For the Pt(tdach)(ecda) (**2c**) complex a different situation exists. While the emission band of Pt(tdach)(ecda) (**2c**) is broad and asymmetric, similar to that observed for the Pt(diimine)(ecda) systems, the absence of π^*(diimine) levels and a large blue shift in the emission maximum relative to the diimine analogues suggest a different orbital origin for its emission. The emission intensity for Pt(tdach)(ecda) (**2c**) also *increases* as the temperature is lowered, consistent with a single emitting state and contrasting with the behavior of the diimine analogues. Furthermore, the shape, energy, and temperature dependence of the emission are similar to those observed for PtL$_2$(ecda) complexes where L$_2$ is a chelating diolefin[35] or phosphine.[22] From the MO calculation of the similar complex Pt(en)(*i*-mnt), it is found that the LUMO possesses mainly dithiolate character and is significantly higher in energy than the diimine-based LUMO of Pt(bpy)(*i*-mnt). Thus, the lowest energy transition for *both* absorption and emission in Pt(tdach)(ecda) (**2c**) is assigned as a metal-to-dithiolate charge transfer, with emission coming from the triplet manifold.

Conclusions

Complexes of the type Pt(diimine)(dithiolate) exhibit both an intense solvatochromic absorption and an intense emission which are observed at room temperature in fluid solution. The solvatochromic absorption is present in Pt(diimine) systems containing saturated dithiolates but disappeares when the diimine is substituted by a saturated diamine. This transition is in all cases ascribed to a $\{d(Pt)/p(S)-\pi^*(\text{diimine})\}$ charge transfer. For all of the diimine complexes except those of mnt, the broad asymmetric emission is assigned as having the same orbital parentage as the solvatochromic absorption but arising from a state of different multiplicity—i.e., $^3\{d(Pt)/p(S)-\pi^*(\text{diimine})\}$. All of the mnt complexes exhibit emissions having similar types and degrees of structuring, leading to the conclusion that they possess a common emitting state. This state is assigned on the basis of systematic ligand variation and MO calculations as $^3\{d(Pt)/p(S)-\pi^*(\text{mnt})\}$.

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Registry No. **1a**, 126929-37-1; **1b**, 126929-39-3; **1c**, 138678-00-9; **2a**, 123623-04-1; **2b**, 123623-05-2; **2c**, 138623-24-2; **3a**, 138678-01-0; **3b**, 138623-25-3; **4a**, 138623-22-0; **4b**, 138623-26-4; **5**, 138623-27-5; **6**, 141249-58-3; **7**, 141249-59-4.

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Contribution from the Department of Chemistry, University of Sassari, Via Vienna 2, 07100 Sassari, Italy, Department of Physical Chemistry, University of Padua, Via Loredan 2, 35131 Padua, Italy, and Istituto per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, CNR, Via Vienna 2, 07100 Sassari, Italy

Structural Information on Chromium(V) Complexes of 1,2-Diols in Solution, As Determined by Isotropic and Anisotropic ^{1}H ENDOR Spectroscopy

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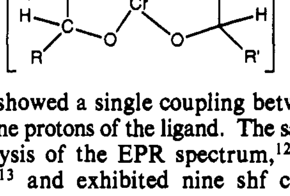
The ^{1}H ENDOR study of complexes formed by 1,2-diols, namely ethylene glycol, (*S*)-(+)-1,2-propanediol, and (2*R*,3*R*)-(−)-2,3-butanediol, has demonstrated the potential of this technique as a structural probe of Cr(V) complexes in solution. The spectra recorded in liquid CD$_3$OD solution demonstrate the ^{1}H superhyperfine (shf) interaction, which, except for the case of the glycolate complex, is not resolved in the EPR spectra. The comparative analysis provides unambiguous evidence for the presence of two classes of protons in the chelated ethylene bridge of the complexes. The analysis shows also that the single ^{1}H ENDOR coupling observed for the bis(ethylene glycolato(2−))oxochromate(V) complex is really an average signal due to a fast axial–equatorial interconversion. Crystallike ENDOR information has been obtained on the anisotropic spectra recorded in frozen solution by using both ^{52}Cr and ^{53}Cr isotopes. The complementary use of the isotropic and anisotropic couplings allow discrimination among all the protons of the ligands and calculation of their distances from the metal ion. The proton ENDOR analysis has been supported by a theoretical simulation of the spectra.

Introduction

Recently, attention has been paid to Cr(V) complexes of polyols or sugars, which are also stable in biological systems.[2-6] Unfortunately, only limited information can be obtained on these complexes by use of EPR spectroscopy. We have tested the usefulness of complementary ENDOR studies, which, as is well-known, can resolve hyperfine splittings not observable by EPR and thus provide information about the interaction between a paramagnetic center and the neighboring magnetic nuclei.[7-10]

The only ENDOR study so far published on Cr(V) complexes reports the isotropic spectrum of the bis(ethylene glycolato(2−))oxochromate(V) species **1**.[11] The spectrum, recorded above



(**1**) R = R' = H

(**2**) R = H; R' = Me

(**3**) R = R' = Me

180 K, showed a single coupling between the metal ion and the methylene protons of the ligand. The same conclusion was reached by analysis of the EPR spectrum,[12] which was also observed earlier[2,13] and exhibited nine shf components indicating the equivalence of the eight protons belonging to the two ligand molecules. Accordingly, almost coincident values were measured

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for the shf constant by two different techniques.

However, despite these results, the equivalence of the ethylene glycolate protons remained doubtful. In fact, accurate theoretical calculations performed by one of the above authors predicted the existence of at least two classes of protons.[12] Actually, also due to this nonequivalence, the ^{1}H shf structure is often unresolved in the EPR spectra of Cr(V) complexes of 1,2-diols.[2]

To solve this problem and to explore further the potential of the ^{1}H ENDOR approach to learning about the Cr(V) complexes in solution, we have undertaken a study on the Cr(V) complexes formed by ethylene glycol and two of its derivatives, namely (*S*)-(+)-1,2-propanediol (**2**) and (2*R*,3*R*)-(−)-2,3-butanediol (**3**).

We have made use of frozen and liquid solutions to measure both the anisotropic and isotropic proton couplings, so that we have been able to distinguish the ligand protons in the metal complexes. The analysis has been successfully supported by the theoretical simulation of the spectra.

Experimental Section

Materials and Instruments. The ligands ethylene glycol, (*S*)-(+)-1,2-propanediol, and (2*R*,3*R*)-(−)-2,3-butanediol were purchased from Aldrich. The Cr(V) complexes were prepared according to procedures reported in ref 11. Namely, K_2CrO_4 and an excess of ligand were dissolved in CD_3OD solution using quartz cells sealed under vacuum and stored in the dark. ^{53}Cr-enriched K_2CrO_4 was prepared from a CrO_3 sample (Icon) having the following isotopic composition: ^{53}Cr, 98.23%; ^{52}Cr, 1.77%. EPR spectra were recorded on a Bruker 220 D instrument operating at the X-band frequency. ^{1}H ENDOR measurements were carried out as described previously[14,15] using the following instrumental settings: microwave frequency power, 60 mW; radiofrequency power, 100 W at 14 MHz; FM modulation depth, 100 kHz.

Simulation of ^{1}H ENDOR Spectra. In the following we outline the methods we used to compute the EPR of ENDOR spectra for a metal complex with $S = {}^1/_2$ in frozen solution. The spin Hamiltonian for this system is written as the sum of the electron Zeeman interaction (Z) and the metal nucleus (M) and ligand protons (L) terms

$$H = H_Z + H_M + H_L$$

with

$$H_Z = \beta_e \mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B}_0 \tag{1}$$

$$H_M = \mathbf{S}\cdot\mathbf{A}_M\cdot\mathbf{I}_M + \mathbf{I}_M\cdot\mathbf{Q}\cdot\mathbf{I}_M$$

$$H_L = \sum_i^{L}(-\beta_H g_H \mathbf{B}_0 I_{iz} + \mathbf{S}\cdot\mathbf{A}_{Hi}\cdot\mathbf{I}_i)$$

where $\mathbf{A}_M$ and $\mathbf{Q}$ are the hyperfine (hf) and the quadrupole coupling tensors of the metal nucleus and $\mathbf{A}_{Hi}$ are the superhyperfine (shf) coupling tensors of the L ligand protons. As is usual, the Zeeman interaction of the metal nucleus has been neglected in H_M. The Zeeman and metal interactions are the principal parts of the spin Hamiltonian, while the proton interactions are usually at least 1 order of magnitude smaller. In general, the proton shf tensors are not diagonal in the reference frame which diagonalizes the $\mathbf{g}$ and $\mathbf{A}_M$ tensors.

The procedure for simulating ENDOR spectra has been described previously.[16,17] Since the method must account for the capability of ENDOR spectroscopy for selection of different orientations by varying the intensity of the magnetic field $\mathbf{B}_0$,[18,19] the following algorithm has been devised:

(i) A grid of molecular orientation is chosen, the orientations being identified by the cosine directors of $\mathbf{B}_0$ in the molecular reference frame.

(ii) At each orientation, the values of the EPR resonance fields are computed by solving the eigenvalue equation for the Hamiltonian (1) by a perturbative technique. The contribution of the metal interaction is treated up to second order in the perturbative expansion, while only first-order corrections from the ligand protons are considered. The difference between the intensity of the applied magnetic field $\mathbf{B}_0$ and the resonance fields for the electron spin $B_r(\theta, \phi)$ determines the weight of the orientation in the buildup of the spectrum:

$$P(\theta, \phi) = \sum_M g(B_0 - B_r^{(M)}(\theta, \phi))$$

Here the summation is over all the hf components of the EPR spectrum. We assume for the functions $g(\delta)$ a Gaussian form:

$$g(\delta) = \sqrt{(^1/_2\pi\sigma^2)e^{-\delta^2/2\sigma^2}}$$

Here σ is an adjustable parameter, which usually is of the order of magnitude of the line width of the EPR spectrum. The greater the distance between the values of the applied and of the resonant fields, the smaller is the weight of the orientation. The proton ENDOR spectrum is also computed at each orientation.

(iii) Finally, the total ENDOR spectrum is given by the weighted sum of the spectra computed at all the orientations.

This algorithm is quite efficient in the computation of frozen matrix spectra, and it accommodates different cases, such as organic free radicals or transition metal complexes, with or without axial symmetry, since it does not rely on the attempt to obtain an analytic expression for the line shape (see ref 20).

To simulate the ENDOR spectra, first an estimate of the proton shf principal values is obtained from the positions of the lines of the experimental spectrum and from the coupling constants which have been measured in solution. Then the theoretical line shape is computed by the method described previously. The σ parameter and principal values and cosine directors of proton tensors $\mathbf{A}_{Hi}$ are adjusted repeatedly until we obtain visual concordance with the experimental spectrum.

Results and Discussion

Isotropic Spectra. The EPR spectra of all the samples, recorded at 200 K in CD_3OD liquid solution with the natural-abundance isotope mixture of Cr (^{52}Cr, 90%, $I = 0$; ^{53}Cr, 10%, $I = {}^3/_2$), exhibit g_0 = 1.9803 (**1**), 1.9799 (**2**), and 1.9798 (**3**) and $A_0(^{53}\text{Cr})$ = 49.86 MHz. However, only for **1** the shf interaction between the paramagnetic metal ion and the ligand protons, $(A_H)_i$ = 1.79 MHz, as confirmed by simulation, is resolved by EPR spectroscopy; see Figure 1a.

The ^{1}H ENDOR spectra recorded at the same temperature (Figure 2) are more revealing because for all complexes they clearly resolve distinct couplings for the different protons. Two coupling constants $(A_H)_i$ = 0.40 and 1.16 MHz are observed for **3**. The finding is consistent with the presence of two classes of nonequivalent protons. The smaller coupling is attributed to the hydrogens of the methyl groups, as expected for a mechanism arising predominantly through atom-to-atom spin polarization.[12] On the other hand, the larger coupling constant derives from the methine protons.

Complex **2** exhibits three proton couplings. The coupling $(A_H)_i$ = 0.40 MHz is the same as that found for **3** and is again attributed to methyl protons. The observation of the couplings of 1.25 and 2.45 MHz indicates that the remaining protons are nonequivalent. Actually, nonequivalent quasi-axial and quasi-equatorial protons are expected in the puckered five-membered chelated ring. This magnetic nonequivalence has been often distinguished in the ethylene bridge of chelated ligands, e.g. *N*,*N*′-ethylenebis(salicylideneaminato) and *N*,*N*′-ethylenebis(acetylacetonatiminato), by solid-state ^{1}H ENDOR studies[21,22] and predicted by theoretical calculations.[12]

An examination of the splitting constants shows that the single coupling for the ethylene glycolate complex, $(A_H)_i$ = 1.79 MHz, is nearly the average of those observed for **2**. This allows us to conclude that two classes of protons exist in the complex **1**, i.e. axial and equatorial, but their interconversion is rather fast at a temperature as high as 200 K. As a consequence, the weighted average of the individual couplings is measured for the protons. In contrast, the presence of the methyl substituents in **2** makes the interconversion sufficiently slow that magnetically different protons may be observed at the same temperature. Since two

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Table I. ESR and ^{1}H ENDOR Parameters of Cr(V) Complexes[a]

complex	g_1, g_2, g_3	$A^1_{Cr}, A^2_{Cr}, A^3_{Cr}$	protons	$(A_H)_i$	$(A^x_H)_a, (A^y_H)_a, (A^z_H)_a$	angle,[b] deg
1	1.9840, 1.9800, 1.9770	20.2, 105.2, 24.2	ax	−1.21[c]	−2.24, −2.24, +4.48	90 ± 13
			eq	−2.45[c]	−2.16, −2.16, +4.33	90 ± 7
2	1.9836, 1.9796, 1.9766	20.2, 105.2, 24.2	ax	−1.21	−2.24, −2.24, +4.48	90 ± 13
			eq	−2.45	−2.16, −2.16, +4.33	90 ± 7
			methyl	+0.33	−0.77, −0.77, +1.50	90 ± 7
3	1.9836, 1.9796, 1.9761	20.2, 105.2, 24.2	ax	−1.21	−2.24, −2.24, +4.48	90 ± 13
			methyl	+0.33	−0.77, −0.77, +1.50	90 ± 7

[a] The g values refer to both ^{52}Cr and ^{53}Cr isotopes; the A_{Cr} values refer to ^{53}Cr. All the A values are in MHz. [b] Angle between the g_2 or A^2_{Cr} axis and the A^z_H axis. [c] Average value: −1.79 MHz.

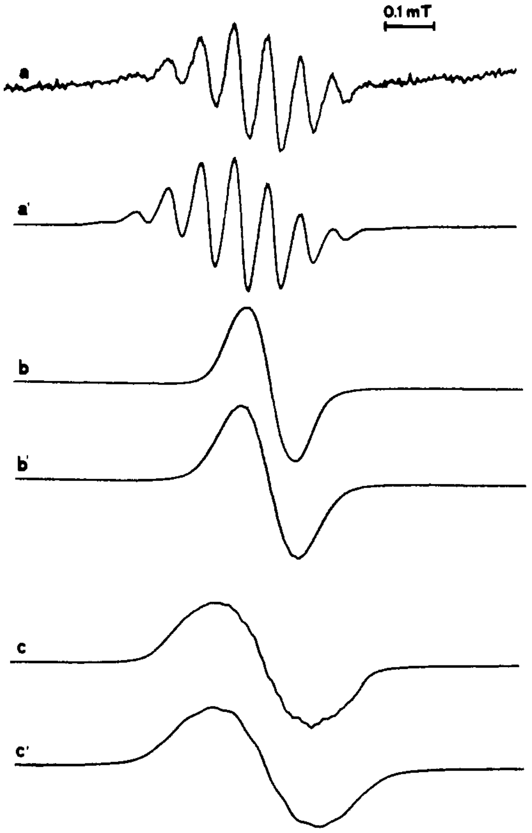

Figure 1. Experimental and simulated (primed) isotropic EPR spectra in CD$_3$OD at 200 K: **1** (a); **3** (b); **2** (c). Spectra a'–c' are simulations obtained by using the following parameters: g_0 = 1.9803, $(A_H)_i$ = 1.79 MHz (a'); g_0 = 1.9798, $(A_H)_i$ = 1.16 MHz, $(A_H')_i$ = 0.40 MHz (b'); g_0 = 1.9799, $(A_H)_i$ = 1.25 MHz, $(A_H')_i$ = 0.40 MHz, $(A_H'')_i$ = 2.45 MHz (c') (See text.)

couplings are detected for complex **3**, it is also inferred that the methyl groups are replacing only a class of the ethylene glycolate protons, most likely the equatorial ones, as is the case of cyclohexanes, and the ring conformation is blocked.

Supporting evidence for the above assignments is given by the computer simulation of the EPR spectra, which obviously should contain all the ^{1}H shf splittings measured by ENDOR. As can be seen in Figure 1b', the line width of the experimental spectrum of **3** is reproduced well by using the coupling constants of 1.16 and 0.40 MHz and assuming a multiplicity of four (methine) and twelve (methyl) protons, respectively. The spectrum of **2** may be interpreted only by attributing the couplings of 1.25, 2.45, and 0.40 MHz to three sets of four, two, and six protons, respectively (Figure 1c). Therefore, the ENDOR-based assignments are also concordant with the results of the EPR measurements.

Anisotropic Spectra. On the cooling of samples to 110 K, anisotropic EPR spectra are observed in CD$_3$OD frozen solution. It is known that in favorable cases, e.g. where there is a large anisotropy of metal g or A tensors, the appropriate selection of the magnetic field for ^{1}H ENDOR observation can allow detection of the proton–metal magnetic interaction along the molecular directions corresponding to the principal values of these tensors.[17–20] EPR spectra indicating a rhombic distortion are observed for ^{52}Cr samples (Figure 3 and Table I). ^{1}H ENDOR measurements have been taken at different points across the EPR spectra. However, because of the small anisotropy of the **g** tensor and the impossibility of an unambiguous assignment of its orientation, a precise evaluation of the ^{1}H shf tensor components based only on the ^{52}Cr EPR resonances is a rather difficult task. The use of ^{53}Cr-enriched samples allows detection of metal hf components well separated from each other in the EPR spectra and also permits selection of the Cr hf axis system for ^{1}H ENDOR observation.

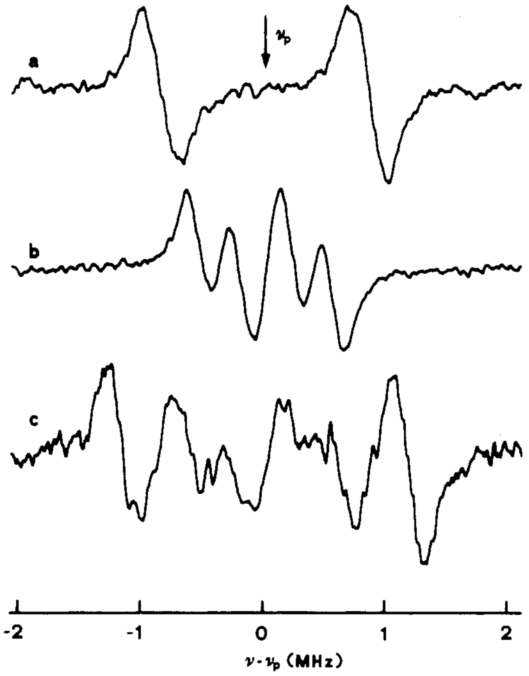

Figure 2. ^{1}H ENDOR isotropic spectra of (a) **1**, (b) **3**, and (c) **2** in CD$_3$OD at 200 K. ν_p indicates the free-proton frequency value (~14 MHz).

The EPR spectra of ^{53}Cr-enriched samples are shown in Figure 3. A computer simulation allowed evaluation the respective parameters and indicated that a rhombic $\mathbf{A}_{Cr}$ anisotropy must be also taken into account (Table I). However, since this is small, the complex can be considered as almost axial. Accordingly, the larger $\mathbf{A}_{Cr}$ principal value (A^2_{Cr}), and the corresponding g_2 component, can be assumed as directed along the tetragonal Cr═O axis and the smaller ones A^1_{Cr} (g_1) and A^3_{Cr} (g_3) in the metal plane, as is the case of complexes of Cr(V)[2,12,23] and analogous d^1 ions, e.g. V^{IV}O.

The comparison of the ^{1}H ENDOR spectra obtained on ^{53}Cr and ^{52}Cr samples (Figures 4–7) permits extraction of information about (i) the mutual orientation of the $\mathbf{A}_{Cr}$ and **g** reference systems and (ii) the selectivity of the ^{1}H ENDOR observation along the different molecular directions. Examination of the spectral patterns shows that, to a reasonable approximation, the two

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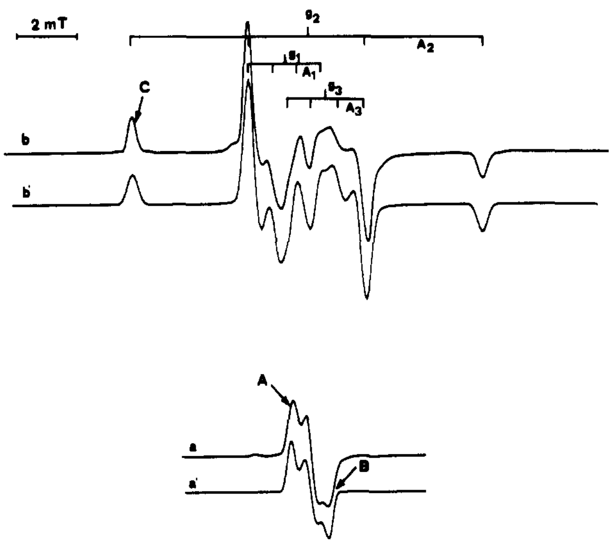

Figure 3. Experimental (a and b) and simulated (a′ and b′) frozen-solution EPR spectra of complex **3** with natural Cr (a and a′) or ^{53}Cr-enriched (b and b′) isotopic composition in CD_3OD at 110 K. The points marked by A–C indicate the magnetic fields selected for ^{1}H ENDOR observation in Figure 4. The spectra have been simulated by using the parameters reported in Table I.

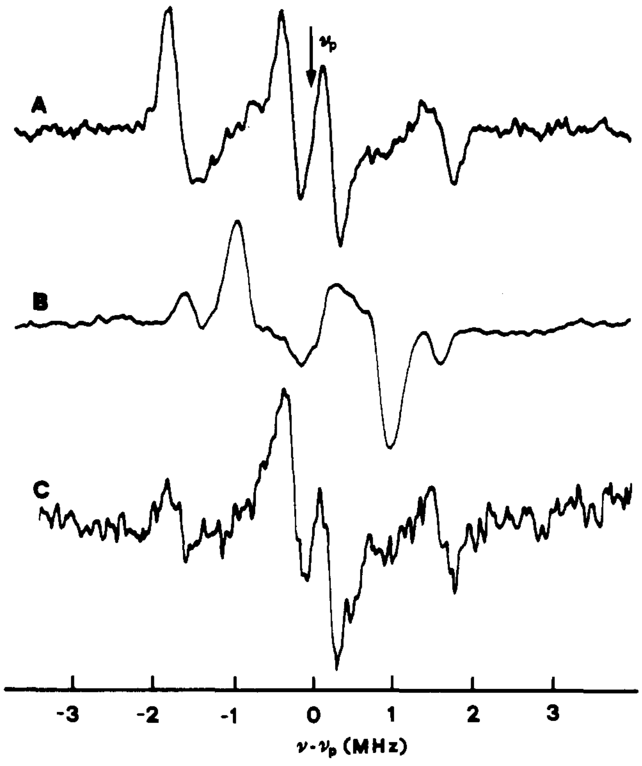

Figure 4. ^{1}H ENDOR spectra of complex **3** measured in CD_3OD at 110 K for the magnetic field settings marked in Figure 3. ν_p indicates the free-proton frequency value (~14 MHz).

reference frames are coincident. However, the proton ENDOR spectra obtained on the low- and high-field $A^2{}_{Cr}$ ^{53}Cr components are dominated by the contribution from a single molecular direction, namely the tetragonal Cr═O axis. Instead, those obtained on g_2 with ^{52}Cr are affected by contributions from the other g components. On the contrary, ENDOR spectra recorded at g_1 and g_3 in the ^{52}Cr EPR spectra have almost pure contributions from the respective directions in the metal plane. Instead, a pure unidirectional ENDOR observation on the $A^1{}_{Cr}$ and $A^3{}_{Cr}$ ^{53}Cr components is hindered by the overlap of several nearby resonances. On the whole, "complete" orientation selection can be

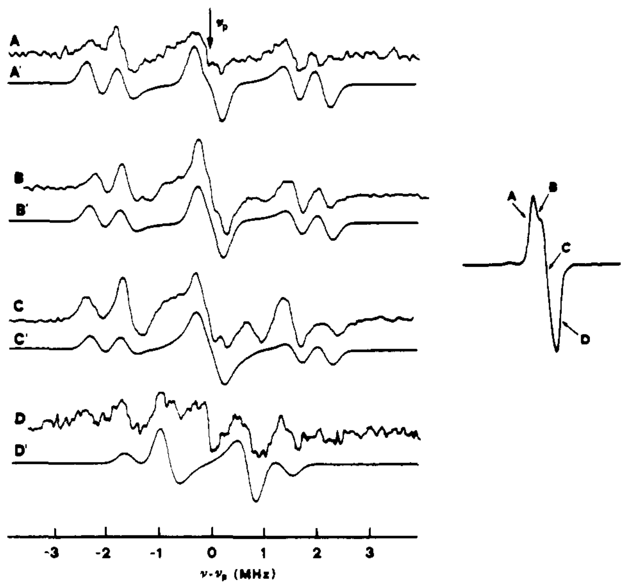

Figure 5. Experimental and simulated (primed) anisotropic ^{1}H ENDOR spectra of complex **2** with Cr natural isotopic composition with varying field setting, as marked on the EPR spectrum. ν_p indicates the free-proton frequency value (~14 MHz). The spectra have been simulated by using the parameters reported in Table I.

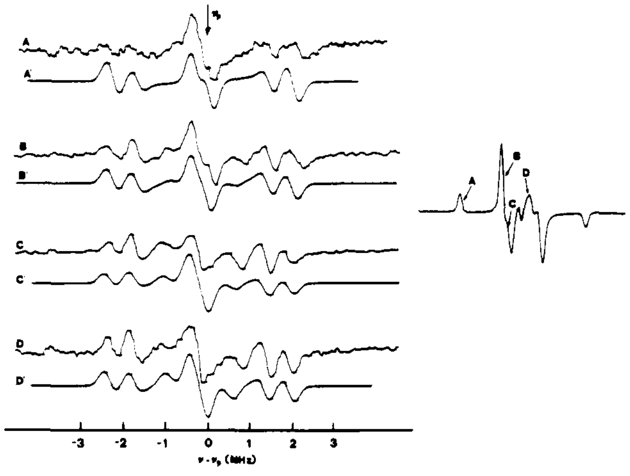

Figure 6. Experimental and simulated (primed) anisotropic ^{1}H ENDOR spectra of the ^{53}Cr-enriched complex **2** with varying field setting, as marked on the EPR spectrum. ν_p indicates the free-proton frequency value (~14 MHz). The spectra have been simulated by using the parameters reported in Table I.

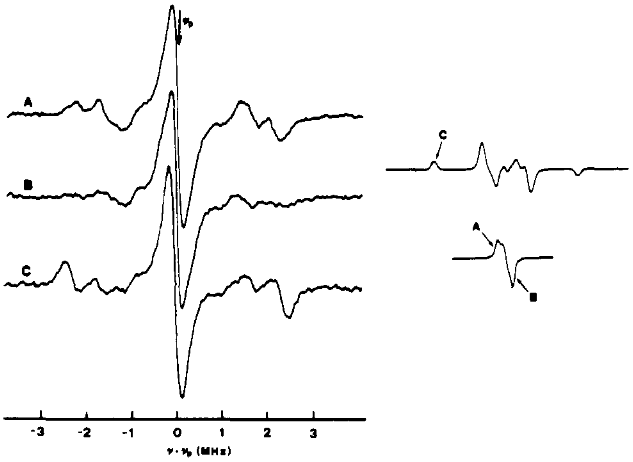

Figure 7. ^{1}H ENDOR spectra of complex **1** measured in CD_3OD at 110 K for the magnetic field settings marked in the EPR spectra. ν_p indicates the free-proton frequency value (~14 MHz).

achieved along all three principal axes of the **g**/**A** matrixes by employing both the ^{52}Cr and ^{53}Cr nuclides and this capability may be unique to Cr(V) complexes.

Because the proton shf interaction A_H is the sum of the isotropic $(A_H)_i$ and anisotropic $(A_H)_a$ contributions, the isotropic couplings measured in liquid solution must be taken into account to derive the relative signs of the observed constants. For instance, the methine protons of complex **3** are responsible for the larger couplings detected in the anisotropic ENDOR spectra (Figure 4). The only reasonable analysis for these protons implies that $(A_H)_i$ is negative (−1.21 MHz; cf. the absolute value of 1.16 MHz at 200 K), as supported by theoretical considerations.[12,21] The best simulation of the spectra is obtained by assuming $(A^x{}_H)_a = -2.24$, $(A^y{}_H)_a = -2.24$, and $(A^z{}_H)_a = +4.48$ MHz as the anisotropic contributions measured within the proton reference system (where z, as is common, refers to the metal–nucleus direction). This procedure yields $A^x{}_H = -3.45$, $A^y{}_H = -3.45$, and $A^z{}_H = +3.27$ MHz as the shf constants, which gives good reproduction of the spectra of both ^{52}Cr and ^{53}Cr samples and their trend with varying observing point. Really, the best fit of the spectra was obtained by introducing a deviation angle (±13°) between the **g** (or $\mathbf{A}_{Cr}$) and the $\mathbf{A}_H$ tensors, e.g. the angle between $A^z{}_H$ and $A^2{}_{Cr}$ is 90 ± 13°. Of course, this angle accounts for the deviation of the protons from the plane containing Cr and the donor atoms.

Since the traceless anisotropic ^{1}H couplings are axial, i.e. by considering the absolute values, the larger coupling is twice the smaller ones, we can extract geometrical information from them. In fact, a metal–proton distance (r) of 0.32–0.33 nm is calculated in the point–dipole approximation by using the well-known equation $(A^z{}_H)_a = 2g_e\beta_e g_n\beta_n/r^3$.[24]

Using the same procedure as above, the ^{1}H ENDOR spectra of the methyl protons of **3** can be interpreted by assuming a positive isotropic constant $(A_H)_i = +0.33$ MHz and anisotropic contributions $(A^x{}_H)_a = -0.77$, $(A^y{}_H)_a = -0.77$, and $(A^z{}_H)_a = +1.50$ MHz. This analysis yields $A^x{}_H = -0.40$, $A^y{}_H = -0.40$, and $A^z{}_H = +1.80$ MHz as the total shf constants. In this case a deviation angle of ±7° gives the best fit, whereas the values for the dipolar interaction are consistent with a metal–proton distance of about 0.47 nm.

The proper assignment of the coupling constants is confirmed by examination of the anisotropic spectra of the complex of (*S*)-(+)-1,2-propanediol (**2**), which, besides the methyl protons, exhibits two types of methylene protons (axial and equatorial) having isotropic constants $(A_H)_i = -1.21$ and −2.45 MHz, respectively. The axial protons are analogous to those of **3** and exhibit similar ^{1}H couplings. The set of couplings for the equatorial protons, after decomposition, yields $(A^z{}_H)_a = +4.85$, $(A^y{}_H)_a = -2.43$, and $(A^x{}_H)_a = -2.43$ MHz as the anisotropic contributions (the calculated proton–metal distance is 0.32 nm). Representative spectra together with computer simulations are shown in Figures 5 and 6.

The same mode of calculation is valid for the ethylene glycolate complex **1**, which also exhibits axial and equatorial protons with splitting values analogous to those of **2**; see Figure 7.

The correctness of the analysis is supported by the comparative examination of the structural and magnetic data for the protons in the ethylene bridge of similar chelated complexes of oxovanadium(IV) and copper(II), e.g. with salen and acen.[21,26,27]

Further information can be extracted from the spectral analysis. The ^{1}H ENDOR patterns of **1** in frozen solution exhibit also a strong matrix line around the nuclear proton frequency value (Figure 7). Since the spectra were recorded in CD_3OD, this signal may only be attributed to a purely dipole–dipole interaction of the metal ion with the protons of neighboring complex or ligand molecules, e.g. due to segregation processes in solution or hydrogen-bonding interactions. Further, as anticipated above, the signs observed for the isotropic couplings of protons are consistent with a spin propagation mechanism arising from successive atom-to-atom polarization from Cr to H atoms with alternating sign. Accordingly, on the basis of the sequence of atoms in the ligand, spin densities of negative and positive sign are expected for the ring and methyl protons, respectively.

In conclusion, the results demonstrate that the power of resolution of proton ENDOR analysis for evaluating the structure of Cr(V) complexes in solution. The approach attempted here and the proper interpretation reached for the proton–metal interaction provide a basis for reasonably complete studies of complexed species formed by complicated and biologically important ligands such as sugars as well as their derivatives or biopolymers. Moreover, the applicability of the point–dipole approximation to 3d^1 systems, allowing estimates of the distance from the metal even for nuclei of outer-sphere bound molecules (see, eg., refs 15 and 28 for V^{IV}O complexes) has been further assessed.

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(24) The applicability of such an approximation, which must be assessed on a case-by-case basis, has been largely demonstrated for 3d^1 spin systems, in particular VO^{2+}. Most important in this regard are crystal ENDOR studies in which the atomic coordinates alternatively determined by X-ray diffraction and by ENDOR were compared.[25]

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