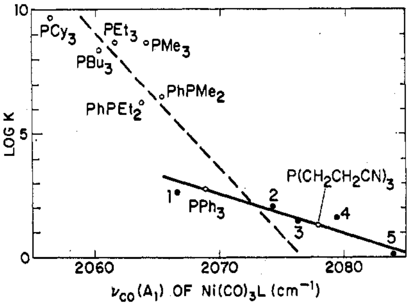

Figure 1.—Variation of protonation equilibrium constant with $\nu_{CO}(A_1)$ of $Ni(CO)_3L$ from ref 6. The solid line and closed circles refer to the NiL_4 complexes listed in Table II. The dashed line and open circles refer to the free phosphines.[10]

those tested, the extent of protonation was below the level of detection in 1 *M* H_2SO_4. The equation of the solid line in Figure 1 is $\log K = 0.16(2086 - \nu_{CO})$. Using this equation it is possible to calculate[8] an approximate hydride formation constant for $HNi(CO)_4^+$ of $\sim 10^{-7}\ M^{-1}$, which explains why the hydride has not so far been observed although nickel hydrides have been proposed as intermediates in acetylene carbonylation reactions using $Ni(CO)_4$.[9]

One interesting aspect of our results is the comparison of NiL_4 basicities with those of the free ligands L. Some phosphine pK_a values measured by potentiometric titration[10] in nitromethane are also plotted in Figure 1. The equation of the dashed line is $\log K = 0.55(2076.6 - \nu_{CO})$. Though our data and those of Streuli[10] were measured in different solvents, two facts clearly emerge from Figure 1. Protonation on nickel in the NiL_4 complexes is only about 0.3 times as sensitive to changes of substituents on phosphorus as is direct protonation of the free phosphine. A greater sensitivity of the electron density on phosphorus to changes in substituents is chemically reasonable and is also indicated by recent ESCA measurements[11] of P $2p^3/_2$ and Ni $2p^3/_2$ binding energies in these complexes. As the substituents become more electron withdrawing, it becomes easier to protonate the NiL_4 complex than the free phosphine. This is why we were able to add excess ligand in the cases of complexes **2**–**5** without interference in determining *K*'s for these complexes. In a mixture of PMe_3 and $Ni(PMe_3)_4$ we anticipate preferential protonation of the phosphine.

The subject of transition metal basicity towards Lewis acids has recently been reviewed by Shriver,[12] who pointed out that metal basicity is expected to increase for more electron-donating ligands. This expectation was based primarily on the effect of replacing CO by PPh_3, as in the series $[Co(CO)_{4-n}(PPh_3)_n]^-$, and has now been confirmed for these NiL_4 complexes. Enhanced basicity is one factor favoring catalytic activity of these complexes for olefin coupling[3] and isomerization[4] reactions, both of which involve formation of $HNiL_4^+$ as a first step, and is also expected to favor oxidative addition reactions of the conventional type involving cleavage of XY bonds.

Acknowledgments.—Donations of $Ni[PPh(OEt)_2]_4$ and $Ni[Ph_2PCH_2CH_2PPh_2]_2$ from Dr. J. J. Mrowca and Dr. R. A. Schunn and assistance from Mrs. Jean L. Read in obtaining the nmr spectra are gratefully acknowledged. The comparison of pK_a's of L and NiL_4 in Figure 1 was suggested by a referee.

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Titanium(III) Chloride in Methanol with Small Amounts of Water

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Very little information concerning the solvation of titanium(III) ions in solution is available in the literature. This information is of interest in the study of corrosion[1] as well as in the chemistry of transition metal ions. As part of some spectroscopic and electrochemical studies of titanium,[2,3] the electron spin resonance (esr) spectra of $TiCl_3$ in methanol–water systems were investigated. We wish to report here the results of an esr investigation of $TiCl_3$ in methanol-*O-d* containing 0–0.1 *M* D_2O.

Titanium(III) chloride has been found to form stable complexes which contain chlorides and alcohols, ethers, nitriles, ketones, or amines as ligands. Those complexes containing 2-propanol and *sec*-butyl alcohol[4] have been assigned the structure $[TiCl_2(alcohol)_4]^+Cl^-$.[5] Complexes with methanol that have been isolated or detected in solution include $[TiCl_n(CH_3OH)_{6-n}]^{3-n}$ where *n* is 0–6 and also several seven- and eight-ligand complexes.[6]

The solvation of titanium(III) has been investigated in acetonitrile,[7] methanol,[8] and water.[8,9] Using nuclear magnetic resonance spectroscopy (nmr), Chmelnick and Fiat[8] found that the average coordination number of methanol on titanium chloride in methanol is 4, which suggests a complex of the form $[TiCl_2(CH_3OH)_4]^+$. These nmr measurements required fairly high concentrations of $TiCl_3$.

In order to investigate the nature of titanium(III) in dilute methanol solutions, esr spectroscopy was selected due to its high sensitivity. Methanol solutions containing from 0.5 to 40 m*M* $TiCl_3$ and from 10 to 100 m*M* D_2O were investigated. Esr studies of titanium(III) complexes in solutions that have been reported include titanium(III) chelates[10] in aqueous

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TABLE I

RESULTS OF ESR INVESTIGATIONS ON Ti(III) IONS IN SOLUTION

Active material	Solvent	a_{Ti}, G	a_H, G	g	ΔH_{pp},[d] G	Ref
$[TiOCH_3]^{2+}$	Methanol	18.2 ± 0.2		1.9532 ± 0.0005		11
$[TiF_2]^+$	Methanol	18.3 ± 0.4		1.9465 ± 0.0004		11
$[TiCl_2(CH_3OH)_4]^+$	Methanol		1.46[a,b]			8
$[Ti(H_2O)_6]^{3+}$	Water		1.76[a,b]			8
$Ti(H_2O)_4X_2$	*tert*-Butyl alcohol–water (1:4)	15.6	1.80[b]	1.9557 ± 0.0010[c]	2.0	12
$Ti(D_2O)_4X_2$	*tert*-Butyl alcohol–D_2O (1:4)				3.0	12
$[TiCl_2(CH_3OH)_4]^+$	Methanol	20.0 ± 1.0		1.951 ± 0.001	7.0	13a
$[TiCl_2(CH_3OH)_4]^+$	Methanol			1.953 ± 0.002	23.0	13e
$[TiCl_2(CH_3CH_2OH)_4]^+$	Ethanol			1.950 ± 0.002	10.0	13e
$\{TiCl_2[(CH_3)_2CHOH]_4\}^+$	2-Propanol			1.952 ± 0.002	10.0	13e
$[TiF_n(H_2O)_{6-n}]^{3-n}$	Water			1.948 ± 0.001		13b
Ti(III) chelates	Water	14.7–15.6		1.93–1.97		10
$[TiCl_2(CH_3OD)_4]^+$	CH_3OD	17.8 ± 0.2		1.9519 ± 0.0005	4.5	*c*
$[TiCl(CH_3OD]_5]^{2+}$	CH_3OD	18.35 ± 0.15		1.9548 ± 0.0003	2.9	*c*
$[TiCl(D_2O)_n(CH_3OD)_{5-n}]^{2+}$	CH_3OD	18.50 ± 0.15		1.9541 ± 0.0003	3.2	*c*

[a] From nmr measurements. [b] Calculated–based on a g factor of 1.95. [c] This work. [d] Peak-to-peak line width of the absorption from the titanium isotopes with no nuclear spin.

solution, $TiOCH_3^{2+}$ and TiF_2^+ in methanol,[11] and $TiCl_3$ in *tert*-butyl alcohol.[12] The concentration dependence in these studies was not discussed. Garif'yanov and coworkers[13] have studied the esr spectra of titanium halides in a wide variety of alcohols and in water. They found that the line widths are nearly constant until a concentration of about 0.3 M titanium salt is reached. Results of esr experiments of Ti(III) in solution are presented in Table I.

During studies of the $TiCl_3$–CH_3OH–H_2O system, the line shape and the apparent g factor appeared to be dependent upon the concentrations of both water and $TiCl_3$ at water concentrations less that 1% (w/w). To investigate this in more detail, CH_3OD and D_2O were substituted for CH_3OH and H_2O in order to sharpen the lines of the spectra. This is similar to the method used by Johnson, *et al.*,[12] to demonstrate the magnitude of the proton hyperfine interactions of water with Ti(III) in solutions of *tert*-butyl alcohol–water. We wish to report here the results of these investigations.

Experimental Section

Materials.—Titanium trichloride powder of 98% purity (Alfa Inorganics) was used as received. Methanol-*O-d* of 99% isotope purity and deuterated water 99.86% iostope purity (Bio-Rad Laboratories) were degassed on the vacuum line before being used in an oxygen-free atmosphere. Water analyses were carried out with an Aquatest II (Photovolt Corp.). The residual D_2O content of the CH_3OD was 0.010 ± 0.001 M. Lithium chloride (reagent grade, J. T. Baker) and tetramethylammonium chloride (polarographic grade, Southwestern Analytical) were dried for 3 days at 135° at 150 mm nitrogen pressure. Sample preparation was carried out in a nitrogen atmosphere.

Electron Spin Resonance.—The esr spectrometer was a modified Varian V4502 X-band spectrometer equipped with a dual cavity and Magnion 15-in. magnet. A frequency meter (Hewlett-Packard X532B) was used for frequency measurements and a power meter (Hewlett-Packard 432A) was used to monitor the power. Spectra were recorded on a dual-channel recorder. The titanium(III) signal was monitored with 100-kHz field modulation and the reference was monitored with 18-kHz field modulation.

The magnetic field was monitored with a Varian F8 fluxmeter and Beckman 6401 frequency counter. To calculate the g factor, diphenylpicrylhydrazyl (DPPH: $g = 2.0037$) was used as the reference and the center of the amplitude of the derivative curve was chosen as the field of resonance. The field difference between cavities was determined from equivalent samples of DPPH placed in each cavity. The field sweep rate was computed by least-squares analysis of the proton resonance frequency with position of the chart. Measurements of the difference between the resonance fields of the sample and DPPH were reproducible to within ±0.2 G (equivalent to $\pm 1.3 \times 10^{-4}$ for the apparent g factor). Because of the distortion of the line shape by contributions from several components, the uncertainty of the difference between the resonance field of DPPH and the resonance field of each titanium species is accurate to ±0.6 G. The relative concentration of material was calculated from the relative line widths and amplitudes required for simulation of the esr spectrum.

Results and Discussion

Figure 1 shows the esr spectra of solutions of various concentrations of $TiCl_3$ and LiCl in CH_3OD at −27°. A low-field line (A) and a high-field line (B) are evident. At temperatures between −15 and −70°, A is nearly gaussian with a peak-to-peak line width of 2.9 G and B is nearly lorentzian with a peak-to-peak line width of 4.5 G. The gaussian line shape of A probably results from hyperfine interactions with the deuterium and the chloride ligands. This complex must also exhibit a longer relaxation time than that of B. As the concentration of $TiCl_3$ is increased or when LiCl or $(CH_3)_4NCl$ is added, the amplitude of B increases relative to A. On the other hand, when the temperature of the sample is decreased, A increases in relation to B. When 0.1 M D_2O is added to a 7 mM solution of $TiCl_3$, the ratio of the absorption at A to that at B increases. The line width of A increases to about 3.2 G, and the g factor of A also appears to decrease by about 6×10^{-4}. Under these conditions, the absorption of B appears only as a shoulder at −27°. At temperatures between −27 and +20° and at high concentrations of $TiCl_3$ or excess chloride, a third absorption begins to appear at the high-field foot of B. The intensity of this line remains small, and the g factor and line width could not be evaluated.

These results suggest an equilibrium between the species responsible for both absorptions, where the high-field absorption arises from a complex containing more chloride than that giving rise to the low-field

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Figure 1.—Esr spectra of solutions of $TiCl_3$ in CH_3OD at $-27°$: (a) 3.1 m*M* $TiCl_3$; (b) 7.8 m*M* $TiCl_3$; (c) 37.5 m*M* $TiCl_3$; (d) 7.0 m*M* $TiCl_3$ with 63.5 m*M* LiCl.

absorption. The fraction of complex containing most chloride increases in the presence of excess chloride or at high concentrations of $TiCl_3$. It is not likely that conversion between cis and trans forms of a complex is responsible for these lines, since this would not be a function of the concentration of either Cl^- or $TiCl_3$. Attempts to calculate the equilibrium constant for the equilibria $TiCl_3 \rightleftharpoons TiCl_2^+ + Cl^-$, $TiCl_2^+ \rightleftharpoons TiCl^{2+} + Cl^-$, or $TiCl_3 \rightleftharpoons TiCl^{2+} + 2Cl^-$ from ratios obtained from the parameters to fit the esr signal resulting from A and B were unsuccessful. This may be due in part to the fact that complexes formed with residual water may be added to the signal of A (*vide infra*) or complexes of Ti(III) which are not detected by esr. Complexes of titanium which have octahedral symmetry and may not be detected could include $Ti(H_2O)_6^{3+}$, $TiCl_6^{3-}$, and $Ti(CH_3OH)_6^{3+}$.[14] If the difference between the crystal field effects of water and methanol were slight, then mixed water–methanol complexes would not be observed or would exhibit broad lines. Thus, the observed absorption lines are expected to be due to chloride complexes of titanium(III).

It is also possible that the residual water displaces a methanol from a complex where both complexes have nearly the same *g* factors. This is supported by the fact that when 0.11 *M* D_2O is added to a solution of $TiCl_3$, A is increased relative to B.

Chmelnick and Fiat[8] measured the chemical shift of the hydroxyl proton of bound methanol in 1.5 *M* $TiCl_3$ solutions at temperatures between -30 and

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[14] J. E. Wertz and J. R. Bolton, "Electron Spin Resonance," McGraw-Hill, New York, N. Y., 1972, Chapter 11.

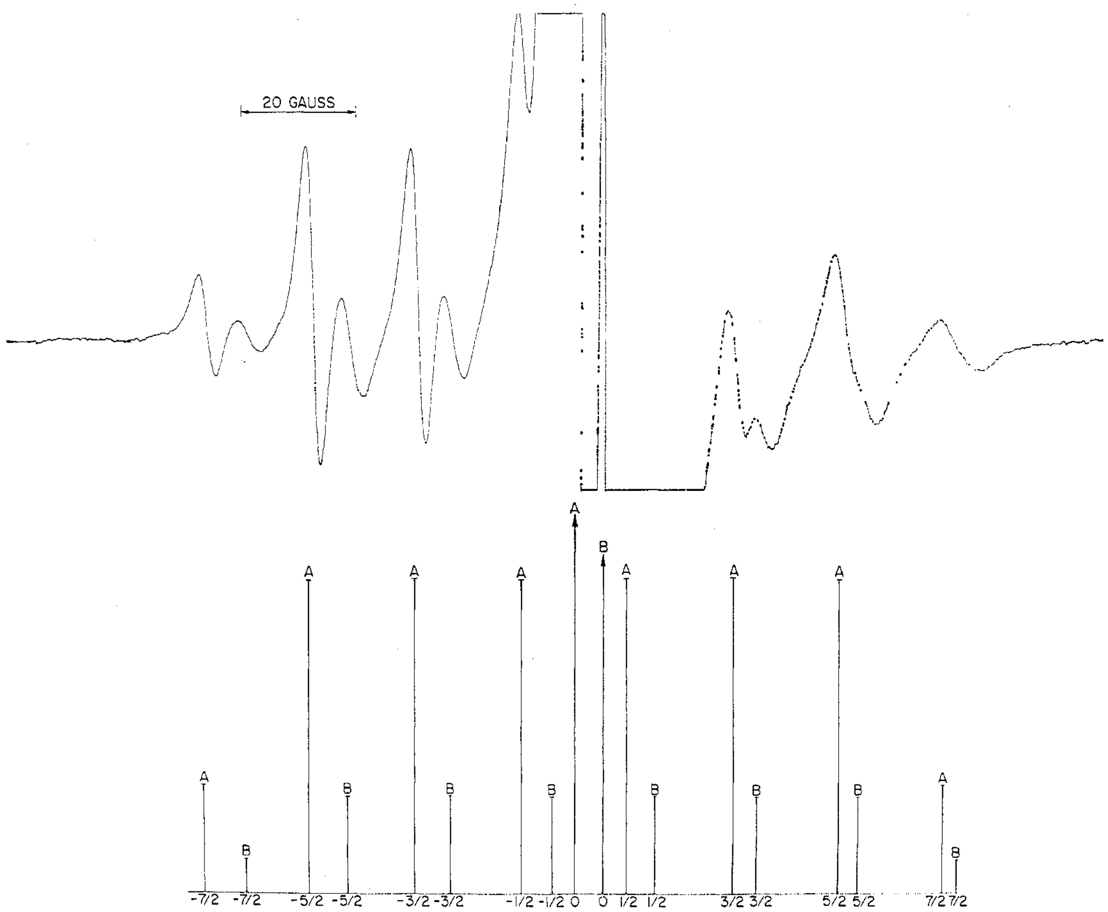

Figure 2.—Esr spectrum of 7.8 m*M* $TiCl_3$ at −9° showing titanium hyperfine structure and a reconstruction of the spectrum in terms of two species (A and B).

−77° (slow exchange rate between the free solvent and the bound solvent). They extrapolated these measurements to the chemical shifts of a 0.13 *M* solution at temperatures between +94 and +27° (fast exchange between free solvent and bound methanol). From the average shift of the resonance line of the methanol, they obtained an average coordination of 4.1 ± 0.2 methanol groups associated with each titanium ion. Based on their results, we tentatively assign absorption B to the complex $[TiCl_2(CH_3OD)_4]^+$ and absorption A to the complex of the form $[TiCl(CH_3OD)_5]^{2+}$. It is also possible that a complex of the form $[TiCl(D_2O)(CH_3OD)_4]^{2+}$ exhibits a spectrum with nearly the same *g* factor as A.

The *g* factor and hyperfine splittings of the ^{49}Ti and ^{47}Ti isotopes obtained from the measurement of the esr spectra are given in Table I. Since the magnetogyric ratios of ^{47}Ti and ^{49}Ti differ by only 0.026%, a difference between the hyperfine splittings is not observed. A typical spectrum and its reconstruction are shown in Figure 2. The titanium splitting due to species B, $a_{Ti}(B)$, is 17.8 ± 0.2 G. This is approximately equal to the splittings of 17.3 G obtained by Davies and Wertz[15] for Ti^{3+} in MgO. The value of $a_{Ti}(A)$ is 18.35 ± 0.15 G and is approximately that found for $TiOCH_3^{2+}$ and TiF_2^+ in methanol.[11] The *g* factors of 1.9547 and 1.9516 (at −9°) for the monochloro (A) and dichloro (B) species show the same trend as the values of 1.9532 for the monosubstituted $TiOCH_3^{2+}$ and 1.9465 for the disubstituted TiF_2^+.[11] There is an increase of the *g* factor of species A of $(1.00 \pm 0.05) \times 10^{-3}$ unit for a 100° decrease of temperature. This may be the result of tighter solvation by methanol at the lower temperatures as well as a reduction in vibronic interaction of the ligand and titanium ions. The difference between the *g* factors of A and B is 0.0031 ± 0.0002 and remains constant with temperature, although at lower temperatures, it is more difficult to assess because of the reduction of a signal due to B.

The values of the *g* factor and of a_{Ti} of the complex formed by the addition of D_2O to $TiCl_3$–CH_3OD solutions are 1.9541 ± 0.0004 and 18.50 ± 0.15 G, respectively. Since both values are close to those of spectrum A, the complex probably has one or more molecules of D_2O replacing CH_3OD. The fact that the *g* factor is smaller than A is consistent with the structure $[TiCl(D_2O)(CH_3OD)_4]^{2+}$ but is not the only possible explanation.[16] The *g* factor of the complex where D_2O replaces one of the CH_3OD ligands in $[TiCl(CH_3OH)_5]^{2+}$ should differ only slightly from the *g* factor of the methanol complex, but it will be much different than if chloride replaces one of the CH_3OD ligands. The increase in the line width is also consistent with those observed for the two complexes but can also

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[15] J. J. Davies and J. E. Wertz, *J. Magn. Resonance*, **1**, 500 (1969).

[16] Recent pulse polarographic and linear sweep electrochemical studies (E. P. Parry, I. B. Goldberg, D. H. Hern, and W. F. Goeppinger, to be submitted for publication in *J. Amer. Chem. Soc.*) have shown that the aquated complex contains one water molecule.

result in part from increased interaction of the unpaired electron with the deuterium on the D_2O adduct.

A temperature-dependent line width was observed by Garif'yanov, *et al.*[18a] For a 0.3 M solution of $TiCl_3 \cdot 6H_2O$ in methanol, the line width increased from 7 G at $-33°$ to 11 G at $+87°$ which they attributed to vibrational interaction between the ligands and the metal. At temperatures above $+15°$, we observe an increase in the line width of both species. This suggests the additional possibility of interconversion between two species as a mechanism of line broadening. At lower temperatures the line shape and the apparent g factor of the spectrum of the $TiCl_3$–H_2O–CH_3OH system would depend on the relative amounts of A and B species present, which is a function of the concentration of $TiCl_3$ and H_2O.

The two dominant complexes of titanium(III) chloride in methanol appear to be the chloro and dichloro complexes. The entire equilibrium, however, may include other complexes as well as cis and trans isomers, and thus we are not ready to evaluate the behavior of the entire system.

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Reinvestigation of Malonate as an Electron-Transfer Bridge. A Medium Effect

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Recent observations made in our laboratory have caused us to examine acid-catalyzed electron-transfer reactions between two positively charged metal complexes. Ignoring the possibility of a three-bodied collision, rate terms of the form $k_h(M_a^{n+})(M_b^{m+})(H^+)$ reflect transition states wherein a cation donates or accepts an electron from another cation which is tightly associated with a proton. Unless some special mitigative factor comes into play, the formation of this transition state will be electrostatically unfavorable relative to formation of the lower charged transition state described by the rate term $k(M_a^{n+})(M_b^{m+})$; *e.g.*, Barrett, Swinehart, and Taube[1] have shown that the rate of chromium(II) reduction of protonated acetatopentaamminecobalt(III) is slower than the rate of reduction of the unprotonated ion. Two such factors which increase the relative efficiency of the k_h pathway have been well documented. (1) Taube and Gould[2] have reviewed the considerable evidence for a k_h term in the chromium(II) reduction of pentaamminecobalt(III) complexes of dicarboxylic acids in which the two carboxylate groups are connected by a conjugated bond system. They suggested that the k_h term reflects chromium(II) attack at the remote carboxylate while the proton resides on the Co(III)-bound carboxylate. This protonation improves conjugation between the two metal centers and thus electron transfer is promoted. (2) Haim and coworkers[3] have studied the inner-sphere reduction of *trans*-A_4CoXY^{n+} complexes, where A is either ammonia or half an ethylenediamine, Y is the bridging ligand, and X is the ligand situated trans to Y. They observed a k_h path whenever X is basic enough (*e.g.*, acetate or azide) to provide a protonation site and ascribed the effect to a lowering of the energy of the acceptor orbital in the protonated form relative to that in the unprotonated species.

There exists in the literature an example of an acid-catalyzed cation–cation electron-transfer reaction that apparently does not fit into either of the above two categories. The reduction of malonatopentaamminecobalt(III) by chromium(II) was originally reported by Svatos and Taube[4] and later confirmed by Butler and Taube[5] to be controlled by a rate law in which there is a k_h term. It was also reported that this term was not present in the reduction of dialkylmalonato complexes. An interpretation of these observations, based on the relative acidity of the methylene protons of malonic acid, has been offered,[4–6] the significance of which has been to extend the general consideration of various factors which may promote the relative efficiency of k_h pathways. This anomalous example of acid-catalyzed electron transfer through a nonconjugated acid is based upon limited data which were obtained with sodium perchlorate as a supporting electrolyte.[7] It is now well established that the use of sodium perchlorate, rather than lithium perchlorate, is likely to have a significant effect on the measured acid dependencies of redox reactions.[5,8] Therefore we thought it worthwhile to reinvestigate the acid dependence of the malonato and dialkylmalonato reactions, using lithium perchlorate to maintain ionic strength constant at 4.00 F where protonation of the malonato complex should be favored.[1,9]

Experimental Section

Materials.—Crude samples of malonatopentaamminecobalt(III) and dimethylmalonatopentaamminecobalt(III) perchlorate salts were prepared as previously described.[5,10] These samples were purified *via* ion-exchange chromatography (Dowex 50W-X2, 200–400 mesh; elution with 2 F $NaClO_4$ separated the desired 2+ band from 3+ impurities) and then were crystallized two times from dilute sodium perchlorate solutions. The purified products exhibited visible absorption spectra typical for this class of compounds[5] (ϵ_{503} 73 M^{-1} cm^{-1}) and the proton magnetic resonance spectra in DMSO-d_6 were completely consistent with the proposed structures (Varian A-60, ambient temperature, CH_2 of malonato

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[1] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971).

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[3] (a) T. J. Przystas and A. Haim, *Inorg. Chem.*, **11**, 1017 (1972); (b) J. R. Ward and A. Haim, *J. Amer. Chem. Soc.*, **92**, 475 (1970); (c) A. Haim, *ibid.*, **86**, 2352 (1964).

[4] G. Svatos and H. Taube, *ibid.*, **83**, 4172 (1961).

[5] R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965).

[6] H. Taube, *Pure Appl. Chem.*, **24**, 289 (1970).

[7] While Taube and Svatos[4] did not identify the supporting electrolyte, their data are consistent with ours if it was sodium perchlorate. Professor H. Taube has kindly communicated to us that the malonato and substituted malonato data of ref 4, and most probably those of ref 5, were obtained in $NaClO_4$ media.

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