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Binuclear Dicyclopentadienyltitanium(III) Complexes: Magnetic Exchange Interactions Propagated by the Methylene Groups of Aliphatic Dicarboxylic Acid Dianions

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The preparation and characterization of a series of eight binuclear titanium(III) metallocenes with the composition $[(\eta^5\text{-}C_5H_5)_2Ti]_2[O_2C(CH_2)_nCO_2]$ (n = 0–4, 6, 8, 10) are reported. In the oxalate case (n = 0), it is shown that the oxalate dianion bridges in a bis bidentate fashion and forms five-membered chelate rings with each titanium ion. In the other cases, the $^-O_2C(CH_2)_nCO_2^-$ anion also bridges in a bis bidentate fashion; however, four-membered chelate rings are formed. The propagation of magnetic exchange interactions by the methylene groups of these aliphatic dicarboxylic acid dianions is investigated. Antiferromagnetic interactions are seen in variable-temperature magnetic susceptibility data for solid samples of the n = 0–3 complexes, whereas no signs of an interaction can be seen in the data for the other complexes. The binuclear nature of the complexes is established by EPR spectra taken for frozen toluene/benzene glasses. Triplet-state spectra are seen, from which estimates of intramolecular Ti–Ti distances can be made. It is suggested that an *intra*molecular exchange interaction is propagated by the methylene groups of the dicarboxylate bridge. Some support for this is found in the data obtained for two binuclear complexes bridged by substituted dicarboxylates. The two ethyl groups of the 3,3-diethylglutarate dianion would be expected to minimize contact of the two $(\eta^5\text{-}C_5H_5)_2Ti$ moieties in a binuclear complex, which is substantiated by the EPR spectra for a glass sample of this complex. It is important then, that the antiferromagnetic exchange interaction is seen to be greater for the 3,3-diethylglutarate complex ($J = -2.9$ cm^{-1}) than for the unsubstituted glutarate complex ($J = -0.82$ cm^{-1}). Similarly, the 2-ethyl-2-methylsuccinate complex gives $J = -2.4$ cm^{-1}, whereas the unsubstituted succinate complex gives $J = -1.6$ cm^{-1}.

Introduction

The possibility of nonadiabatic electron transfer between two transition-metal ions that are well separated is of growing interest. Nonadiabaticity[4] in electron transfer will occur in a solution redox reaction, for example, when the electrostatic interaction between the electronic manifolds of the two metal ions in the precursor complex is small, i.e., less than ca. 200 cm^{-1}. Such a weak interaction could occur if the bridging group between the two metal ions is very extended. The evidence for and against nonadiabatic electron transfer in solution redox reactions between metal complexes has been discussed.[5,6] In biological electron-transport chains it is generally believed that, in several cases, electrons are transferred between metal ions that are separated by distances greater than ca. 20 Å and nonadiabaticity is suspected.[7,8]

By studying magnetic exchange interactions in binuclear complexes with extended bridging groups, it might be possible to indirectly characterize the viability of a given extended organic bridge for propagating an interaction between the two metal ions in a precursor complex. Binuclear transition-metal complexes with very extended bridging groups are of limited supply. An antiferromagnetic exchange interaction of 3 cm^{-1} was identified recently for a binuclear copper(II) complex bridged by a 4,4′-diaminobiphenyl group.[9] The two copper(II) ions in this complex are separated by more than 12 Å. It appears from this and related studies[10] that the orbital compositions and energies of the extended bridging unit should interface well with those of the two metal centers. In a very recent paper,[11] the literature is reviewed to establish an experimentally determined limit function for long-range antiferromagnetic and ferromagnetic superexchange interactions between two paramagnetic centers. It was concluded that the exchange parameter depends exponentially on the distance between the two paramagnetic centers.

The present study was undertaken to ascertain whether a magnetic exchange interaction between two metal ions could be propagated by a chain of methylene carbon atoms. In the case of electron-transfer metalloproteins, it is possible that electrons transfer via saturated residues in polypeptide chains. A very convenient approach to prepare a series of binuclear Ti(III) complexes with methylene chain bridges was found with the oxidative addition of 1 mol of an aliphatic dicarboxylic acid to 2 mol of $(\eta^5\text{-}C_5H_5)_2Ti^{II}(CO)_2$. The preparation and characterization of the titanium(III) metallocenes I–IX are reported in this paper. In the following two papers the magnetic exchange interaction present in binuclear titanium(III) metallocenes bridged, on the one hand, by aliphatic cyclic and polycyclic dicarboxylate dianions and, on the other hand, by aromatic dicarboxylate dianions will be investigated.

At the outset of this paper it is important to note that EPR and magnetic susceptibility work[12,13] on organic biradicals is relevant to the present study. Two basic types of information have been obtained from EPR and magnetic susceptibility data for organic biradicals. Zero-field splitting in the triplet state is used to assess the distance between the two unpaired electrons in the biradical. The magnitude of magnetic exchange interaction and whether it is *intra*molecular in origin have also been evaluated.

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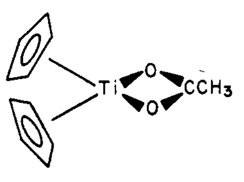

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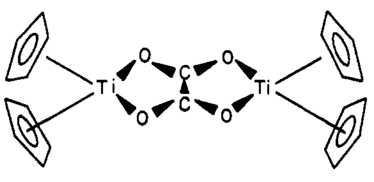

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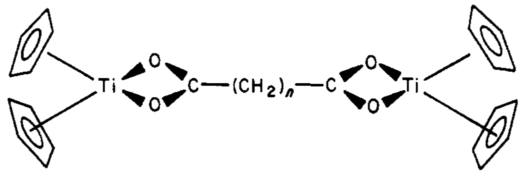


III, $n = 1$
IV, $n = 2$
V, $n = 3$
VI, $n = 4$
VII, $n = 6$
VIII, $n = 8$
IX, $n = 10$

Experimental Section

Compound Preparation. Most of the bridging dicarboxylic acid ligands were purchased from Aldrich and were used as received. Acetic acid (Baker) was distilled under N_2 prior to use. Bis(η^5-cyclopentadienyl)titanium dichloride was used as received from Pressure Chemical Co. Solvents were distilled from sodium and benzophenone under a nitrogen atmosphere. The titanium(III) metallocenes are air sensitive and most synthetic work was performed in a Vacuum Atmospheres Corp. inert-atmosphere glovebox with a helium-gas atmosphere. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences.

Samples of bis(η^5-cyclopentadienyl)titanium(III) chloride, $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$, were prepared according to literature methods.[14] Samples of bis(η^5-cyclopentadienyl)titanium(II) dicarbonyl, $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, were also prepared by literature methods[15] except with a slight modification. The aluminum sheets were activated by stirring overnight with a toluene solution of I_2 prior to use.

The preparations of the one mononuclear and 10 binuclear complexes discussed in this paper employ $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ as a reagent and are all very similar. Consequently, only one example synthesis will be given. A sample of (μ-succinato)-bis[bis(η^5-cyclopentadienyl)titanium(III)] (IV) was prepared by reacting a THF solution of 0.24 g (2 mmol) of succinic acid with 0.92 g (4 mmol) of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$. Additional THF was added until the total volume was ca. 40 mL. The solution was heated to ca. 50 °C and stirred for 15–20 min, whereupon gas was emitted (i.e., bubbles were observed). During this time, the solution changed from red-brown (the color of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ dissolved in THF) to blue-green. The solution was stirred overnight at ambient temperature, and then the solvent was pulled off in vacuo to yield a green-blue powder. The powder was slurried in boiling hexanes, filtered, and finally dissolved in hot toluene. Dark blue needlelike crystals were obtained by cooling and evaporating the solution.

Physical Measurements. Variable-temperature (4.2–244 K) magnetic susceptibility data were obtained with use of a Princeton Applied Research Model 150A vibrating-sample magnetometer operating at 13.5 kG. A calibrated GaAs diode was used for temperature determination. In all measurements, $CuSO_4{\cdot}5H_2O$ was used as a standard together with determinations on other compounds previously reported in the literature. Because the compounds are somewhat air sensitive, the samples for susceptibility determination were loaded into press-fit Kel-F sample cells in the inert-atmosphere box and introduced into the helium atmosphere of the magnetometer immediately after removal from the glovebox. Because the compounds change color upon exposure to air, it was easy to detect decomposition.

EPR spectra were recorded for liquid-nitrogen temperature glasses and for room-temperature solutions. Generally, a combination of toluene and benzene (4:1) was used as the solvent; however, 2-methyltetrahydrofuran was also occasionally used. X-Band data were measured with a Varian E-9 spectrometer operating in the range of 9.1–9.5 GHz. The X-band frequency was determined with a Hewlett Packard Model 5240A 12.4-GHz digital frequency meter. Q-Band data were measured with a Varian E-15 spectrometer employing an E-110 bridge and an E-266 cavity. Powdered DPPH was used as a reference. A few spectra were recorded for frozen glasses at S-band frequency (3.725 GHz) at the NIH regional EPR center at the University of Wisconsin, Milwaukee.

Mass spectral data were obtained on a MAT-Varian CH-5 spectrometer. Infrared spectra were recorded with a Perkin-Elmer Model 467 spectrophotometer.

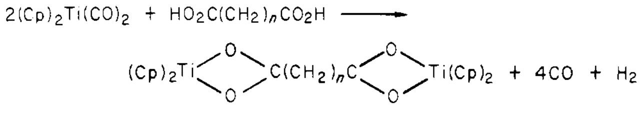
All of the compounds in this study are air sensitive both in the solid state and in solution. The samples for IR spectra were prepared as Nujol mulls in the helium-charged inert-atmosphere box. The samples for EPR measurements were loaded as solutions into quartz tubes in the inert-atmosphere box. The tubes were connected to a vacuum stopcock assembly and then removed from the box to be degassed and sealed on a glass vacuum line.

An iterative computer program[16] employing a function minimization routine was used to least-squares fit magnetic susceptibility and EPR data. Certain EPR spectra were computer simulated with a previously reported program.[17]

Results and Discussion

Compound Preparation. Three of the molecules described in this paper have been reported previously. The mononuclear complex I and the two binuclear complexes II (oxalate) and IV (succinate) were prepared by reacting $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ and the sodium salt of a carboxylic acid in an aqueous medium.[18]

Recently we found[19] a more convenient preparation of titanium(III) metallocenes with carboxylate ligands. The carboxylic acid is reacted directly with $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ to produce the binuclear titanium(III) metallocene with the evolution of CO and H_2 in the reaction



$$2(Cp)_2Ti(CO)_2 + HO_2C(CH_2)_nCO_2H \longrightarrow (Cp)_2Ti\langle O_2\rangle C(CH_2)_nC\langle O_2\rangle Ti(Cp)_2 + 4CO + H_2$$

The product gases were verified with gas chromatography. It is important to note that $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ has already been found to be a useful reagent.[20–23] Interestingly, $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ reacts with excess acetic acid to give the titanium(IV) complex $(\eta^5\text{-}C_5H_5)_2Ti(O_2CCH_3)_2$.[24]

Complexes I–IX were characterized by both analytical data, which are given in Table I, and mass spectral data. The mass spectrum for each compound shows an intense pattern of peaks assignable to the parent ionization peak.

Infrared Spectroscopy and Structural Considerations. The infrared spectra of complexes I (acetate) and IV (succinate) in THF have been reported[18] to exhibit an antisymmetric carboxyl stretching band (ν_{as}) at ca. 1520 cm^{-1} and a symmetric carbonyl stretching band (ν_s) at ca. 1430 cm^{-1}. The difference between these two frequencies is less than that for free acetate (1560 and 1416 cm^{-1}), which indicates that each carboxylate is chelating one Ti(III) ion.[25] If the carboxylate

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Table I. Analytical Data

		% C		% H		% Ti	
compd	bridge	calcd	obsd	calcd	obsd	calcd	obsd
I	acetate(2–)	60.78	60.78	5.53	5.41	20.20	20.04
II	oxalate(2–)	59.51	61.76	4.50	4.70	21.58	20.03
III	malonate(2–)	60.31	59.18	4.80	4.87	20.92	20.97
IV	succinate(2–)	61.07	61.33	5.08	5.24	20.29	19.80
V	glutarate(2–)	61.78	61.78	5.35	5.30	19.71	19.47
VI	adipate(2–)	62.45	63.16	5.60	5.71	19.16	18.66
VII	suberate(2–)	63.68	63.79	6.06	6.27	18.14	17.64
VIII	sebacate(2–)	64.80	65.12	6.47	7.20	17.23	15.31
IX	dodecanedioate(2–)	65.80	65.24	6.85	6.86	16.40	15.64
X	3,3-diethylglutarate(2–)	64.21	63.65	6.33	6.12	17.66	17.82
XI	2-ethyl-2-methylsuccinate(2–)	63.04	62.56	5.89	5.78	18.62	17.76

moieties were monodentate in these complexes, it is known that the difference in these frequencies would be much larger than in the free ion.

Nujol-mull IR spectra were run for our complexes III, IV, and VI, and in each case bands were seen at ca. 1520 and 1450 cm^{-1}. Each carboxylate moiety apparently interacts with a Ti(III) ion to give four-membered chelate rings as pictured in the Introduction. It is clear that complexes III–IX do *not* have a copper(II) acetate structure. First, the EPR and magnetic susceptibility data for complexes III–IX (vide infra) are not in keeping with a copper(II) acetate structure where a strong interaction is expected. Second, the carboxyl frequencies for complexes III–IX are quite different from those observed for the monocyclopentadienyl carboxylate complexes $[(\eta^5\text{-}C_5H_5)Ti(O_2CR)_2]_2$.[26–28] These latter complexes are presumed to have the copper(II) acetate structure and have a difference in ν_{as} and ν_s in the range of 150–200 cm^{-1}. Third, a copper(II) acetate structure for complexes III–IX would require a polymeric structure which is not in keeping with the mass spectral data, the fact that the complexes are soluble in toluene, and the EPR spectra which are characteristic of binuclear complexes (vide infra).

The oxalate-bridged complex II exhibits an IR spectrum which is appreciably different from those observed for the dicarboxylate compounds. An intense band is seen at 1650 cm^{-1} which can be assigned as ν_{as} for the CO_2 moiety. A sharp, but weak, feature is found at 1340 cm^{-1}, and this is assigned to ν_s. This is the pattern of ν_{as} and ν_s expected[29] if the oxalate ion is bridging in a bis bidentate fashion with five-membered chelate rings as illustrated in the Introduction. Further support for this structure of the oxalate-bridged complex II will be given in the EPR section.

An unsuccessful attempt was made in this study to determine the single-crystal X-ray structure of one of the dicarboxylate-bridged complexes. X-ray quality crystals of the adipate-bridged complex VI were grown, and a data set was collected. Repeated efforts to solve the structure by either heavy-atom or direct techniques were frustrated by pseudosymmetry.

Magnetic Susceptibility. Data have been measured previously for the oxalate-bridged complex II.[27] The effective magnetic moment per Ti(III) ion, μ_{eff}/Ti, was reported to be spin only and independent of temperature from room temperature down to 130 K. The workers in this study assumed a four-membered chelate structure for the oxalate bridging and concluded that the presence of only one C–C single bond in the bridge precluded the presence of a magnetic exchange interaction. No EPR data were reported.

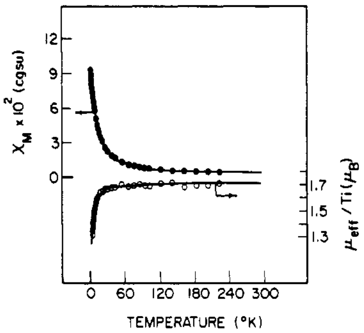

Figure 1. Plots of effective magnetic moment per titanium(III) ion, μ_{eff}/Ti, and molar paramagnetic susceptibility per binuclear complex, χ_M, vs. temperature for (μ-oxalato)-bis[bis(η^5-cyclopentadienyl)titanium(III)]. The solid lines result from least-squares fits of the data to the theoretical equation.

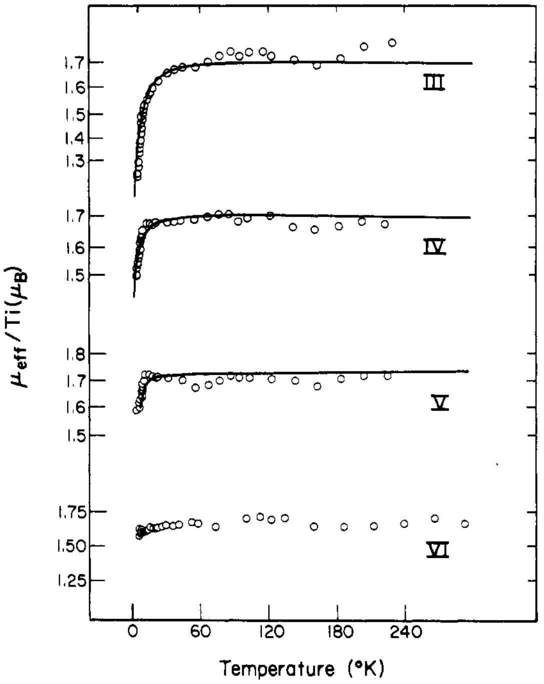

Figure 2. Plots of μ_{eff}/Ti vs. temperature for the binuclear titanium(III) metallocenes bridged by malonate(2–) (III), succinate(2–) (IV), glutarate(2–) (V), and adipate(2–) (VI). The solid lines represent the theoretical fits of the data.

The magnetic susceptibility for the oxalate-bridged complex II was measured from 224 to 4.2 K; the data are given in Table II.[30] Figure 1 shows that there is, in fact, a weak antiferromagnetic exchange interaction present in this compound.

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The value of μ_{eff}/Ti drops from spin only at high temperatures to 1.33 μ_B at 4.2 K. Least-squares fitting to the Bleaney–Bowers equation (via $\hat{H} = -2J\hat{S}_1{\cdot}\hat{S}_2$) for an $S_1 = S_2 = {}^1/_2$ binuclear complex gives an exchange parameter of $J = -2.2$ cm^{-1} and $g = 1.99$. The solid lines in Figure 1 represent this fit.

The susceptibility data for dicarboxylate-bridged complexes III–VI are given in Tables III–VI.[30] It was of interest to establish whether a magnetic exchange interaction exists in this series of complexes and just how extended the methylene chain can become before the magnetic exchange interaction disappears. Illustrated in Figure 2 are the μ_{eff}/Ti vs. temperature curves for the first four members (n = 1–4) of the series. It can be seen that, as the length of the methylene chain is increased, the antiferromagnetic exchange interaction decreases until there is no sign of an interaction with the adipate-bridged (n = 4) complex VI. There is a decrease in μ_{eff}/Ti at low temperatures for the malonate-bridged (n = 1) complex. At 4.2 K, μ_{eff}/Ti is 1.25 μ_B, and fitting the data gives $J = -2.6$ cm^{-1} and $g = 2.00$. Fitting the data for the succinate (n = 2) complex gives $J = -1.6$ cm^{-1} and $g = 2.00$, whereas the data for the glutarate (n = 3) complex lead to $J = -0.82$ cm^{-1} and $g = 2.01$. Because there is no sign of an interaction in the case of the adipate (n = 4) complex, the exchange parameter for an antiferromagnetic interaction is limited by $-J < \sim 0.3$ cm^{-1}.

Tables VII–VIII[30] give the data for complexes VII and IX, where the length of the methylene chain increases from 6 to 10. Figure 3[30] shows that there is no sign of an antiferromagnetic exchange interaction in either of these two compounds.

The monotonic decrease in magnitude of antiferromagnetic exchange interaction as the methylene chain is varied from n = 1 to n = 3 and the absence of interactions for the n = 4, 6, and 10 complexes suggest that the magnetic exchange is *intra*molecular rather than *inter*molecular in nature. The results of the following paper substantiate this. The X-ray structure for the analogous complex (2,4-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)] shows that the cyclopentadienyl ligands provide a certain amount of steric bulk to separate the binuclear complexes.[31] This complex exhibits a weak ferromagnetic interaction which was shown to be not due to an extended intermolecular interaction by studying the magnetization of the compound as a function of magnetic field.[32] It is difficult to definitively demonstrate that the antiferromagnetic exchange interactions seen for the solids are *intra*molecular in nature. As will be seen in the next section even EPR spectra taken for frozen glasses of these compounds do *not* definitively establish the presence of an *intra*molecular exchange interaction in these binuclear complexes.

If it is accepted that the antiferromagnetic exchange interactions observed for the solids are *intra*molecular, this does not necessarily mean that the interactions are propagated by the methylene carbon chains. It is possible that the molecules with long methylene chains are positioned head to tail in the solid. The *intra*molecular interaction between two Ti(III) ions could, then, be propagated by contact of two η^5-C_5H_5 ligands. CPK models show, however, that, by introducing substituents on the methylene carbon atoms, this could be prevented. Two additional binuclear complexes were prepared, one bridged by the dianion of 3,3-diethylglutaric acid and the other by the dianion of 2-ethyl-2-methylsuccinic acid. Magnetic susceptibility data for these two complexes are illustrated in Figures 4 and 5,[30] respectively (Tables IX[30] and X[30]). It was found that the antiferromagnetic interaction for the 3,3-diethylglutarate bridged complex ($J = -2.9$ cm^{-1}) is greater than what was seen for the unsubstituted glutarate complex ($J = -0.82$ cm^{-1}). This is in keeping with the idea that the interaction is propagated by the methylene carbon chain. The same comparison is found for the binuclear complex bridged by 2-ethyl-2-methylsuccinate. This complex exhibits a greater interaction ($J = -2.4$ cm^{-1}) than was seen for the unsubstituted succinate complex ($J = -1.6$ cm^{-1}).

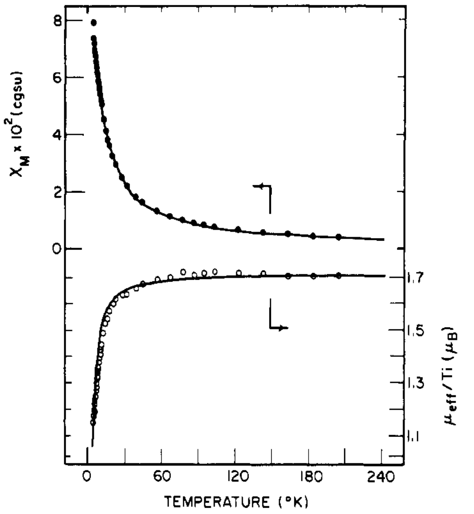

Figure 4. Plots of effective magnetic moment per titanium(III) ion, μ_{eff}/Ti, and molar paramagnetic susceptibility per binuclear complex, χ_M, vs. temperature for the binuclear titanium(III) metallocene bridged by the dianion of 3,3-diethylglutaric acid. The solid lines result from a least-squares fit of the data to the theoretical equation.

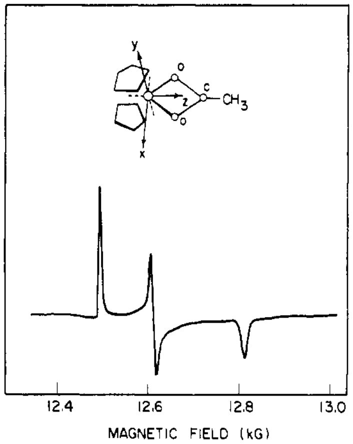

Figure 6. Q-Band EPR spectrum of a liquid-nitrogen-temperature toluene/benzene (4:1) glass of (acetato)bis(η^5-cyclopentadienyl)titanium(III), mononuclear complex I. The inset shows molecular orientation of the **g** tensor, where the x and z axes lie in the TiO_2C plane.

Electron Paramagnetic Resonance. Figure 6 shows the Q-band liquid-nitrogen temperature spectrum of a toluene/benzene glass of complex I, the mononuclear acetate. The spectrum is characteristic of a rhombic **g** tensor with g values of 2.002, 1.953, and 1.983. These values are typical of mononuclear dicyclopentadienyltitanium(III) complexes, even those where the two noncyclopentadienyl ligands are not the same, i.e., $(\eta^5\text{-}C_5H_5)_2Ti(X)(Y)$.[33,34] A single-crystal EPR

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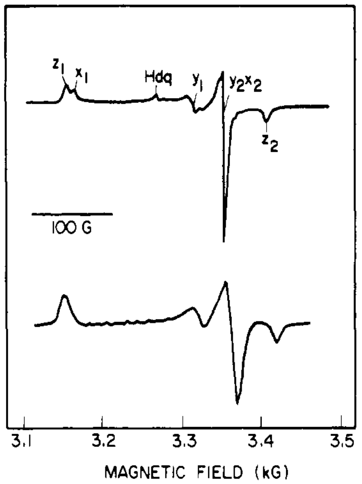

Figure 7. X-Band EPR spectrum (upper tracing) taken at liquid-nitrogen temperature of a toluene/benzene (4:1) glass of oxalate-bridged complex II. The lower tracing illustrates the computer-simulated spectrum.

study of bis(η^5-cyclopentadienyl)vanadium(IV) dichloride doped into the corresponding diamagnetic Ti(IV) host resulted in very similar values for the principal components of the **g** tensor.[35,36] In fact, the principal g values for the molecules $(\eta^5\text{-}C_5H_5)_2V^{IV}(L')(L'')$ do not depend on the nature of the ligands L′ and L″. It is safe to conclude that the molecular orientation of the principal components of the **g** tensor is the same for the acetate complex I as found for $(\eta^5\text{-}C_5H_5)_2VCl_2$. The drawing inset in Figure 6 shows the directions of the **g**-tensor components. If we make the reasonable assumption that the four-membered carboxylate chelate ring is planar, one component of the **g** tensor, defined here as g_z, lies in the plane and bisects the O–Ti–O angle. The g_x axis also lies in this plane. It is to be noted that the axes of the **g** tensor, as they are identified here, are relabeled from those in the single-crystal $(\eta^5\text{-}C_5H_5)_2VCl_2$ work. The intermediate field $g = 1.983$ signal is the g_z component, whereas $g_x = 2.002$ and $g_y = 1.952$. This selection of the orientation of the z axis is convenient for the discussion of binuclear complexes.

The spectrum for a binuclear titanium(III) metallocene consists of six $\Delta M_s = 1$ signals which arise from a splitting of each of the three monomer signals into two signals. This so-called zero-field splitting is due to a through-space magnetic dipole interaction between the two unpaired electrons in the binuclear complex. In addition to the six $\Delta M_s = 1$ transitions, a formally forbidden $\Delta M_s = 2$ transition is seen at half the magnetic field. The intensity of this transition depends on the magnitude of the zero-field splitting of the triplet state. The analysis of the EPR spectrum of a binuclear $S_1 = S_2 = {}^1/_2$ complex generally can be very involved.[37] The relative orientations of the **g** tensors on the two metal centers and the zero-field splitting tensor $\hat{D}$ must be considered. The symmetry of the complex dictates three limiting cases. If the binuclear complex is centrosymmetric, then the **g** tensors on the two metal centers will be collinear and they will also be collinear with the **D** tensor, the z component of which lies along the metal–metal vector. A second limiting situation arises when the **g** tensors on the two metal centers are collinear but *not* collinear with the **D** tensor. In this case there is a nonzero angle between g_z of one metal and D_z. The third limiting situation occurs when the **g** tensors on the two metal centers are not collinear with each other or the **D** tensor.

The spin Hamiltonian for the $S = 1$ state of the binuclear complex is

$$\hat{H} = \beta\hat{S}\cdot\hat{g}\cdot\hat{H} + D(\hat{S}_z^2 - {}^1/_3S^2 - {}^1/_3) + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (1)$$

where D is the axial zero-field splitting parameter and E is the nonaxial (rhombic) zero-field splitting parameter. Wasserman et al.[38] derived the equations for the resonance fields of the six $\Delta M_s = 1$ transitions for a randomly oriented sample where the molecular **g** and **D** tensors are parallel or, at least, nearly parallel. In terms of H_0, the magnetic field expected for a free electron, the six resonance fields are given by eq 2.

$$H_{x_1} = \frac{2.0023}{g_x}[(H_0 - D + E)(H_0 + 2E)]^{1/2} \quad (2a)$$

$$H_{y_1} = \frac{2.0023}{g_y}[(H_0 - D - E)(H_0 - 2E)]^{1/2} \quad (2b)$$

$$H_{z_1} = \frac{2.0023}{g_z}[(H_0 - D)^2 - E^2]^{1/2} \quad (2c)$$

$$H_{x_2} = \frac{2.0023}{g_x}[(H_0 + D - E)(H_0 - 2E)]^{1/2} \quad (2d)$$

$$H_{y_2} = \frac{2.0023}{g_y}[(H_0 + D + E)(H_0 + 2E)]^{1/2} \quad (2e)$$

$$H_{z_2} = \frac{2.0023}{g_z}[(H_0 + D)^2 - E^2]^{1/2} \quad (2f)$$

Equation 2 was incorporated into an iterative least-squares computer program to fit the spectra for values of g_x, g_y, g_z, $|D|$, and $|E|$. It is important to note that the values of g_x, g_y, and g_z for the triplet state will be equal to those of the individual metal centers that make up the binuclear complex only if the complex is centrosymmetric.

In addition to fitting observed resonance fields to the above equations, the X-band and Q-band spectra for a few selected complexes in this and the following two papers were simulated by a computer program written by Gibbons.[17] This program is based on the direct eigenfield method of Belford et al.[39] and at its present stage of development requires the **g** tensors on the two metal centers to be aligned. The relative orientation of the **g** tensor and the titanium–titanium vector (z axis of the **D** tensor) can be varied in this program. The two angles η and ξ relate the principal g axes to those of the zero-field D tensor. The input parameters to the program are g_x, g_y, g_z, the Ti–Ti distance which is used to calculate D, a value for the nonaxial zero-field parameter E, linewidth data, and the η and ξ angles, as well as the number of orientations of the binuclear complex relative to the magnetic field.

EPR spectra of complexes I–IX have been run at liquid-nitrogen and room temperatures with use of X-band frequencies (ca. 9.1 GHz) and at liquid-nitrogen temperature with use of Q-band frequencies (ca. 35 GHz). A few samples were also examined at liquid-nitrogen temperature with use of the S-band frequency of 3.725 GHz. All samples were dissolved in a toluene/benzene (4:1) solution. Powder spectra run at room temperature and liquid-nitrogen temperature only gave broad unresolved derivative-like signals.

The oxalate-bridged complex II is expected to be rigid and approach a centrosymmetric structure. The top tracing in Figure 7 illustrates the liquid-nitrogen temperature X-band EPR spectrum for a glass containing this compound. The spectrum is clearly that of a triplet-state molecule. An assignment of the various features is indicated in Figure 7. The

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Table XI. Theoretical Fit of X-Band and Q-Band EPR Spectra for a Liquid-Nitrogen-Temperature Toluene/Benzene Glass (4:1) of (μ-Oxalato)-bis[bis(η^5-cyclopentadienyl)titanium(III)][a]

		field, G	
	peak[b]	obsd	calcd
X-band	X1	3 310	3 309
	Y1	3 166	3 151
	Z1	3 157	3 159
	X2	3 352	3 355
	Y2	3 354	3 354
	Z2	3 408	3 410
	half-field ($\Delta M_s = \pm 2$)	1 680	1 643
Q-band	X1	12 792	12 719
	Y1	12 396	12 404
	Z1	12 498	12 502
	X2	12 836	12 837
	Y2	12 610	12 607
	Z2	12 756	12 753

[a] Fit to $D = 0.0116$ cm^{-1}, $E = 0.0024$ cm^{-1}, $g_x = 1.952$, $g_y = 2.000$, and $g_z = 1.981$. [b] The X-band features (except $\Delta M_s = 2$ transition) are identified in Figure 5 and Q-band features in Figure 6.

z axis of the **g** tensor is collinear with the z axis of the **D** tensor, i.e., Ti–Ti vector. As per our previous study[32] of binuclear titanium(III) metallocenes, the zero-field splitting seen for the dicarboxylate-bridged complexes is most likely due to a through-space dipole–dipole interaction. Dipole–dipole zero-field splitting, D_{dd}, is related to the Ti–Ti distance R by eq 3.[40] In this equation, θ is the angle between the principal axis

$$|D_{dd}| = \frac{0.325g^2}{R^3}\langle 1 - 3\cos^2\theta\rangle \qquad (3)$$

of the **D** tensor and the applied magnetic field, D_{dd}, is given in cm^{-1} and the Ti–Ti distance in Å. The maximum zero-field splitting occurs for a centrosymmetric complex when $\theta = 0°$, that is, when the magnetic field is along the z axis (**R** vector). Thus, the g_z signal exhibits the greatest splitting with a magnitude of $2D$. The separation between the Z_1 and Z_2 signals is 251 G with g_z calculated as 1.981 from the field position equally spaced between these two signals. Equation 3 gives a Ti–Ti distance of 5.97 Å with these values. This distance is in agreement with the structure suggested above, where the oxalate bridges in a bis bidentate fashion and forms five-membered chelate rings with each titanium ion. A Ti–Ti distance of 5.85 Å was calculated from a model for this type of bridging by assuming reasonable bond lengths and angles. Five-membered chelate rings are also found in (μ-biimidazolato)-bis[bis(η^5-cyclopentadienyl)titanium(III)]. The X-ray structure[40] of this compound gives a Ti–Ti distance of 6.02 Å.

The best check of our assignment for the signals seen in the X-band spectrum of the oxalate complex is obtained by computer simulating the X-band spectrum and then using the same parameters to simulate the Q-band spectrum. The procedure that we followed is to use eq 2 and the X-band spectral assignment given in Figure 7 to obtain values for $g_x = 2.000$, $g_y = 1.952$, $g_z = 1.981$, $|D| = 0.011\,60$ cm^{-1}, and $|E| = 0.0024$ cm^{-1}. As can be seen in Table XI, a good fit of the observed resonances to eq 2 was obtained. These spin-Hamiltonian parameters were then used as input into the computer simulation program to give the lower tracing in Figure 7. The angles η and ξ were both taken as zero. As can be seen, the appearance of the X-band spectrum is simulated by these parameters. The derivative feature at 3270 G ($g = 1.99$) appears consistently from one sample preparation to another and is most likely a double quantum transition.

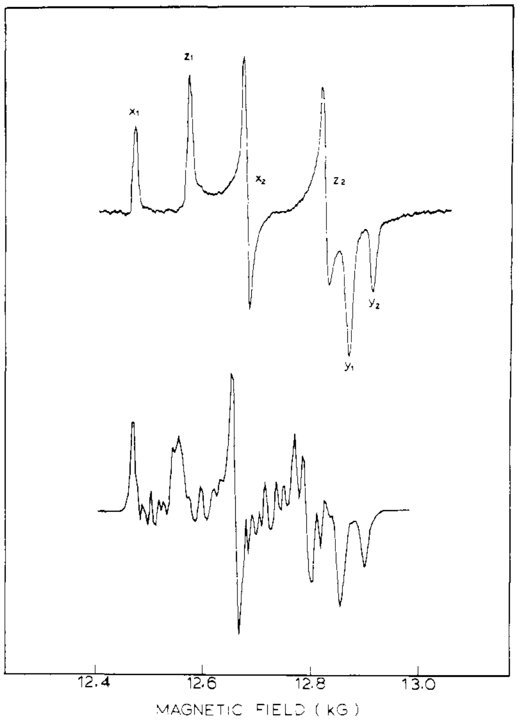

Figure 8. Q-Band EPR spectrum (upper tracing) taken at liquid-nitrogen temperature of a toluene/benzene (4:1) glass of oxalate-bridged complex II. The lower tracing illustrates the computer-simulated spectrum.

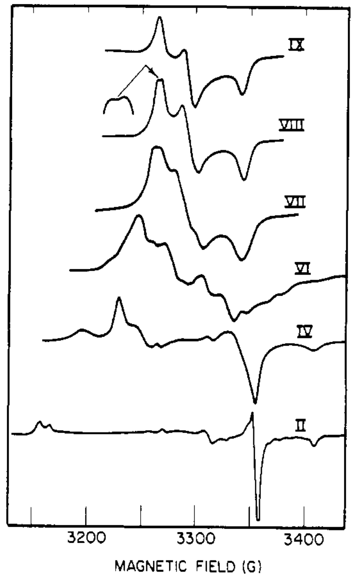

Figure 9. X-Band EPR spectra taken for liquid-nitrogen-temperature toluene/benzene glasses of the binuclear complexes bridged by $^-O_2C(CH_2)_nCO_2^-$, where n = 0, 2, 4, 6, 8, and 10. Compound numbers are indicated next to each spectrum.

The Q-band spectrum seen in Figure 8 for the oxalate-bridged complex has a textbook appearance. The lower tracing in this figure shows the simulation using the same parameters as above. The simulation is quite reasonable. Cost limitations dictated the number of molecular orientations used in the simulation, and nonaveraging peaks are seen between the features in the simulated spectrum. The features in the Q-band spectrum encompass a larger magnetic field range than in the X-band case, and, consequently, a larger number of molecular orientations is required to eliminate nonaveraging effects. It is to be noted that, when the X-band and Q-band spectra of the oxalate complex are compared, the zero-field splitting in

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(40) Fieselmann, B. F. Ph.D. Thesis, University of Illinois, 1977.

a given *g*-component signal is independent of the microwave frequency used.

A comparison of the X-band EPR spectra taken at liquid-nitrogen temperatures for toluene/benzene (4:1) glasses for the series of binuclear titanium(III) metallocenes bridged by $^{-}O_2C(CH_2)_nCO_2^{-}$ is seen in Figure 9. The lowest tracing is for the oxalate-bridged complex, and as one moves up the figure two methylene groups are added in each successive tracing. There is a monotonic change in the spectrum as the methylene chain is extended. Large zero-field splittings are seen for the complexes with the shortest bridges and as the bridge length is increased, the zero-field splitting decreases. The spectrum for complex IX, which is bridged by $^{-}O_2C(CH_2)_{10}CO_2^{-}$, does *not* show any resolved zero-field splitting, and the three signals seen are essentially at the same *g* values as those found for the acetate monomer.

The concentration dependence of the frozen-glass spectra was checked for the glutarate (n = 3) and adipate (n = 4) complexes. Solutions were prepared in the concentration range of 0.001–0.1 M and then frozen to give glasses. There were no changes seen in either the full-field ($\Delta M_s = 1$) or the half-field region of the frozen glass spectra. It is clear from these results that the zero-field splittings that are seen result from *intra*molecular magnetic dipole interactions.

A computer simulation of each spectrum would be needed in order to accurately determine the zero-field splittings and consequently the Ti–Ti distances for all of the complexes frozen in the glass media. This is made very difficult by two factors. First, some of the binuclear complexes with extended dicarboxylate bridges can exist in more than one molecular conformation in the frozen glass. Second, several of the complexes probably have a conformation in which the **g** tensors on the two metal centers are not aligned. The computer simulation program presently available to us can*not* handle this situation. However, it is still possible to analyze the Q-, X-, and S-band data available for several of the complexes to get moderately accurate assessments of the zero-field splittings and Ti–Ti distances for the complexes in the frozen glasses.

The frozen-glass X-band spectrum of the malonate-bridged (n = 1) complex is poorly resolved and, consequently, difficult to interpret. The outermost features, one at high and the other at low field, are most likely due to the zero-field split g_z signal. The separation between those two signals gives a $|D|$ value of 0.0102 cm^{-1}. This D value corresponds to a Ti–Ti distance of 6.28 Å. A CPK model for this molecule is fairly rigid and gives a calculated distance of ca. 6.5 Å.

The EPR data for the succinate-bridged complex IV show how it is possible to assess the zero-field splitting for a complex without detailed computer simulations. Figure 10 shows the frozen-glass X-band and Q-band spectra for this complex which has two methylene groups in the bridge. The X-band spectrum is well resolved, and this indicates that only one conformation of the complex is present in the glass. The three low-intensity signals in the middle of the spectrum are due to monomeric species resulting from a partial dissociation of the complex upon dissolution. These three signals vary in intensity relative to the other signals in spectra for different sample preparations. The appearance of the X-band spectrum does not change if the solution is cooled very slowly (ca. $1^1/_2$ h) to form the glass.

The X-band spectrum for the succinate complex has close to an axial appearance; that is, the g_x and g_y field positions are close to each other and they would be expected to have the same magnitude of zero-field splitting. The signals marked 1 and 6 could, thus, be assigned to the zero-field split g_z resonances. A pairing of signal 2 with 4 and 3 with 5 comprise the split g_x and g_y resonances. The separation between signals 1 and 3 of the Q-band spectrum corresponds well to the separation (215 G) between the *z* features of the X-band spectrum. The separations between Q-band signals 1 and 2 and between 3 and 4 are ca. 100 G. This is close to the splitting of the g_x and g_y signals as tentatively assigned above for the X-band spectrum. Although these assignments of possible zero-field splittings appear to be consistent between the X-band and Q-band spectra, the correspondence of *g* values between the two assignments is very poor. It is likely that the **g** tensor for the binuclear succinate-bridged complex results from an averaging of *misaligned* **g** tensors on the two titanium centers. This is substantiated by the fact that we could not find a single set of parameters for the computer simulation program that would simultaneously fit the X-band and Q-band spectra.

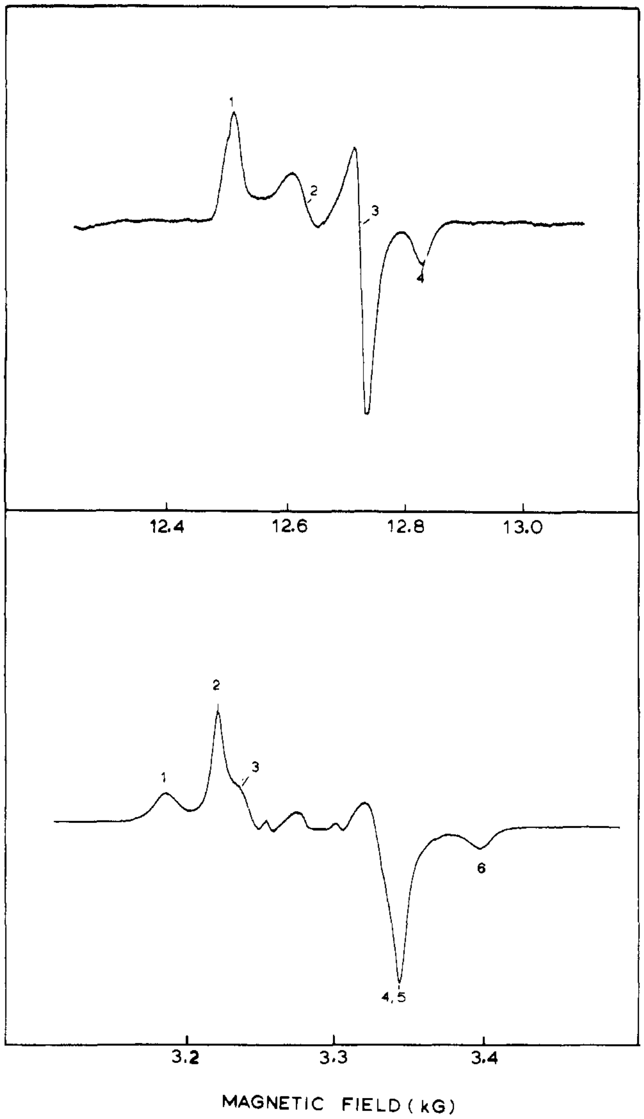


Figure 10. Q-Band (upper tracing) and X-band (lower tracing) EPR spectra of a ca. 80 K toluene/benzene glass of the succinate-bridged binuclear complex IV.

It is still possible to assess the zero-field splitting for the succinate-bridged complex. This can be done by further deemphasizing the Zeeman interaction compared to the zero-field interaction, which is accomplished by going to microwave frequencies that are even less than X band (ca. 9 GHz). At S-band (ca. 4 GHz) frequencies, the magnetic field positions of the three *g* values for our titanium(III) metallocenes only encompass a range of 20–30 G, which approaches the observed line widths. In short, the noncollinearity of the **g** tensors will be less important relative to the zero-field splitting at S-band frequencies. The spectrum should then

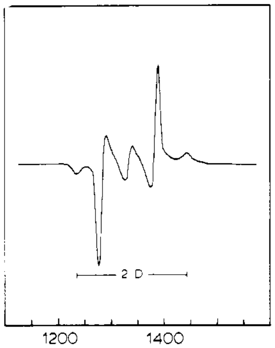


Figure 11. S-Band EPR spectrum of a frozen toluene/benzene glass of the succinate-bridged binuclear complex IV.

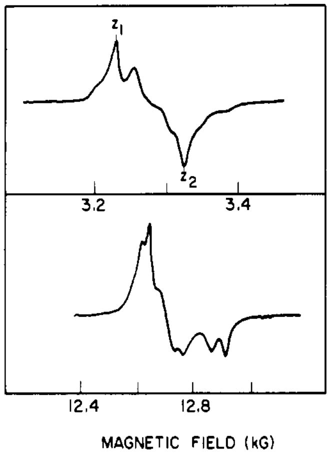


Figure 12. X-Band (upper) and Q-band (lower) EPR spectra for a liquid-nitrogen-temperature toluene/benzene glass of the glutarate-bridged complex V.

approach an axial limit. From eq 3 it can be seen that, when the magnetic field is along the principal axis of the **D** tensor, that is, along the Ti–Ti vector, a dipolar zero-field splitting should be observed which is twice as large as that observed when the magnetic field is along the other two axes (x, y) of the **D** tensor. This is what is seen in the S-band (3.725 GHz) spectrum illustrated in Figure 11 for a frozen glass of the succinate complex. The separation between the two outermost features (bumps) in this spectrum is 215 G and between the two innermost features is ca. 104 G. These separations are very close to those obtained from the X-band spectrum. Apparently, X-band frequencies almost provide the limit for deemphasizing the **g** tensor anisotropy and noncollinearity effects relative to the zero-field splitting.

From the separation between the outermost features in the S-band (or X-band) spectrum of the succinate-bridged complex, a D value of 0.0100 cm^{-1} can be calculated. Equation 3 with $g_z = 1.98$ was used to calculate a Ti–Ti distance of 6.33 Å. As per a CPK model, this distance corresponds to some intermediate conformation of the binuclear succinate complex. In the most outstretched form of the molecule the maximum Ti–Ti distance of ca. 8.5 Å can be obtained from a CPK model. Additional discussion of the conformation of the succinate complex will appear in the following paper where complexes bridged by the dicarboxylic acids of cyclohexane are described. The X-band and Q-band EPR spectra for a frozen glass of the 2-ethyl-2-methylsuccinate-bridged complex are very similar to those seen for the unsubstituted succinate complex.

Figure 12 illustrates the X-band and Q-band spectra of a frozen glass of the glutarate-bridged complex dissolved in toluene/benzene (4:1). Both of these spectra appear to have seven features. This is evidence for the fact that at least two conformations of the binuclear complex are frozen out in the glass. No S-band data were measured for this complex. The X-band spectrum does approach an axial appearance. A suggested zero-field splitting for the z component of the **g** tensor of one conformer is indicated in the figure. This peak-to-peak separation gives $|D| = 0.0041$ cm^{-1} which yields a Ti–Ti distance of 8.53 Å. However, it was not possible to arrive at an assignment of the various signals that would fit to eq 2 or which agreed with a computer simulation. It is likely that the **g** and **D** tensors are misaligned for this complex and S-band data are needed.

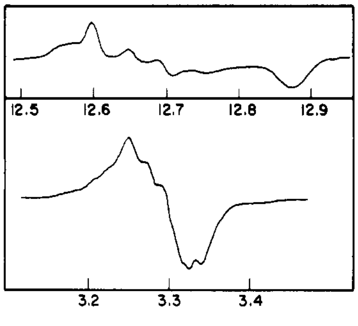
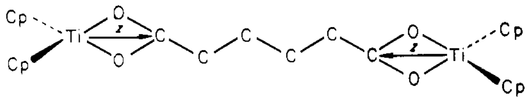


Figure 13. X-Band (lower) and Q-band (upper) EPR spectra for a liquid-nitrogen-temperature toluene/benzene glass of the adipate-bridged complex VI.

EPR spectra at both X-band and Q-band frequencies were recorded for a frozen glass of the 3,3-diethylglutarate-bridged complex. It was anticipated (vide supra) that the introduction of the two ethyl substituents would lead to a predominance of the more outstretched form of this binuclear complex. This is borne out by the EPR spectra which show a larger proportion of conformer with a large Ti–Ti distance for the substituted complex than for the unsubstituted complex.

The data for the adipate-bridged complex are indeed interesting. The complicated X-band and Q-band spectra for a frozen glass are shown in Figure 13. There are clearly enough signals in each of these spectra to indicate the presence of two conformations of the complex in the glass. An outstretched conformation of this complex has a Ti–Ti distance of ca. 11.2 Å as estimated from a CPK model. The X-band spectrum approaches an axial appearance; that is, it is close to being symmetric about a mirror plane perpendicular to the plane of the spectrum and located at a central magnetic field position. Again, however, the S-band spectrum, which is illustrated in Figure 14, more closely approaches the axial limit. The S-band spectrum is clear evidence for the presence of two different conformations of the adipate-bridged complex in the glass. Signals 1, 2, 7, and 8 reflect the presence of one conformer where $2|D| = 240$ G. This magnitude of zero-field splitting corresponds to a Ti–Ti distance of 6.10 Å. Signals in the regions indicated 3, 4, 5, and 6 are due to the second conformer. The separation between 3 and 6 gives $2|D| =$ ca. 85 G which leads to an assessment of a Ti–Ti distance of 8.6 Å. The above assignments were verified by computer simulation. The S-band spectra for both conformations were simulated independently for g values of ca. 1.98. The two computer-simulated spectra were then superimposed to give the spectrum illustrated in Figure 15. The resultant simulated spectrum agrees well with the experimental spectrum. Conformers of the adipate-bridged complex with Ti–Ti distances of 6.1 and 8.6 Å are bent, and



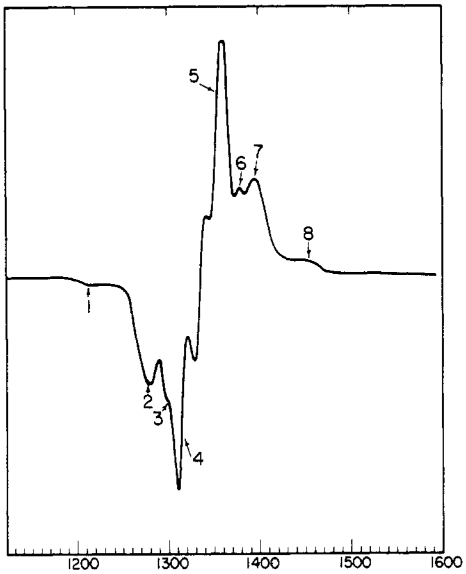


Figure 14. S-Band EPR spectrum for a liquid-nitrogen-temperature toluene/benzene glass of the adipate-bridged complex VI.

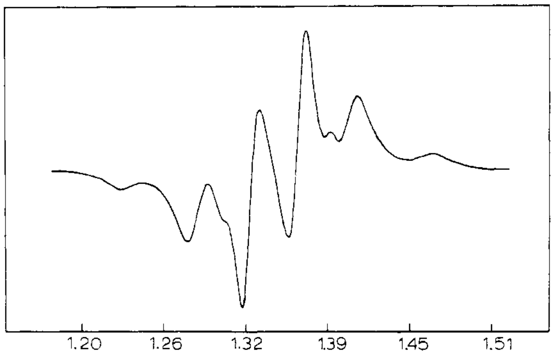


Figure 15. Computer-simulated S-band spectrum for a liquid-nitrogen-temperature toluene/benzene glass of the adipate-bridged complex VI. See text for details.

consequently the two $(\eta^5$-$C_5H_5)_2$Ti moieties are brought into closer proximity than would be present in the outstretched conformation.

The $\Delta M_s = 2$ transitions observed for the oxalate(II), succinate(IV), and adipate(VI) complexes in liquid-nitrogen-temperature toluene/benzene glasses are shown in Figure 16. The appearance of the $\Delta M_s = 2$ signal changes from one complex to another. It is known that the intensity patterns and field positions of "half-field" lines are affected considerably by variation in the symmetry of the molecule.[41] Half-field transitions were seen for all of the binuclear complexes except complexes VIII and IX. The $\Delta M_s = 2$ transition gains intensity from zero-field splitting, and it follows that, as the methylene chain length increases, the intensity of the $\Delta M_s = 2$ signal would decrease.

Comments and Comparison with Related Systems. In this work we studied a series of binuclear titanium(III) metallocenes bridged by $^-O_2C(CH_2)_nCO_2^-$. For solid samples, an antiferromagnetic exchange interaction is seen which monotonically decreases as n is varied from 1 to 3. There is no evidence for an interaction in the solid state for complexes with four, six, or ten methylene groups as indicated by susceptibility data measured down to 4.2 K. Appreciable *inter*molecular interactions do not appear to be present. However, it is not known exactly what conformations these complexes assume in the solid state. In a toluene/benzene frozen-glass media, there is only one conformer of the succinate-bridged ($n = 2$) complex present, whereas, in the case of the adipate-bridged ($n = 4$) complex the EPR data clearly point to the presence of two different conformers. It seems that for both of these cases the molecular conformations that are present are *not* the most stretched out form of the molecules. On the other hand, the EPR spectra of the glasses of the longer chain ($n = 6$, 8, 10) species do *not* exhibit signs of appreciable zero-field splitting. Thus, in these three cases, the molecules are not freezing out in the glass such that the two titanium(III) metallocenes are in close proximity.

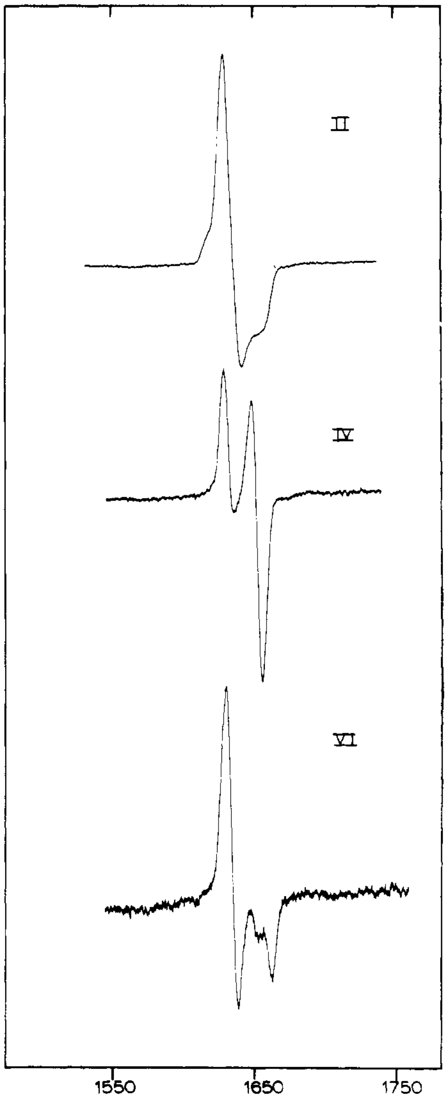


Figure 16. Frozen-glass X-band EPR spectra for the oxalate(II)-, succinate(IV)-, and adipate(VI)-bridged complexes, showing the half-field $\Delta M_s = 2$ transitions.

In conclusion, the data in this paper suggest that there is an *intra*molecular antiferromagnetic exchange interaction present in these dicarboxylate-bridged titanium(III) metallocenes and that the interaction is propagated by a chain of methylene carbon atoms. However, the presence of the interaction is not definitively established by the data. In the following paper rigid, saturated dicarboxylate dianions are employed as bridges. EPR spectra for room-temperature solutions of these complexes exhibit nuclear hyperfine structure

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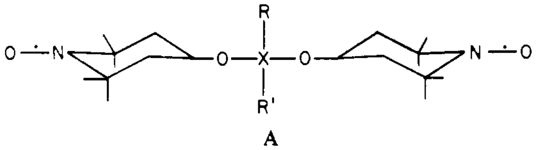
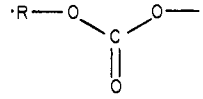
[41] Cookson, D. J.; Smith, T. D.; Pilbrow, J. R. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2832. Boyd, P. D. W.; Toy, A. D.; Smith, T. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1549. Carr, S. G.; Smith, T. D. *Ibid.* **1972**, 1887.

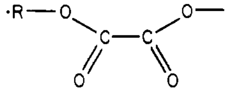
which conclusively establishes the presence of an *intra*molecular exchange interaction propagated by methylene carbon atoms. Room-temperature EPR spectra were also run for solutions of the binuclear complexes bridged by $^-O_2C(CH_2)_nCO_2^-$; however, due to the ineffective tumbling of these binuclear complexes, we could not completely resolve the nuclear hyperfine. Several additional experiments, including X-ray crystallographic work on the 3,3-diethylglutarate and variable-temperature EPR studies on glasses in the 4.2 K region, are planned.

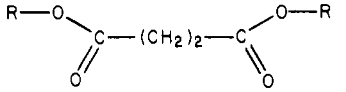
The same types of problems have been encountered in various studies of organic biradicals.[12,13] Nitroxide biradicals have been studied that have long bridging units interposed between the two radical centers. In general, the magnitude of a magnetic exchange interaction in such a biradical is determined by examining the EPR spectrum for the solution state species. When the exchange parameter J is on the order of the nitrogen hyperfine coupling constant A (ca. 15 G = 0.0014 cm^{-1}), a second-order spectrum is obtained, from which one can evaluate J. There are now several well-documented cases where the magnetic exchange interaction is *intra*molecular in nature and is propagated by a chain of σ bonds connecting the two nitroxyl centers. For example, a series of biradicals with piperidine rings joined to one another by one X = S, Si, or P atom have been studied where the molecular structure A is indicated (R and R′ are either alkyl groups or oxygen atoms).[42] The J values measured from solution EPR spectra are relatively temperature and solvent independent and vary according to the nature of atom X. The values of $|J|$ range from ($\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ Hamiltonian) ca. 70 G (=0.0066 cm^{-1}) for X = Si to ca. 49 G (=0.0046 cm^{-1}) for X = P.

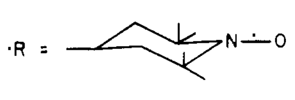

A

Data have been reported for another series of iminoxyl biradicals that are related to the present series of binuclear titanium(III) metallocenes. These molecules have been studied by several groups,[12,42-45] and most of the conclusions are in agreement. The carbonate diester (B) has an *intra*molecular exchange parameter of 15–20 G (ca. 0.0014–0.0019 cm^{-1}), as determined by EPR spectra of solutions. The oxalate diester (C) has an *intra*molecular J value that is approximately 6 times smaller than that for the carbonate. This attenuation is in agreement with the value predicted by McConnell for the addition of a single σ bond.[46] Both of these exchange parameters are independent of temperature at low temperatures, which indicates that the molecular conformations are fixed at the low temperatures. The succinate diester (D) and other biradicals with larger methylene chains exhibit exchange parameters that are very temperature dependent. Apparently these molecules can bend into a conformation in solution where the two nitroxyl radicals are close enough to interact directly. This was substantiated by a study of these same biradicals in a liquid crystal. Glarum and Marshall[43] oriented the biradicals in a liquid crystal and from an analysis of zero-field splitting calculated that the *intra*molecular nitroxide–nitroxide distance is 15 and 16 Å for the carbonate and oxalate diesters, respectively. The two unpaired electrons in the succinate molecule, on the other hand, were found to be separated by 14 Å, which indicates that this biradical folds to some degree. It was indicated that the distances they found for the carbonate and oxalate diesters were in keeping with models for the outstretched forms of the molecules.

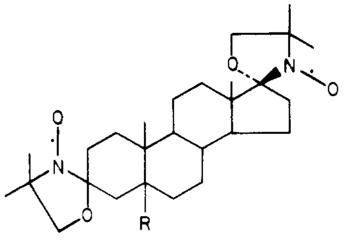

B


C

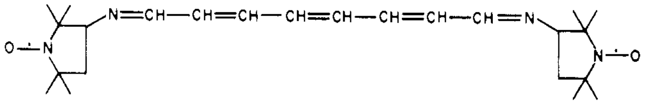

D

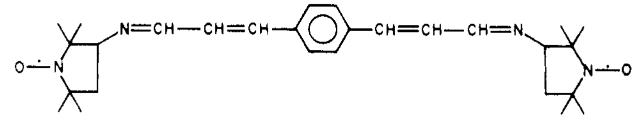


Very recently, the preparation of several extended and rigid biradicals has been reported. Calvin et al.[47] presented evidence to show that *intra*molecular through-bond mechanism was operative for the magnetic exchange interaction seen for two isomers of biradical E and various analogous biradicals. The value of $|J|$ varies from ca. 12 to ca. 80 G for the two different isomers of E.


E

Shapiro et al.[48-50] have reported the presence of magnetic exchange interactions propagated by very extended bridging units in several biradicals. Biradicals F and G exemplify the type of molecular architecture that they used. We have used CPK models to estimate the nitroxide–nitroxide distances in the stretched-out form of these two molecules as 20–24 Å for biradical F and 23–28 Å for biradical G. EPR spectra were used to determine the $|J|$ values as 0.0013 and 0.000 35 cm^{-1}, respectively.


F


G

Magnetic exchange interactions that are propagated over such large distances were the focus of a very recent paper by Coffman and Buettner.[11] They reviewed the literature and established an experimentally determined limit function for long-range ferromagnetic and antiferromagnetic superex-

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[48] Shapiro, A. B.; Goldfield, M. G.; Rozantsev, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1973**, 960; *Tetrahedron Lett.* **1973**, 2183.

[49] Shapiro, A. B.; Novozhilova, G. A.; Rozantsev, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 452.

[50] Shapiro, A. B.; Novozhilova, G. A.; Dombrovskii, V. A.; Volodarskii, L. B.; Rozantsev, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 2124.

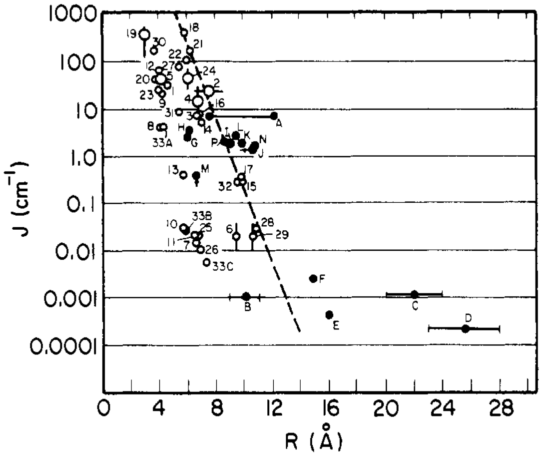

Figure 17. Plot of log *J* vs. the distance between paramagnetic centers. The straight line is from Coffman and Buettner.[11] The points labeled with letters represent data from titanium dimers bridged by dicarboxylic acids and organic biradicals mentioned in the text.

change. In other words, they entered available data on a plot of log *J* vs. distance between paramagnetic centers and then drew a straight line such that all known systems fell to the left of this line. Figure 17 shows a reproduction of their plot to which we have added points for the binuclear titanium(III) complexes studied in this work and the organic biradicals mentioned above. These additional compounds are labeled with letters A–P and are identified in Table XII. It is important to note that Coffman and Buettner used an $\hat{H} = J\hat{S}_1 \cdot \hat{S}_2$ Hamiltonian, and, consequently, the *J* values reported in this paper need to be multiplied by a factor of −2 to correspond to the *J* values they report.

We have relabeled in Figure 17 the one point that Coffman and Buettner reported which could represent an example "of superexchange of longer range than previously known" or "could simply be in error". The point A is for [(tren)Cu–BZD–Cu(tren)]$(NO_3)_4$, where the BZD bridge between the two copper(II) centers is 4,4′-diaminobiphenyl and tren is 2,2′,2″-triaminotriethylamine. An X-ray structure[51] for this compound shows binuclear copper(II) complexes with *intra*molecular distances in excess of ca. 12.1 Å. Magnetic susceptibility data[9] for this compound were fit to the Bleaney–Bowers equation to give $J = -4.5$ cm⁻¹. Coffman and Buettner decided that, in view of the statistical evidence, the data for this compound were misinterpreted, and the interaction is *inter*molecular. The closest Cu–Cu *inter*molecular distance is 7.5 Å, which is indicated in Figure 17 as a second way of plotting this point.

It is our opinion that the interaction in [(tren)Cu–BZD–Cu(tren)]$(NO_3)_4$ is *intra*molecular. Several reasons were given.[9] In short, susceptibility data were reported for three different salts of the [(tren)Cu–BZD–Cu(tren)]$^{4+}$ cation. Coffman and Buettner suggested that the exchange pathway in the nitrate salt involved nitrate ions and a double hydrogen-bonded pathway. In spite of this, we found that the exchange interaction is very similar for the ClO_4^- ($J = -3.7$ cm⁻¹) and PF_6^- ($J = -3.3$ cm⁻¹) compounds. Crystal structures are not available for these two salts, but it would be very unlikely that any exchange pathway involving the counterion would be the same in these three salts.

Two other pieces of evidence support the idea that the interaction is *intra*molecular. Nitrate and perchlorate salts of [(tren)Cu–MDA–Cu(tren)]$^{4+}$ were also studied, where MDA is 4,4′-methylenedianiline. A single methylene group was inserted into the middle of the 4,4′-diaminobiphenyl bridge. Both of these salts show no signs of an exchange interaction in susceptibility data measured down to 4.2 K, which means that $-J >$ ca. 0.3 cm⁻¹ for these two compounds. Why did the interaction drop off by 1 order of magnitude with the introduction of a methylene group into the bridge if the interaction is *inter*molecular in nature? We also found that replacing BZD by *p*-phenylenediamine, i.e., one less phenyl group, increases the interaction by a factor of ca. 5–10. The interaction clearly depends on the aromatic diamine bridge.

There is one other curious fact about the Coffman and Buettner plot. They did not include any data for organic biradicals. Points for a few extended biradicals are included in Figure 17. It can be seen that the data for several of these molecules, notably biradicals F and G (points C and D, respectively, in the figure), fall to the right of the line. Further work is needed; however, it is clear that there is *not* a simple distance dependence for the magnetic exchange parameter.

Table XII. Data Added to Coffman–Buettner Plot for Figure 17[a]

plotting code	compd identification	*J*,[b] cm⁻¹	*R*,[c] Å
A	$[Cu_2(tren)_2(BZD)](NO_3)_4$	9.0[9]	12.2–12.3[9]
B	E[c]	0.0011[47]	9–11[d]
C	F	0.0013[50]	20–24[d]
D	G	0.00035[50]	23–28[d]
E	C	0.00065[43]	16[43]
F	B	0.0039[43]	15[43]
G	oxalate(2−)[e]	4.4	5.97
H	phthalate(2−)	5.6	6.02
I	isophthalate(2−)	2.8	9.2
J	terephthalate(2−)	<1.4	10.55
K	bicyclopentane-1,3-dicarboxylate(2−)	2.8	9.97
L	adamantane-1,3-dicarboxylate(2−)	4.6	9.6
M	*trans*-1,2-cyclohexane-dicarboxylate(2−)	<0.6	6.35
N	*trans*-1,4-cyclohexane-dicarboxylate(2−)	2.2	10.8
P	fumarate(2−)	3.2	8.8

[a] See ref 11 for identification of numbered points in Figure 17.
[b] The isotopic exchange Hamiltonian is defined as $\hat{H}_{ex} = +J\hat{S}_1 \cdot \hat{S}_2$
[c] *R* represents the distance between unpaired spin density, which in the case of the binuclear titanium(III) metallocenes is assumed to be the Ti–Ti distance. [d] Distance calculated from CPK models.
[e] The compounds are identified by the bridging dicarboxylic acids.

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Registry No. I, 12248-00-9; II, 55009-31-9; III, 77071-17-1; IV, 12249-07-9; V, 77071-18-2; VI, 77071-19-3; VII, 77071-20-6; VIII, 77071-21-7; IX, 77071-22-8; X, 77071-23-9; XI, 77071-24-0; $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, 12129-51-0.

Supplementary Material Available: Tables II–X (magnetic susceptibility data), Figure 3 (plots of μ_{eff}/Ti vs. temperature), and Figure 5 (plots of μ_{eff}/Ti and χ_M vs. temperature) (20 pages). Ordering information is given on any current masthead page.