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Exchange of Axial and Equatorial Carbonyl Groups in Pentacoordinate Metal Carbonyls in the Solid State. The Variable Temperature Magic Angle Spinning Carbon-13 NMR Spectroscopy of $Fe(CO)_5$, $[Ph_3PNPPh_3][HFe(CO)_4]$, and $[NEt_4][HFe(CO)_4]$

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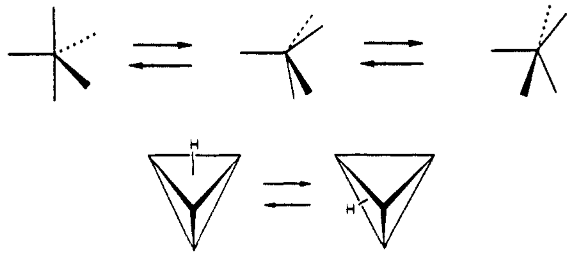
Abstract: The pentacoordinate anion, $[HFe(CO)_4]^-$, undergoes rapid axial-equatorial exchange of carbonyl groups in the solid state as demonstrated by variable temperature magic angle spinning carbon-13 NMR spectroscopy. The exchange occurs in crystalline samples with either $Ph_3PNPPh_3^+$ (PPN^+) or NEt_4^+ as the counterion. From the variation in line width as a function of temperature in the fast-exchange region the activation energy for axial-equatorial exchange in $[HFe(CO)_4][NEt_4]$ is estimated to be 7.0 ± 0.7 kcal mol^{-1}. A comparison of coalescence temperatures suggests that the activation barrier is higher in the PPN^+ salt. The crystal structure of the PPN^+ is known and shows a pentacoordinate iron atom with a geometry that can be described as intermediate between a face-capped tetrahedron and a trigonal bipyramid. Although the structure for the NEt_4^+ salt is not known it is likely that the anion has essentially the same geometry determined in the PPN^+ salt. A hydride tunnelling mechanism is considered to be most likely for the exchange of carbonyl ligands. In contrast the related molecule, $Fe(CO)_5$, shows no evidence for rapid axial-equatorial exchange of carbonyl groups in the solid state. Previous broadline NMR results estimated the rate of axial-equatorial exchange in solid $Fe(CO)_5$ to be 2.4×10^4 s^{-1} at -60 °C. However, magic angle spinning NMR results suggests that the rate of axial-equatorial exchange in solid $Fe(CO)_5$ cannot be greater than 10^2 s^{-1}.

The solution behavior of pentacoordinate metals is now well established from NMR investigations of many transition-metal phosphine complexes.[1-3] These complexes have trigonal-bipyramidal ground-state structures and are observed to undergo rapid intramolecular exchange of axial and equatorial groups. Two permutationally distinct models for the exchange are possible for molecules having a D_{3h} trigonal-bipyramidal geometry: a 2 for 2 exchange of axial and equatorial ligands and a 1 for 1 exchange of these groups. The best-known physical model for the 2 for 2 exchange is the Berry pseudorotation.[4] This is represented in Scheme I. For the phosphine and phosphite transition-metal complexes that have been observed in the slow exchange limit at low temperature the experimental line shapes as a function of temperature favor the Berry mechanism or one of its permutationally equivalent models. Trigonal-bipyramidal hydrido olefin phosphine complexes of iridium also undergo rapid exchange of axial and equatorial groups. A Berry-type mechanism is proposed for these complexes.[5] However, when the ground-state geometry of the pentacoordinate complex deviates from idealized trigonal-bipyramidal geometry the applicability of the Berry mechanism breaks down. Thus the HML_4 (M = Rh, Co and L = PR_3) molecules, which have a geometry best described as a face-capped tetrahedron,[1-3] are proposed to undergo a hydride tunnelling mechanism. The tunnelling mechanism moves the face-capping hydride from face to face in the tetrahedron. This mechanism is also described in Scheme I.

Iron pentacarbonyl has a ground-state structure of a trigonal bipyramid as determined by electron diffraction in the gas phase and X-ray diffraction in the solid state.[6,7] Previous broadline NMR results on frozen samples of neat $Fe(CO)_5$ suggested that rapid axial-equatorial exchange of carbonyl groups occurs in the solid.[8] A rate of 2.4×10^4 s^{-1} was estimated at -60 °C. In solution the rate is estimated to be as high as 10^{12} s^{-1},[9,10] and activation barriers of 0.5 to 2 kcal mol^{-}1 have been estimated by a number of methods for the exchange of axial and equatorial carbonyls.[9-13] If the chemical shift difference between axial and equatorial carbonyl groups is less than 1000 Hz then the rate estimated by broadline NMR in the solid state should be sufficiently fast to average axial and equatorial carbonyls on the NMR time scale.

Scheme I



The hydrido iron carbonyl, $[HFe(CO)_4]^-$, has a structure that is best described as a distorted trigonal bipyramid with the hydride ligand occupying an axial site.[14] The axial carbonyls are bent toward the hydride, indicating that the distortion is in the direction of a face-capped tetrahedron. The bond angles suggest that the

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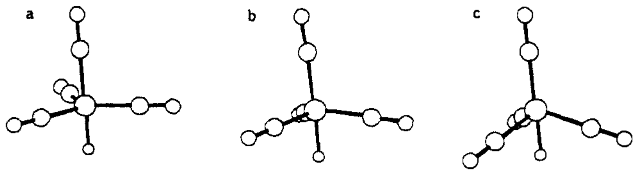

Figure 1. (a) Representation of the structure of $[HFe(CO)_4]^-$ as an idealized trigonal bipyramid with hydrogen in an axial position. (b) Representation of the structure of the anion as determined by X-ray crystallography in $[PPN][HFe(CO)_4]$.[14] (c) An idealized tetrahedron with hydrogen capping a triangular face.

structure is nearly midway between the two idealized structures. This is particularly evident when comparing the structure of $[HFe(CO)_4]^-$ in $[PPN][HFe(CO)_4]$ with the isoelectronic molecule $HCo(PF_3)_4$ in which the phosphorus atoms form an almost ideal tetrahedron.[15] The actual structure of the $[HFe(CO)_4]^-$ ion and the idealized trigonal-bipyramid and face-capped tetrahedral structures are shown in Figure 1.

In this paper we examine the dynamic behavior of $[NEt_4][HFe(CO)_4]$, $[PPN][HFe(CO)_4]$, and $Fe(CO)_5$[16] in the solid state by magic angle spinning carbon-13 NMR spectroscopy. The evidence suggests that certain motions of pentacoordinate molecules may be allowed in the solid state.

Experimental Section

Iron pentacarbonyl (Pressure Chemical Co.) was filtered to remove any solid particles before enrichment in carbon-13 carbon monoxide. The enrichment was accomplished by stirring the neat liquid under 99% ^{13}CO in the presence of Pd on carbon. The level of enrichment was estimated to be 15 to 20% as judged by infrared spectroscopy. The iron pentacarbonyl was then distilled to give the pure liquid. The anion, $[HFe(CO)_4]^-$, was synthesized by literature methods[17] from enriched $Fe(CO)_5$ and isolated as either the $Ph_3PNPPh_3^+(PPN^+)$ or the NEt_4^+ salt. The salts were transferred in a nitrogen atmosphere drybox to standard MAS NMR rotors made of delrin and sealed with plasticine. Iron pentacarbonyl was transferred by syringe to a delrin rotor packed in dry ice and blanketed by a stream of argon. The addition was dropwise at a rate that allowed the freezing of one drop before the addition of another.

All NMR spectra were recorded on a spectrometer consisting of a JEOL FX90Q console interfaced to a Chemagnetics 2.1 T superconducting magnet and Chemagnetics probe tuned to an observation frequency for carbon of 22.53 MHz. A Chemagnetics temperature controller with a thermocouple in the drive gas stream was used to maintain the temperature of the sample. The drive and bearing gases were dry nitrogen provided from liquid nitrogen boil off. Spinning rates varied from 2.5 to 4.0 kHz. A simple Bloch decay sequence (a carbon 90° pulse and a 1 to 60 s pulse delay) was used to record all spectra. Gated ^1H decoupling was used only for the $[HFe(CO)_4]^-$ salts. For the hydride samples 100 to 1000 scans were recorded for each spectrum with the larger number of scans and shorter pulse delays used at higher temperatures. For iron pentacarbonyl all spectra obtained at −30 °C and lower are the result of a single carbon 90° pulse. The spectrum shown at −25 °C is the result of two pulses with a 10 min pulse delay. At temperatures between −20 and −30 °C a second pulse contributed significantly to the signal to noise only after pulse delays of 20 min. The spin–lattice relaxation time, T_1 for $Fe(CO)_5$ was previously estimated to be 30 min at −60 °C.[8] Thus for all spectra shown at temeperatures lower than −30 °C the sample had first been held at −25 °C for 20 min and then cooled to the reported temperature and held constant for an additional 10 min. Before attempting to record another low-temperature spectrum the sample was warmed to −25 °C to allow the carbon magnetization to relax.

Results

Iron Pentacarbonyl. The MAS ^{13}C NMR spectrum for solid $Fe(CO)_5$ is shown in Figure 2 at several temperatures.[16] At temperatures of −38 °C and lower, two signals at 216.0 and 208.1 ppm are observed. The relative integrated intensities, including spinning sidebands, are 2:3 for the two signals. This is consistent with a trigonal-bipyramidal structure.[6,7]

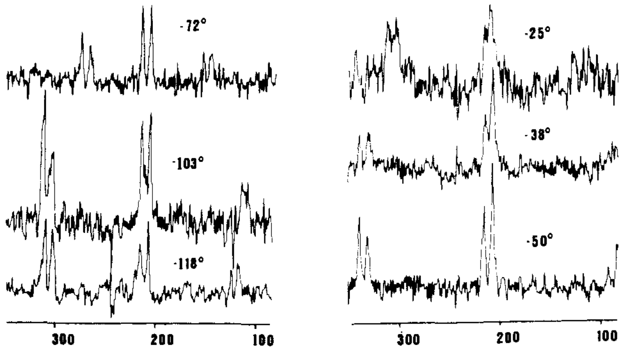

Figure 2. Variable temperature MAS NMR spectra for $Fe(CO)_5$. The spinning rates varied as follows: at −118 °C, 2140 Hz; at −72 °C, 1360 Hz; and at −25 °C, 2700 Hz.

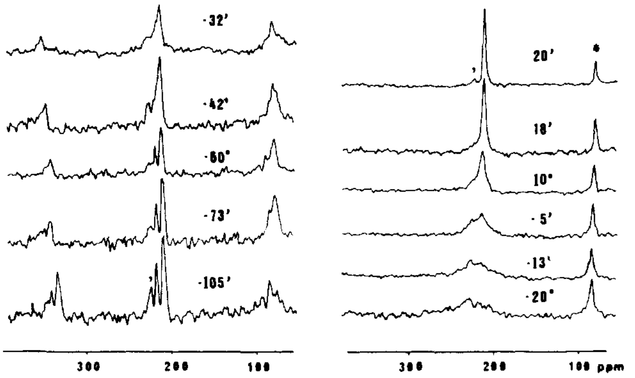

Figure 3. Variable temperature MAS NMR spectra for $[NEt_4][HFe(CO)_4]$. The asterisked peak is due to delrin; the peak denoted with a dagger is due to an unidentified impurity.

The melting point of $Fe(CO)_5$ is approximately −21 °C.[18] All MAS spectra recorded between −23 and −30 °C show three signals in the carbonyl region. These occur at 216, 208.1, and 211.6 ppm. The last of these corresponds to the isotropic shift of iron pentacarbonyl. The presence of this signal however is not necessarily indicative of rapid axial–equatorial exchange in the solid state. Rather the simultaneous observation of three signals is most consistent with the presence of two phases in the sample at these temperatures. The second phase is most likely the liquid state although the possibility of a second solid phase in which axial–equatorial exchange is rapid cannot be eliminated. In the spectrum at −25 °C the sidebands corresponding to the static solid phase are observed but a sideband representing the average of axial and equatorial signals is not present. It is apparent from these results that axial–equatorial exchange of carbonyls is not rapid on the NMR time scale in solid $Fe(CO)_5$ at temperatures of −38 °C and lower.

$[M][HFe(CO)_4]$ ($M = PPN^+$, NEt_4^+). Several years ago one of us (K.H.W.) recorded the room temperature MAS ^{13}C NMR spectrum for the anion in $[NEt_4][HFe(CO)_4]$. Contrary to what is expected from the structure of the anion the spectrum showed a single line in the carbonyl region suggesting a dynamic process in the solid state. The variable temperature ^{13}C NMR MAS NMR spectra for this compound are shown in Figure 3 and demonstrate that the compound is indeed fluxional in the solid state.

At temperatures of −60 °C and lower two carbonyl resonances are seen at 228.0 and 220.0 ppm. The peak at 235.0 ppm appears to be independent of the other two and is most likely due to an impurity. The peaks at 228.0 and 220.0 ppm are in a 1 to 3 ratio consistent with 1 axial and 3 equatorial carbonyl groups as expected. Coalescence for the two-site exchange occurs at approximately −40 °C. After coalescence the signal broadens extensively at temperatures near −13 °C. Simulation of the spectra

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with the assumption of two-site exchange describes the experimental behavior to −42 °C but cannot account for the extensive broadening observed at higher temperatures. This phenomenon is described by Rothwell and Waugh and is a consequence of magic angle spinning with high-power proton decoupling.[19] These authors show that in the short correlation time limit the line width, Δ, is related to τ_c, the molecular correlation time, according to the equation

$$\frac{1}{T_2} = \frac{4\gamma_I^2\gamma_S^2\hbar^2}{15r^6}[I(I+1)]\tau_c$$

Since Δ is a function of τ_c ($\Delta = 2/T_2$ for a Lorentzian line) an Arrhenius plot of log Δ vs $1/T$ yields an activation energy. The line widths from four spectra recorded at 10 °C and higher[20a] were fitted to the Arrhenius equation to obtain an activation energy for the process responsible for the exchange.[19] This was calculated to be 7.0 ± 0.7 kcal mol^{-1}. It is assumed that the dynamic process responsible for the Rothwell–Waugh broadening also causes exchange of axial and equatorial sites.

This type of broadening has also been observed in other fluxional metal carbonyl complexes.[21] On top of the broad line observed at −13 °C the peak at 235.0 ppm persists as a fairly sharp signal. At 30 °C the peak due to the anion is seen at 221.6 ppm which is close to the weighted average position predicted from the chemical shifts at −105 °C. The impurity gives a small peak at 233.1 ppm. Over the temperature range studied the signal due to the impurity broadens and resharpens indicating that it is dynamic also.

The solid-state structure for $[HFe(CO)_4]^-$ has been reported only as the PPN$^+$ salt. Examination of the bond angles in this structure shows that the geometry at the iron lies between the ideal cases of a C_{3v} trigonal bipyramid and a face-capped tetrahedron (Figure 1). It is anticipated that the geometry at iron is similar in the tetraethylammonium salt examined by solid-state NMR. The crystal structure for $[PPN][HFe(CO)_4]$ shows no unusual features whereas preliminary results on the crystal structure of $[NEt_4][HFe(CO)_4]$ indicate an unexpectedly high symmetry for the space group.[20b] Unfortunately attempts to solve this structure have not yet been successful. This may suggest that the anion lies at a special position that requires some degree of disorder. To see if the nature of the crystal lattice influences the dynamic behavior of the anion in $[NEt_4][HFe(CO)_4]$ we examined the NMR spectrum of $[PPN][HFe(CO)_4$ in the solid state as well. These spectra are shown in Figure 4.

At low temperature only a single line is seen in the NMR spectrum in contrast to the result for the NEt_4^+ salt. From the width of the resonance it is likely that the axial and equatorial signals are simply not resolved. The nature of the cation may be responsible for some of the broadening; the PPN$^+$ cation contains an asymmetric quadrupolar nucleus, ^{14}N, and two ^{31}P nuclei that are not decoupled. As the temperature is raised the signal broadens substantially and does not begin to narrow again until 60 °C. The behavior of the signal as a function of temperature clearly indicates that the anion is dynamic. The point of maximum broadening is about 40 deg higher than for the $[NEt_4][HFe(CO)_4]$ sample, which suggests a higher activation barrier for exchange in the [PPN] salt. The substantial broadening observed is greater than anticipated from two-site exchange and most likely results from the Rothwell–Waugh broadening as described above. Unfortunately the data were not sufficiently good to estimate an activation barrier accurately.

Discussion

Iron Pentacarbonyl. Iron pentacarbonyl has been studied by broadline NMR at temperatures from 4.2 to 213 K.[8] Evaluation of the spin–lattice relaxation times over part of this temperature range and calculation of the expected line shapes led to the conclusion that a molecular rearrangement occurs in solid $Fe(CO)_5$. Two possible mechanisms for the motion were considered, a pseudorotation, as described above, and a rotation about the molecular 3-fold axis of the trigonal-bipyramidal molecule. The authors concluded that a Berry pseudorotation better described the experimental data.[8] The exchange frequency for the motion was measured to be 2.4 × 10^4 s^{-1} at −60 °C. From the reported variation of the rate with temperature an activation energy of 0.5 kcal mol^{-1} can be calculated. Although this is similar to what is estimated for axial–equatorial exchange of carbonyls in liquid $Fe(CO)_5$ the exchange frequency is much slower than the corresponding rate of molecular reorientation in liquid $Fe(CO)_5$ at −20 °C, i.e. 1.1 × 10^{10} s^{-1}.[9,10] However, the rate estimated in the solid state at −60 °C is sufficiently provided the isotropic chemical shifts of these groups are within 1000 Hz. At an observation frequency of 22.53 MHz it is reasonable to expect the chemical shift difference between axial and equatorial carbonyls to be less than this value since the range of chemical shifts observed for terminal carbonyl ligands in neutral iron carbonyl derivatives is ca. 208 to 220 ppm.[22] As seen from the low-temperature NMR spectra (Figure 2) the actual difference between axial and equatorial signals is 182 Hz. Clearly then the rate estimated by broadline NMR must be for a process that does not exchange axial and equatorial carbonyls. If axial–equatorial exchange were taking place at this rate (2.4 × 10^4 s^{-1}) then the spectra obtained at temperatures of −60 °C and higher would consist of a single exchange narrowed line. We conclude then that the process detected by broadline NMR most likely involves the alternative explanation proposed by Spiess et al.,[8] that is, the simple rotation of the trigonal-bipyramidal molecule about its 3-fold rotation axis. At temperatures of −38 °C and lower the rate of axial–equatorial exchange in solid $Fe(CO)_5$ is estimated to not exceed 10^2 s^{-1} since significant line shape changes are not observed in the MAS spectra.

M[HFe(CO)$_4$] (M = PPN, NEt$_4$). As noted above the structure observed for $[HFe(CO)_4]^-$ is intermediate between face-capped tetrahedral and trigonal bipyramidal. The fact that $Fe(CO)_5$ does not undergo rapid axial–equatorial exchange in the solid state leads us to the conclusion that a pseudorotation or similar process such

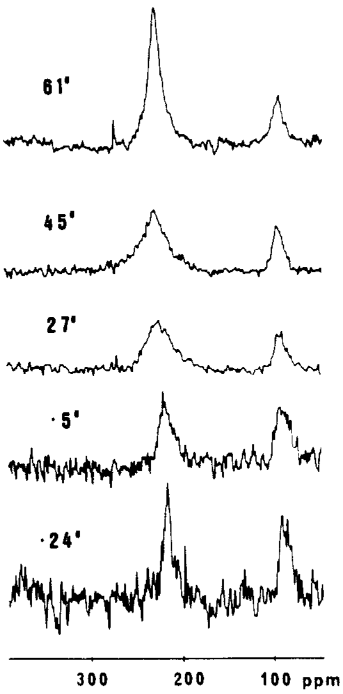

Figure 4. Variable temperature MAS NMR spectra for $[PPN][HFe(CO)_4]$. The broad peak at ca. 120 ppm is due to the phenyl groups in the PPN cation. At −24 °C the chemical shift observed for the anion is 218.9 ppm and in the spectrum at 61 °C it is 222.7 ppm.

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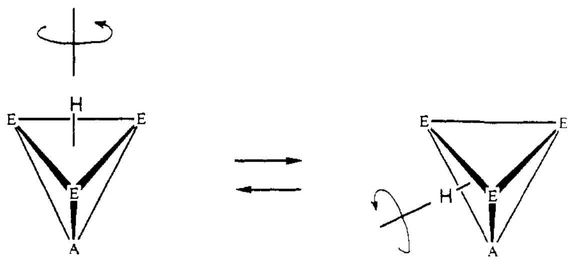

Figure 5. Representation of a mechanism that interchanges all carbonyl groups in the solid state for a face-capped tetrahedron.

as a twist mechanism is unlikely in the solid state for $[HFe(CO)_4]^-$. A hydride tunnelling mechanism appears to be more likely since it requires minimal movement of the carbonyl ligands.

A similar conclusion was reached from the study of HML_4 complexes in solution.[1-3] It was argued that for transition-metal complexes the Berry rotation applies to structures of rigorous square-pyramidal or trigonal-bipyramidal structure. On this basis then the hydride tunnelling mechanism is also more likely in the solid since the structure of the carbonyl hydride is distorted away from an ideal trigonal bipyramid.

Hydride tunnelling has also been proposed to occur in the closely related complexes $H_2Fe(CO)_4$[23] and $H_2Fe(PR_3)_4$.[24] For these distorted-octahedral complexes hydride tunnelling exchanges axial and equatorial carbonyl groups. In solution the barrier to hydride tunnelling for $H_2Fe(CO)_4$ was estimated to be 8.1 kcal mol^{-1}.[23] Axial-equatorial exchange is also rapid in solution for the anion, $[HFe(CO)_4]^-$; the average chemical shift observed in solution is 220.8 ppm at room temperature.[23] In the solid state the barrier for axial-equatorial exchange is 7.0 ± 0.7 kcal mol^{-1} for $[NEt_4][HFe(CO)_4]$, significantly higher than the appearent solution value, and the isotropic chemical shift in the fast exchange limit is 221.6 ppm, in good agreement with the solution value.

Closer examination of the dynamic processes that may take place in the solid state suggests that, in addition to the hydride tunnelling, another motion is required to make the carbonyl environments truly equivalent. Since the anion in $[PPN][HFe(CO)_4]$ lies on a general position the four carbonyl ligands are crystallographically unique. This suggests that either the resonances due to the three equatorial carbonyls in the anion are degenerate at low temperature or there is an additional motion that makes these groups magnetically equivalent. It is well established that chemically identical but crystallographically unique carbonyl ligands can show different resonances in the solid state.[25] If rotation about the 3-fold axis in the anion is fast in the solid state then all four carbonyls can in fact become equivalent in the solid state when hydride tunnelling and the 3-fold rotation are combined. This is shown schematically in Figure 5. Rotation about molecular 3-fold axes is established in $(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3$ and related metal carbonyls[19] as well as in $Fe(CO)_5$ (vide supra).

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Hydration Structure of Titanium(III) Ion. ESR and Electron Spin-Echo Study

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Abstract: ESR, ENDOR, and electron spin-echo studies have been carried out for determining the hydration structure of the Ti^{3+} ion in the amorphous solid of a 2-propanol/D_2O mixture. It is found that the hydrated ion is in D_{3d} symmetry with the unpaired electron mainly in the d_{z^2} orbital. Six water molecules coordinate to the central metal ion with the Ti^{3+}–O distance of about 2.2 Å to form an octahedron with a slight compression along the C_3 axis. Because of the strong repulsive interaction between the d_{z^2} orbital and the n_π orbitals of the coordinating D_2O molecules, the D–O–D planes are almost parallel to the C_3 axis. The angle between the C_3 axis and the Ti^{3+}–O bond is about 60°. The value of $g_\parallel$ is 1.994, but the value of $g_\perp$ is distributed around 1.896. The hydrated ion with lower $g_\perp$ value shows weaker isotropic hyperfine coupling with the coordinated water deuterons, which is well interpretted as due to the displacement of the D–O–D planes from the parallel configuration.

The trivalent titanium ion, Ti^{3+}, is one of the simplest paramagnetic metal ions and has been frequently cited as a good example for explaining crystal field or ligand field theory. However, ESR studies of the Ti^{3+} ion are rather few, probably because of its chemical instability. The ESR spectrum of the hydrated Ti^{3+} ion in cesium alum, $CsTi(SO_4)_2 \cdot 12H_2O$, was measured below 8 K by Bijl,[1] who reported the $g_\parallel$ of 1.25 and $g_\perp$ of 1.14. Since the structure of the hydrated ion in the alum crystal was expected to be nearly regular octahedron,[2-4] the g anisotropy was explained as due to the splitting of the $^2T_{2g}$ state into the $^2A_{1g}$ state by a slight compression of the coordinated water molecules about the C_3 axis and by covalent bonding between the metal ion

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