; Rocek, J. *J. Am. Chem. Soc.* **1978**, *100*, 145.
- (3) Krumpolc, M.; Rocek, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.
- (4) Judd, R. J.; Hambley, T. W.; Lay, P. A. *J. Chem. Soc., Dalton Trans.* **1989**, 2205.
- (5) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.
- (6) Easom, K. A.; Bose, R. N. *Inorg. Chem.* **1988**, *27*, 2331.
- (7) Krumpolc, M.; Rocek, J. *Inorg. Chem.* **1985**, *24*, 617.
- (8) Bramley, R.; Ji, J.-Y.; Judd, R. J.; Lay, P. A. *Inorg. Chem.* **1990**, *29*, 3089.
- (9) Bramley, R.; Ji, J.-Y.; Lay, P. A. *Inorg. Chem.* **1991**, *30*, 1557.

- (10) Branca, M.; Micera, G.; Dessi, A. *J. Chem. Soc., Dalton Trans.* **1990**, 457.
- (11) Branca, M.; Micera, G.; Segre, U.; Dessi, A. *Inorg. Chem.* **1992**, *31*, 2404.

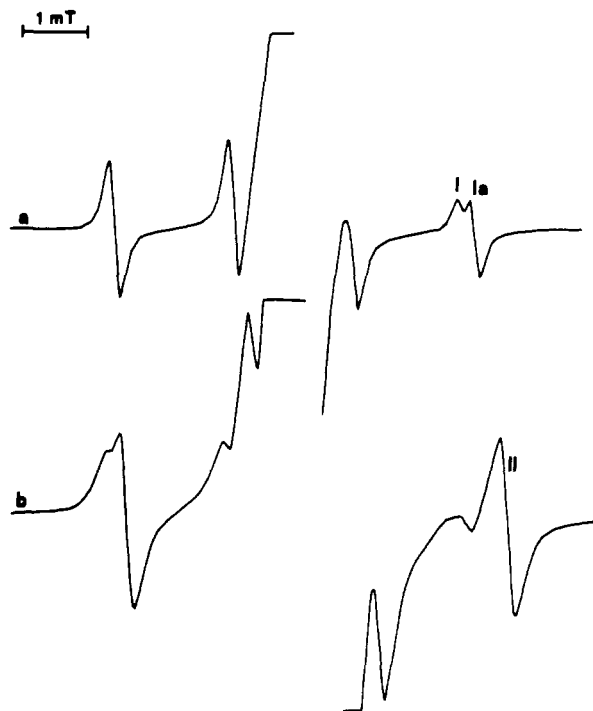


Figure 1. X-Band EPR spectra recorded at 298 K in CH₃OH: (a) Na[CrO(ehba)₂] \cdot H₂O (4×10^{-3} M); (b) Na[CrO(ehba)₂] \cdot H₂O (4×10^{-3} M) in the presence of 4×10^{-3} M CH₃O⁻.

sets of ⁵³Cr ($I = 3/2$; 9.50%) hyperfine couplings, indicating the equilibrium between two complexes were detected (Figure 1a). The minor species I exhibited $g_0 = 1.978$ and $A_0 = 16.5 \times 10^{-4}$ cm⁻¹, whereas the outer multiplet of resonances was characterized by a higher coupling constant ($g_0 = 1.978$ and $A_0 = 17.0 \times 10^{-4}$ cm⁻¹) (Ia). The addition of ligand, up to a 100-fold molar excess with respect to the metal, did not affect significantly the relative intensity of the two sets of ⁵³Cr satellites and caused only some broadening of the hyperfine lines without loss of resolution. Analogously, the addition of either bases (CH₃O⁻, *t*-BuO⁻, and NEt₃) or acids (CH₃COOH) produced minor spectral changes.

For a solution of Na[CrO(ehba)₂] \cdot H₂O in CD₃OD, it was found that Ia was the only EPR-detectable species in freshly prepared solutions and then it equilibrated with I, yielding a distribution identical to that in CH₃OH. The equilibrium was reached after ca. 10 min at 298 K, but as the temperature was diminished, the rate of interconversion also diminished.

A further species (II) was found in a dilute methanolic solution of Na[CrO(ehba)₂] \cdot H₂O (Figure 1b). This complex, which was the only EPR-detectable species at a metal concentration as low as 1×10^{-4} M, was favored by the addition of bases. Compared to I and Ia, complex II exhibited g_0 and A_0 values (1.975 and 18.1×10^{-4} cm⁻¹, respectively) that were in good agreement with those for the species assigned previously as a monochelated complex of chromium(V) bound, besides to a bidentate ehba anion, to methoxide ligands.⁸

Solutions of Na[CrO(ehba)₂] \cdot H₂O in nonprotic solvents (acetone, acetonitrile, dichloromethane, and dimethyl sulfoxide) showed a behavior that was somewhat different from that reported by Bramley et al.⁸ These authors observed a mixture of I and Ia on dissolving a compound described as a partially protonated form of [CrO(ehba)₂]⁻. In our case, only Ia was obtained immediately after dissolving Na[CrO(ehba)₂] \cdot H₂O, whereas I was slowly formed with elapsing time. Analogously to Bramley, we also observed that the addition of bases (NEt₃, CH₃O⁻, or *t*-BuO⁻) resulted in the growth of the EPR signals of I. However, exactly the same spectral changes were obtained on adding acids, e.g. CH₃COOH.

When the formation of Cr(V) by reaction of potassium dichromate with 2-ethyl-2-hydroxybutanoic acid was followed

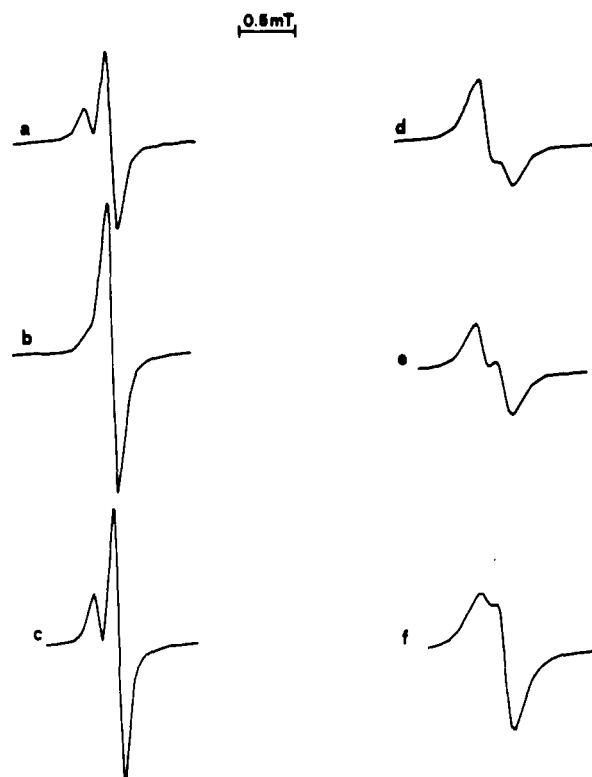


Figure 2. $M_1 = -3/2$ ⁵³Cr hf components of X-band isotropic EPR spectra: Na[CrO(ehba)₂] \cdot H₂O, 2.2×10^{-3} M in H₂O, pH 3.9, in the presence of a 100-fold excess of ligand (a); Na[CrO(ehba)₂] \cdot H₂O, 4×10^{-3} M in DMSO, immediately after dissolution (b) and after a 300-min interval (c); a solution of 1×10^{-3} M K₂⁵³Cr₂O₇ and 3×10^{-3} M ehba in CD₃OD irradiated with 258-nm light for 0.5 min at 180 K and left standing for 20 min at 240 K (d) and then brought to 298 K (e); the same solution after equilibrium was reached (20 min at 240 K + 20 min at 298 K) (f). Spectra were recorded at 298 K except (d), which was obtained at 240 K.

directly in either protic (CH₃OH, CD₃OD, C₂H₅OH) or nonprotic solvents, an equilibrium between I and Ia was again detected with relative populations comparable to those observed on dissolving the solid complex. However, the exposure of the solutions to UV radiation (258 nm) remarkably increased the amount of I relative to Ia; that is, the minor component became the major one (Figure 2) and the equilibrium between the two complexes was reestablished only after elapsing time. Moreover, the interconversion of I to Ia was very slow at low temperature; e.g., the extent of the transformation was almost negligible within a 40-min interval at 200 K, contrary to the expectation for a normal acid-base process. In contrast, no effect on the species distribution was observed on cooling a solution after the equilibrium had been reached. Moreover, the distribution in solutions of Na[CrO(ehba)₂] \cdot H₂O was not changed by the exposure to UV radiation, indicating that the light absorption had an effect only on the formation rate of the Cr(V) complexes.

Finally, the Cr(V) complexes I and Ia were examined in aqueous solutions of Na[CrO(ehba)₂] \cdot H₂O. Both the species, Ia with a higher proportion than in methanol or DMSO solutions, were found in water. Because no significant pH dependence of the equilibrium distribution was observed over the range pH 2–10, as noticed also elsewhere,¹² the existence of a deprotonation equilibrium may be ruled out. In comparison, both 1:1 and 1:2 complexes have been observed by potentiometric and spectroscopic techniques in the aqueous V^{IV}O-ehba system, the formation of the bischelated species with the fully deprotonated ligand being almost complete above pH 7.¹³ Since ligand deprotonation should

(12) Farrell, R. P.; Lay, P. A. *Comments Inorg. Chem.* **1992**, *13*, 133.

(13) Kiss, T.; Buglyó, P.; Micera, G.; Dessì, A.; Sanna, D. Unpublished results. For related systems, see ref 14.

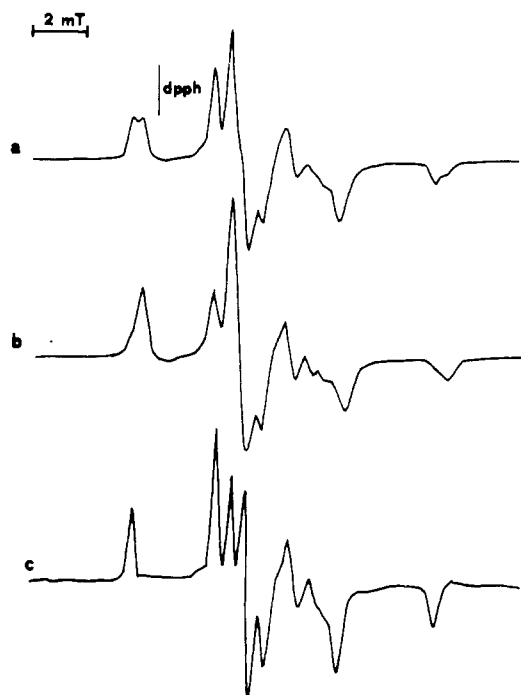


Figure 3. X-Band EPR spectrum recorded at 110 K for a solution of 1×10^{-3} M $K_2^{53}Cr_2O_7$ and 3×10^{-3} M ehba in CD_3OD irradiated with 258-nm light for 0.5 min at 110 K (a). Individual spectra of Ia (b) and I (c) were obtained by computer subtraction.

be more favorable with oxochromium(V) than with oxovanadium(IV), it is unlikely that in the present case the two EPR signals may be associated with an acid–base equilibrium.

No evidence for a type-II complex, with a 1:1 ligand-to-metal ratio, was obtained by diluting the aqueous solution and adding NaOH. Indeed, the EPR signals of I and Ia vanished almost completely on increasing the pH above 10. The resonances appeared again, although with diminished intensity due to Cr(V) decay, upon addition of acid, substantiating a completely reversible process, at least for unreacted Cr(V). This behavior is consistent with the formation of a dimeric 1:1 Cr(V) complex.¹² Most likely, its structure is similar to that of the EPR-silent complex formed by the perfluoropinacolate(2-) ligand, where two oxo groups act as bridges between two oxochromium(V) ions.¹⁵

The results obtained for the Cr(V) complex of 2-hydroxy-2-methylbutanoate, which differs from ehba in having a methyl in the place of one of the ethyl groups, were precisely analogous to those for the Cr(V)–ehba system.

The anisotropic EPR spectra for a frozen methanolic solution of I and Ia formed by reaction of ^{53}Cr -enriched dichromate with the ligand are shown in Figure 3. The individual spectra of the species, obtained by computer subtraction, exhibit a rhombic anisotropy, as expected for a strongly distorted geometry at the metal ion, and the following parameters have been obtained for the g and $A(^{53}Cr)$ values. I: $g_1 = 1.975$, $g_2 = 1.975$, $g_3 = 1.987$, $A_1 = 35.7 \times 10^{-4} \text{ cm}^{-1}$, $A_2 = 4.6 \times 10^{-4} \text{ cm}^{-1}$, $A_3 = 9.3 \times 10^{-4} \text{ cm}^{-1}$. Ia: $g_1 = 1.973$, $g_2 = 1.976$, $g_3 = 1.986$, $A_1 = 35.9 \times 10^{-4} \text{ cm}^{-1}$, $A_2 = 8.6 \times 10^{-4} \text{ cm}^{-1}$, $A_3 = 6.0 \times 10^{-4} \text{ cm}^{-1}$. The corresponding parameters for II are $g_1 = 1.969$, $g_2 = 1.975$, $g_3 = 1.983$, and $A_1 = 38.3 \times 10^{-4} \text{ cm}^{-1}$ (A_2 and A_3 not resolved).

1H ENDOR spectroscopy has been used to measure hyperfine proton couplings which are not resolved in EPR spectra. Unidirectional ENDOR observation is possible by selection of the magnetic fields corresponding to the directions of the A_C principal values. However, due to the overlap of the hyperfine structure in the middle part of the spectrum, only the external

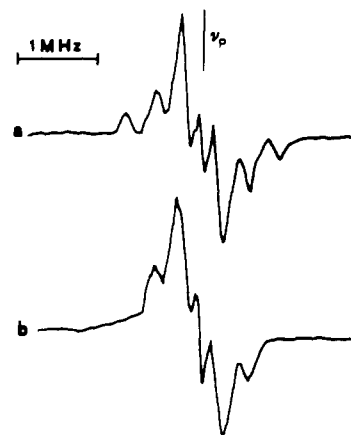


Figure 4. 1H ENDOR spectra recorded at 110 K for solutions of 1×10^{-3} M $K_2^{53}Cr_2O_7$ and 3×10^{-3} M ehba in CH_3OH (a) and CH_3OD (b) after irradiation with 258-nm light for 0.5 min at 110 K. The observing magnetic field was set on the $M_1 = 3/2$ component(s) of the EPR spectra of I and Ia; ν_p indicates the free-proton frequency value (~ 14 MHz).

$M_1 = \pm 3/2$ components of the largest ^{53}Cr coupling can yield a crystal-like ENDOR spectrum, and by analogy with other complexes of Cr(V) and related d^1 ions, e.g. V^{IV} ,^{16–18} the observing direction may be assumed to be the Cr=O axis. The strongest 1H ENDOR couplings recorded in CH_3OH by setting the magnetic field on the $M_1 = +3/2$ turning point exhibit absolute magnitudes of 2.51 and 3.76 MHz (Figure 4). The first is not affected by deuteration, whereas the second disappears in CD_3OD and CH_3OD but is still observed in CD_3OH . On this basis, the 2.51-MHz splitting is likely due to the ligand protons and that of 3.76 MHz to the alcoholic proton of methanol. The latter proton shows tensor anisotropy typical of a nucleus located approximately along the Cr=O direction. By neglecting the isotropic contribution to the coupling constant, which is expected to be small for the nucleus of an outer-sphere molecule, one can estimate a distance of ca. 0.40 nm from the metal for this proton with the point-dipole approximation, which has been shown to be valid for d^1 ions and distant interacting nuclei.^{10,11,19,20} This finding suggests that the solvent molecule is hydrogen-bonded through the hydroxyl group to the oxo ligand of chromium; cf. the distance of 0.34 nm estimated by proton ENDOR for a similar proton bound to V^{IV} .²⁰ Since no difference is observed by varying the I-to-Ia ratio in solution and sweeping the magnetic field setting on either of the $M_1 = 3/2$ components, it is likely that these ENDOR features are common to both species I and Ia.

The 1H ENDOR features of the monochelated species II (^{53}Cr -enriched samples) in methanolic solution are remarkably different compared to those of the bischelated complexes. First of all, since no exchangeable, i.e. hydroxyl, proton lying at a measurable distance from the metal is detected, the presence of coordinated or hydrogen-bonded CH_3OH molecules may be ruled out. However, analysis of the spectra indicates two types of methyl protons, located approximately in equatorial and axial positions, as suggested by splittings of 3.36 and 2.60 MHz recorded for the field alignment perpendicular (g_2 and g_3) or parallel (g_1 and A_1) to the Cr=O direction, respectively. The ENDOR-determined metal–proton distances, about 0.36 and 0.39 nm for equatorial and axial protons, respectively, suggest that both of them belong to methoxide ligands bound to chromium. On the whole, the results make acceptable Bramley's hypothesis that the monochelated species II has three (two equatorial and one axial) methoxide groups bound to the metal ion (see structure II).

(16) Derouane, E. G.; Ouhadi, T. *Chem. Phys. Lett.* **1975**, *31*, 70.

(17) Winscom, C. J. *Mol. Phys.* **1974**, *28*, 1579.

(18) Kon, H.; Sharpless, N. E. *J. Chem. Phys.* **1965**, *42*, 906.

(19) Atherton, N. M.; Shackleton, J. F. *Mol. Phys.* **1980**, *39*, 1471.

(20) Mustafi, D.; Makinen, M. V. *Inorg. Chem.* **1988**, *27*, 3360.

(14) Teixeira, M. H. S. F.; Costa Pessoa, J.; Vilas Boas, L. F. *Polyhedron* **1992**, *11*, 697.

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

Conclusions

In conclusion, the results of this study clearly rule out that two Cr(V)-ehba or -hmha species are formed stepwise in solution due to protonation-deprotonation equilibria involving the chelating ligand molecule. In such a case, opposite effects on the ratio of the species should be expected upon acid or base addition. The insensitivity of the spectral parameters of the species to the solution composition (solvent, added base, etc.) makes it also unlikely that the splitting of ESR signals reflects the formation of adducts with coordinating solvents.⁸

The kinetics of the $I \rightleftharpoons Ia$ interconversion are affected by the nature of the solvent, being quite rapid in protic solvents and remarkably slower in nonprotic media, where the process is accelerated, without any significant difference, by either acids or bases. The transformation of Ia, the species observed immediately after dissolving $Na[CrO(ehba)_2] \cdot H_2O$, to I is slower in CD_3OD than in CH_3OH , suggesting an isotopic effect. On the contrary, with irradiation of Cr(VI) in the presence of ligand, I seems to be favored over Ia.

Although definite evidence concerning the structures of I and Ia cannot be obtained, all the experimental data support the alternative hypothesis that, irrespective of the solvent, the two sets of EPR signals must be assigned to geometric isomers. As suggested by Bramley et al., several types of isomerism could be taken into account, e.g., in the limit of a regular geometry, those

involving an equilibrium between a square pyramidal and a trigonal bipyramidal complex or between two trigonal bipyramidal complexes. The major species Ia, which is the one existing in freshly prepared solutions of the crystals, is likely to have the same basic structure as that in the solid state, and thus it is assigned as the distorted five-coordinated species with two ligands coordinated in trans positions. On the basis of the minor differences in the EPR parameters for frozen solutions, it is rather unlikely that species I, which equilibrates with Ia as the result of a slow process, is a complex where the geometry is relaxed toward the square pyramid. Moreover, the presence of a solvent molecule, even loosely bound, in the sixth coordination position of chromium should be likely in methanol. Proton ENDOR spectra fail to give evidence for such a solvent molecule in spite of the fact that they distinguish the one bound to the oxo group. This finding may support Bramley's proposal that the unknown isomer also exhibits steric clashes so as to inhibit the approach of a sixth ligand to the metal, and this is in favor of a distorted five-coordinated structure. On this basis, all the results point to the conclusion that I is a cis isomer of Ia having a similar geometry at the metal ion.⁸

The formation of monochelated complexes of hexacoordinate Cr(V) has been confirmed by this study, which has also shown that oxo bridging may occur in such species to yield strong magnetic coupling between the metal ions.