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

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The preparation and characterization of six binuclear titanium(III) metallocenes are described. The complexes have the composition $[(\eta^5\text{-}C_5H_5)_2Ti]_2B$, where B is the dianion of a cyclic aliphatic dicarboxylic acid which bridges the two titanium(III) ions in a bis bidentate fashion with the formation of four-membered chelate rings. Five of the binuclear complexes exhibit a weak antiferromagnetic exchange interaction in the solid state as evidenced by magnetic susceptibility data measured down to 4.2 K. It is suggested that the adamantane-1,3-dicarboxylate-bridged complex has an intramolecular antiferromagnetic exchange interaction characterized by $J = -2.3$ cm^{-1}. The rigid structure of the bridging dianion in this complex ensures that, if the interaction is intramolecular in nature, it is propagated by the chain of methylene carbon atoms in the adamantane moiety. In the same vein the exchange interaction ($J = -1.4$ cm^{-1}) observed for the binuclear complex bridged by the dianion of bicyclo[1.1.1]pentane-1,3-dicarboxylic acid is most likely "through bond", as opposed to "through space", since the antiferromagnetic coupling is weaker than observed for the adamantane-bridged complex. The binuclear complex bridged by the cyclohexane-*trans*-1,4-dicarboxylate dianion shows a weak interaction with $J = -1.1$ cm^{-1}, whereas there is no sign ($-J < 0.3$ cm^{-1}) of an exchange interaction in the susceptibility data for the analogous complex bridged by the *trans*-1,2-dicarboxylate. The binuclear complex bridged by the 3-methylcyclopropane-*trans*-1,2-dicarboxylate dianion is found to have a weaker magnetic exchange interaction ($J = -1.3$ cm^{-1}) than is present in the complex bridged by the cyclobutane-*trans*-1,2-dicarboxylate dianion where $J = -2.2$ cm^{-1}. X-Band, Q-band, and in some cases S-band EPR data are presented for liquid-nitrogen-temperature toluene/benzene glasses of the complexes to document the presence of binuclear triplet-state species, and in some cases the observed zero-field splitting is used to calculate an intramolecular Ti–Ti distance. Nuclear hyperfine splitting due to the small amount of binuclear complexes with ^{47}Ti ($I = {}^5/_2$) and ^{49}Ti ($I = {}^7/_2$) isotopes was seen for room-temperature toluene/benzene solutions of the various binuclear complexes. This definitely establishes the presence of intramolecular exchange interactions where $-J \gg 10^{-3}$ cm^{-1}.

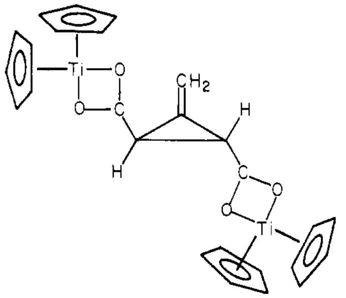
Introduction

In the preceding paper EPR and magnetic susceptibility data were presented for a series of binuclear titanium(III) metallocenes bridged by the dianions of aliphatic acids. It was suggested that a magnetic exchange interaction between the two titanium(III) ions in a binuclear complex could be propagated by the methylene groups of the aliphatic dicarboxylic acid dianion. More than one molecular conformation was indicated for some of the binuclear complexes bridged by the long-chain dicarboxylate ions. The aliphatic backbone of the bridging unit can be made more rigid by employing the dicarboxylic acids of cyclohexane, cyclobutane, cyclopropane, bicyclo[1.1.1]pentane, and adamantane. In this paper, the preparation and characterization of the new mononuclear and binuclear titanium(III) metallocenes I–VII are reported with the goal of further establishing the viability of chains of methylene groups as propagators of magnetic exchange interactions.

The dianions of adamantane-1,3-dicarboxylic acid and bicyclo[1.1.1]pentane-1,3-dicarboxylic acid were selected as bridges in the complexes for several reasons. Not only do they possess a rigid construction which restricts the number of different molecular conformations for the binuclear complexes, but they introduce the possibility of through-space interactions between orbitals on the bridgehead carbon atoms. The terminology of "through-space" and "through-bond" interactions was devised by Hoffmann[4] to distinguish between the modes of interaction of remote orbitals. Direct through-space interactions should be greater in bicyclo[1.1.1]pentane-1,3-dicarboxylic acid because this molecule possesses the shortest known formally nonbonded carbon–carbon distance; the bridgehead–bridgehead C–C distance is 1.845 Å.[5] The relatively large proton–proton hyperfine coupling constant of 18 Hz between the bridgehead hydrogen atoms has been taken as evidence of through-space interactions in bicyclo[1.1.1]pentane.[6] Several molecular orbital calculations have also been carried out for bicyclo[1.1.1]pentane.[6-8]

Results and Discussion

Synthesis of Cyclopropane Complex. All of the binuclear complexes in this paper were prepared in the same manner as indicated in the preceding paper. One mole of the dicarboxylic acid is oxidatively added to 2 mol of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ to give a binuclear titanium(III) complex. However, there was an interesting observation made in the preparation of complex VII which is bridged by the dianion of 3-methylcyclopropane-*trans*-1,2-dicarboxylic acid. The reactant used to prepare this compound was 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid.



An analysis of mass spectral data alerted us to the fact that the double bond in the initial dicarboxylate acid had been hydrogenated during the course of the reaction. This result was not totally unexpected as titanium compounds are known

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[3] A. P. Sloan Foundation Fellow, 1976–1978.

[4] Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779.

[5] Chiang, J. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 1614.

[6] Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773.

[7] Whitman, D. R.; Chiang, J. F. *J. Am. Chem. Soc.* **1972**, *94*, 1126.

[8] Lehn, J. M.; Wipff, G. *Chem. Phys. Lett.* **1972**, *15*, 450.

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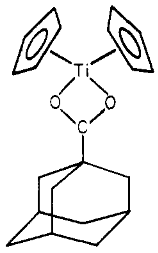

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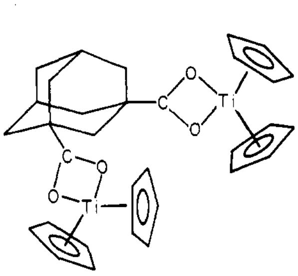

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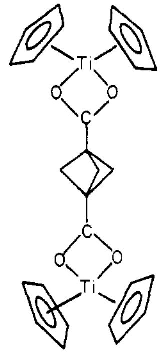

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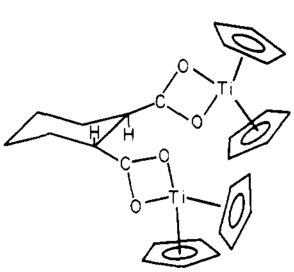

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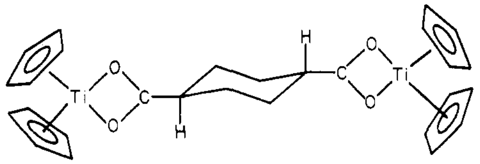

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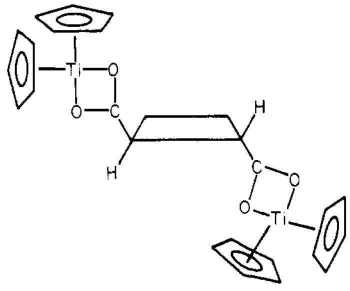

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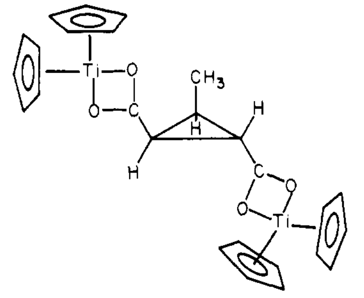

VII

to hydrogenate multiple bonds;[9,10] however, in the case of ene–dicarbonyl compounds, previous work had suggested that hydrogenation occurred only in conjugated species. Additional results dealing with the hydrogenation by $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ will be the subject of a later paper.[11]

Magnetic Susceptibility. Data were collected for solid samples of the six binuclear titanium(III) complexes and are given in Tables I–VI.[12] Figure 1 illustrates the data for (μ-(adamantane-1,3-dicarboxylato))-bis[bis(η^5-cyclopentadienyl)titanium(III)] (II). The plot of effective magnetic moment per titanium(III) ion, μ_{eff}/Ti, vs. temperature gives clear evidence of the presence of an antiferromagnetic exchange interaction. The moment per Ti(III) ion is 1.73 μ_B at 245 K and remains relatively constant down to ca. 50 K, whereupon μ_{eff}/Ti decreases with decreasing temperature to a value of 1.25 μ_B at 4.2 K. These data were least-squares fit to the Bleaney–Bowers equation[13] for the molar paramagnetic susceptibility of an $S_1 = S_2 = {}^1/_2$ binuclear complex experiencing an isotropic magnetic exchange interaction ($\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$). The resulting least-squares fitting parameters are $J = -2.3$ cm^{-1} and $g = 1.99$. The solid lines in Figure 1 represent this fit. The goodness of the fit to the equation for an interaction in a binuclear complex supports the idea that the interaction is intramolecular in nature.

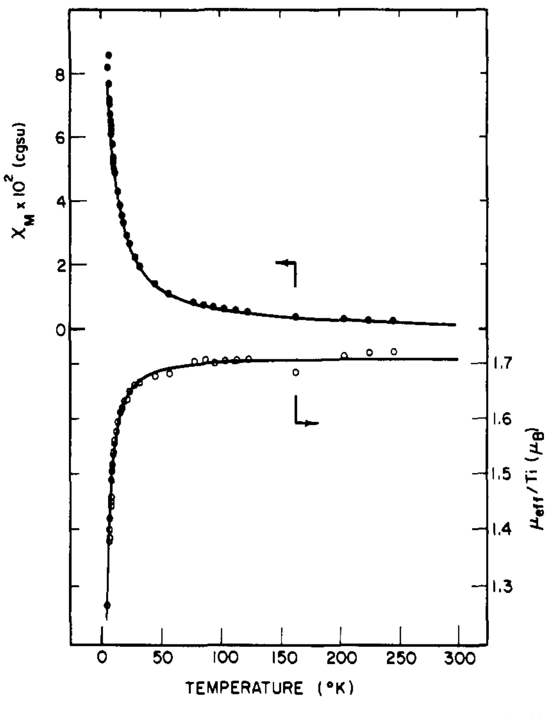

Figure 1. Plots of molar paramagnetic susceptibility, χ_M, and effective magnetic moment per titanium(III) ion, μ_{eff}/Ti, vs. temperature for the adamantane-1,3-dicarboxylate-bridged complex II. The solid lines result from a least-squares fit to the theoretical equation.

The orientation of the unpaired-electron orbital and the shielding by the cyclopentadienyl ligands would tend to minimize intermolecular interactions. The rigid construction of the adamantane bridge is such that the Ti–Ti distance is fixed. A CPK space-filling molecular model was used to estimate a Ti–Ti distance of 9.0 Å for this complex. It is clear that, if the antiferromagnetic is intramolecular, then it is propagated by a three-methylene-carbon fragment of the adamantane unit rather than through direct interaction between the titanium ions or contact of cyclopentadienyl rings. The unpaired electron of the titanium(III) ion is located in a d orbital which is in the plane of the carboxylate moiety and is properly phased for a σ-type of bonding.

Binuclear complex III, which has a bicyclo[1.1.1]pentane-1,3-dicarboxylate bridge, also has a three-methylene-carbon fragment interposed between the two $(\eta^5\text{-}C_5H_5)_2TiO_2C$ moieties. The variable-temperature magnetic susceptibility data for the binuclear bicyclo[1.1.1]pentane complex are illustrated in Figure 2.[12] The antiferromagnetic exchange interaction that is present in this complex is weaker than that seen for the adamantane complex as evidenced by the fact that

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(9) Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1178.
(10) Blaszczak, L. C.; McMurry, J. E. *J. Org. Chem.* **1974**, *39*, 258.
(11) Corbin, D. R.; Stucky, G. D., paper in preparation.
(12) Supplementary material.
(13) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

Table VIII. Analytical Data

compd no.	bridge	% C calcd	% C obsd	% H calcd	% H obsd	% Ti calcd	% Ti obsd
I	adamantane-carboxylate(1−)	70.58	66.55	7.06	6.78	13.40	13.15
II	adamantane-1,3-dicarboxylate(2−)	66.45	66.71	5.92	5.99	16.56	15.70
III	bicyclo[1.1.1]pentane-1,3-dicarboxylate(2−)	63.54	63.11	5.14	4.88	18.77	18.36
IV	cyclohexane-*trans*-1,2-dicarboxylate(2−)	63.93	64.50	5.70	5.79	18.21	18.13
V	cyclohexane-*trans*-1,4-dicarboxylate(2−)	63.93	63.88	5.70	5.58	18.21	17.55
VI	cyclobutane-*trans*-1,2-dicarboxylate(2−)	62.66	62.17	5.27	5.26	19.22	18.43
VII	3-methylcyclopropane-*trans*-1,2-dicarboxylate(2−)	62.66	62.52	5.27	5.44	19.22	18.16

μ_{eff}/Ti only decreases to 1.50 μ_B at 4.2 K for the bicyclo[1.1.1]pentane complex. Fitting the data to the Bleaney–Bowers equation gives $J = -1.4$ cm^{-1} and $g = 1.97$.

Complexes IV and V were prepared by reacting $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ with cyclohexane-*trans*-1,4-dicarboxylic acid and cyclohexane-*trans*-1,2-dicarboxylic acid. An interesting observation was made with the magnetic susceptibility data for these two binuclear complexes. There is little sign of an interaction for the 1,2-disubstituted complex, whereas the 1,4-disubstituted complex gives evidence of a weak antiferromagnetic exchange interaction. Figure 3[12] shows the data for the 1,4-disubstituted complex; there is a small drop in μ_{eff}/Ti below ca. 10 K to a value of 1.52 μ_B at 4.8 K. Least-squares fitting of the data gives $J = -1.1$ cm^{-1} and $g = 1.98$. The solid lines in Figure 3[12] represent this fit. On the other hand, there is not much drop in μ_{eff}/Ti seen at low temperatures for the 1,2-disubstituted complex (see Figure 4[12]). In this case μ_{eff}/Ti only drops from an average value of ca. 1.74 μ_B to a value of 1.69 μ_B at 4.5 K, which means that $-J <$ ca. 0.3 cm^{-1}.

Compounds VI and VII contain cyclic bridging units which separate the titanium fragments by two methylene groups. Compound VI, which is bridged by the cyclobutane-*trans*-1,2-dicarboxylate dianion, displays an antiferromagnetic interaction as shown by the magnetic susceptibility data in Figure 5.[12] The magnetic moment per Ti(III) ion is 1.72 μ_B at 245 K and decreases to a value of 1.32 μ_B at 4.7 K. These data were least-squares fit to give $J = -2.2$ cm^{-1} and $g = 2.00$. Compound VII, which is bridged by 3-methylcyclopropane-*trans*-1,2-dicarboxylate dianion, also displays an antiferromagnetic interaction. The value of μ_{eff}/Ti starts at 1.70 μ_B at room temperature and drops to 1.52 μ_B at 4.2 K. Fitting these data gives $J = -1.28$ cm^{-1} and $g = 1.97$.

EPR of Frozen Glasses. Frozen toluene/benzene (4:1) glasses of all six binuclear complexes were examined at Q-, X-, and, in certain cases, S-band frequencies. For reference purposes, the frozen-glass X-band spectrum of *mononuclear* (adamantane-1-carboxylato)bis(η^5-cyclopentadienyl)titanium(III) (I) is shown as the lower tracing in Figure 6. The signal is characteristic of a rhombic **g** tensor, and g values calculated (2.000, 1.982, 1.955) are in accordance with g values seen for other such mononuclear complexes (see preceding paper). The magnetic susceptibility data for a solid sample of this complex in Table VII[12] give little indication of a interaction.

Figure 6 (upper tracing) also illustrates the X-band spectrum for the binuclear adamantane complex. It is clear that this spectrum results from a binuclear species since the spectrum is quite different from that observed for the mononuclear complex. Zero-field splitting is evident, and because the spectrum was taken for a dilute frozen glass, the zero-field interactions are not intermolecular in nature. However, the spectrum for the binuclear adamantane complex is disappointing, as many more than the expected six signals are seen. There is no question that the adamantane carbon atom framework is rigid, but in spite of this several different molecular conformations are present. This is to be expected, for there is probably relatively free rotation of each of the two carboxylate moieties in solution. Freezing a solution of the binuclear adamantane complex would probably give a glass wherein the binuclear complexes each have different relative orientations of their two carboxylate planes. In other words, a binuclear complex having its two carboxylate planes coplanar will give a different EPR spectrum (g values and zero-field splittings) than a binuclear complex having its two carboxylate planes oriented in a perpendicular fashion. It would be necessary to modify the complex sterically in order to lock the complex into one molecular conformation and get a simple six-line spectrum. It is important to emphasize that, irrespective of the above problems, the rigidity of the adamantane framework ensures that, if the observed magnetic exchange interaction is intramolecular in nature, it is propagated by a three methylene carbon chain.

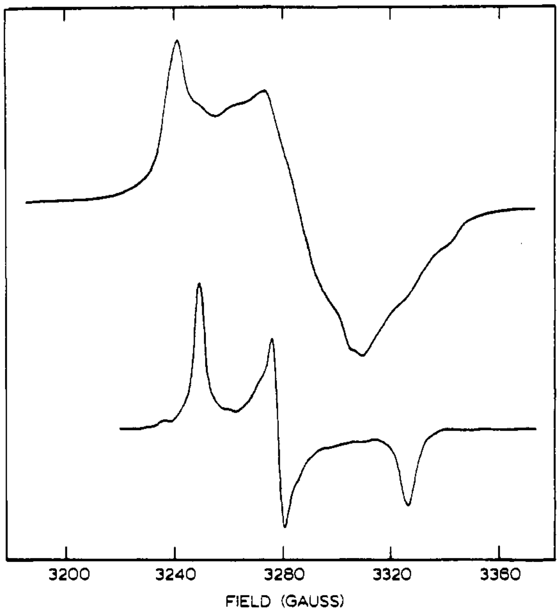


Figure 6. X-Band EPR spectra for liquid-nitrogen-temperature toluene/benzene (4:1) glasses of the adamantane-1-carboxylate complex I (lower tracing) and adamantane-1,3-dicarboxylate-bridged complex II (upper tracing).

Figure 7 illustrates the frozen-glass X-band spectrum of the binuclear bicyclo[1.1.1]pentane complex III. It is clear that more than one rotamer is also present for this complex in the

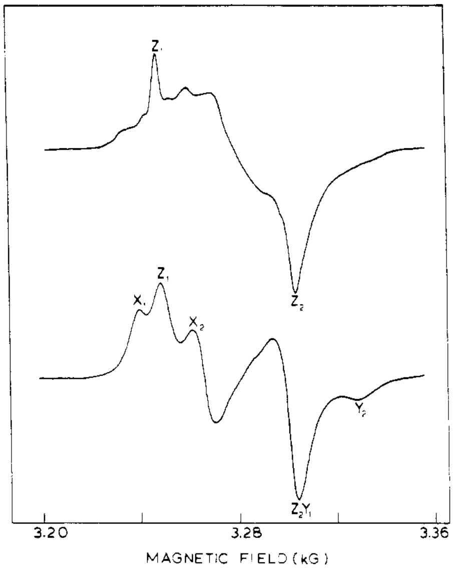


Figure 7. X-Band EPR spectrum (upper tracing) for a liquid-nitrogen-temperature toluene/benzene (4:1) glass of the bicyclo[1.1.1]pentane-1,3-dicarboxylate-bridged complex III. The computer-simulated spectrum is shown in the lower tracing; see text for parameters.

frozen toluene/benzene glass since the spectrum (upper tracing in Figure 7) has more than 10 overlapping features. There are two relatively sharp features in the spectrum which have been labeled Z_1 and Z_2. If these two features correspond to the zero-field split g_z signal for the rotamer which has the two carboxylate planes coplanar (i.e., centrosymmetric complex), then the spacing between these two features gives $2|D| = 55$ G (D value of 27.5 G = 0.0026 cm^{-1}) and a g_z value of 1.986. A Ti–Ti distance of 9.98 Å can be calculated from these values, which is in good agreement with a Ti–Ti distance of ca. 9.9 Å calculated from the available[5] bridgehead–bridgehead C–C distance of 1.845 Å and reasonable estimates of the other bond distances and angles. Both complexes II and III exhibit $\Delta M_s = 2$ transitions in the frozen-glass media.

The X-band spectrum was simulated for the centrosymmetric rotamer of the binuclear bicyclo[1.1.1]pentane complex. A Ti–Ti distance of 9.98 Å was assumed together with $g_x = 2.000$, $g_y = 1.960$, and $g_z = 1.986$ to give the simulated spectrum in Figure 7. It can be seen that reasonable selections of line widths ($W_x = W_z = 5$ G and $W_y = 10$ G) give a spectrum with resolved signals which could be present in the experimental spectrum.

The Q-band EPR spectra for frozen glasses of the binuclear adamantane and bicyclo[1.1.1]pentane complexes have very broad features. Little information can be gleaned from these two spectra.

Binuclear complex IV, (μ-(cyclohexane-*trans*-1,2-dicarboxylato))-bis[bis(η^5-cyclopentadienyl)titanium(III)], exhibits X-band and Q-band EPR spectra that are remarkably similar to those seen for the succinate-bridged complex of the preceding paper. Figure 8 should be compared to Figure 10 of the preceding paper to see that the two X-band spectra are nearly superimposable. Both of these complexes obviously have two methylene carbon atoms interposed between the two carboxyl–titanium moieties, and it appears that similar molecular conformations are present.

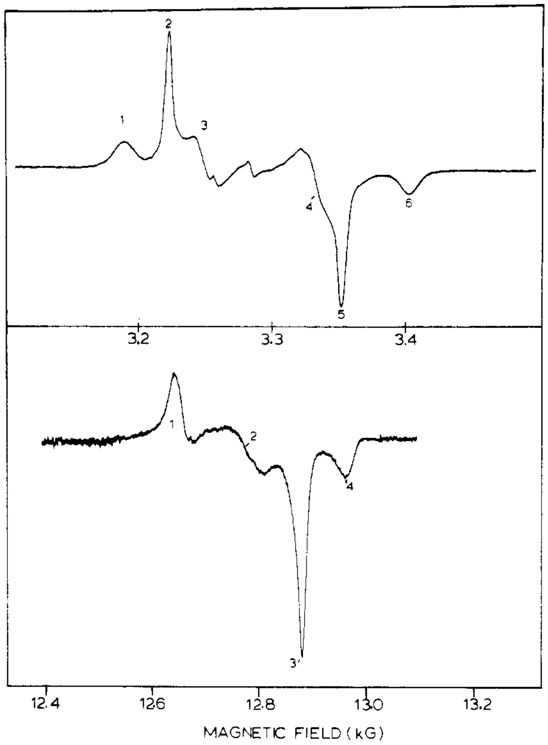


Figure 8. X-Band (upper tracing) and Q-band (lower tracing) EPR spectra for a liquid-nitrogen-temperature toluene/benzene (4:1) glass of the cyclohexane-*trans*-1,2-dicarboxylate-bridged complex IV.

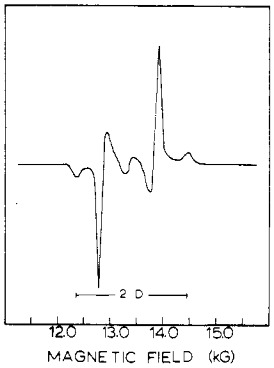
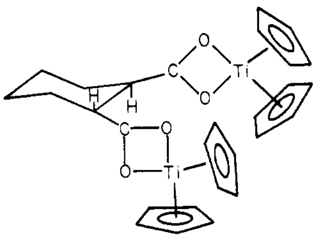


Figure 9. S-Band EPR spectrum for a frozen glass of the cyclohexane-*trans*-1,2-dicarboxylate-bridged complex IV.

The S-band spectrum for the μ-(cyclohexane-*trans*-1,2-dicarboxylato) complex is shown in Figure 9. As we found from the S-band spectrum for the succinate-bridged complex, the axial zero-field splitting can be extracted from the difference in magnetic field positions for the outermost turning points (bumps) on the spectrum. This spacing is $2D$ which gives $D = 106$ G = 0.0099 cm^{-1}. A Ti–Ti distance of 6.35 Å can be calculated from this D value. There are two reasonable configurations for the bridging cyclohexane-*trans*-1,2-dicarboxylate dianion. It is likely that the cyclohexane is in a chair form and the two carboxyl moieties could be either diaxial or diequatorial. A CPK space-filling model was used to estimate the Ti–Ti distances for these two conformations. In the case of the chair diaxial form, a Ti–Ti distance of 8.4 Å is found, whereas, the chair diequatorial form gives 6.4 Å. The distance for the diequatorial form is clearly closer to the 6.35 Å experimental value. Complex IV most likely has the structure



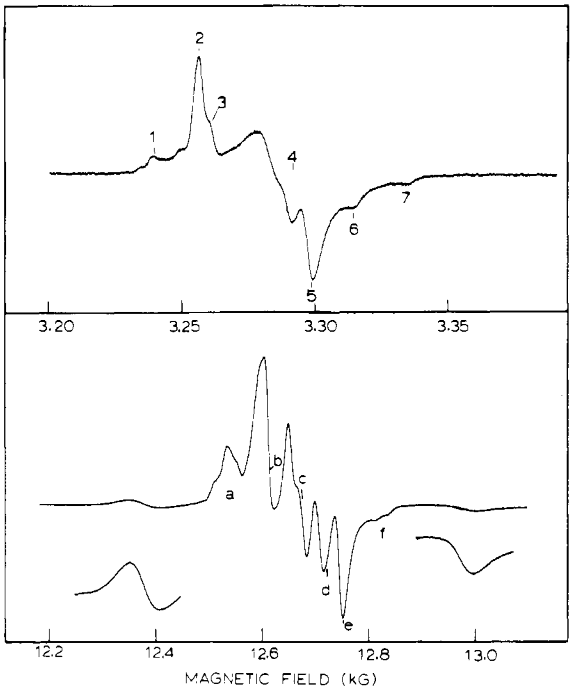
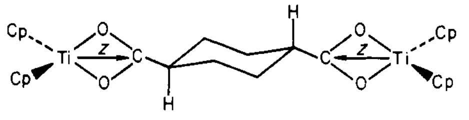


Figure 10. X-Band (upper tracing) and Q-band (lower tracing) EPR spectra for a frozen glass of complex V which is bridged by the dianion of cyclohexane-*trans*-1,4-dicarboxylic acid.

The succinate-bridged complex must have the same molecular conformation for the $O_2CCHCHCO_2$ moiety. It is relevant to note that the diequatorial conformation was found for cyclohexane-*trans*-1,2-dicarboxylic acid.[14] It is also well-known that bulky substituents on cyclohexane prefer equatorial positions.[15]

The X-band and Q-band spectra for the cyclohexane-*trans*-1,4-dicarboxylate-bridged complex V (see Figure 10) present a problem. Equilibrium and thermochemical studies of various trans 1,4-disubstituted cyclohexanes indicate that the most prevalent form in solution is the chair diequatorial conformation.[16] In addition, a recent crystal structure[17] of cyclohexane-*trans*-1,4-dicarboxylic acid shows that the two carboxylic acid groups are in diequatorial positions of the chair form of cyclohexane. The chair diequatorial conformation would intuitively seem to be the favored one for the cyclohexane-*trans*-1,4-dicarboxylate-bridged binuclear complex V, as illustrated by



The Ti–Ti distance calculated from models for this centrosymmetric conformation is 10.5 Å. It is clear from the spectra in Figure 10 that more than one conformation of the binuclear complex is present in the glass. Two prominent features, 2 and 5, are evident in the X-band spectrum and could be assigned as the zero-field split g_z signal for the chair diequatorial conformer. Other features in the X-band and Q-band spectra can tentatively be assigned as part of the signal for this same conformer; see Table IX. The resonance field assignments given in Table IX were least-squares fit to eq 2 in the preceding paper to give the calculated fields also listed in Table IX and the parameters $g_x = 2.001$, $g_y = 1.969$, $g_z = 1.984$, $D = 0.020$ cm^{-1}, and $E = 0.00005$ cm^{-1}. This D value gives a Ti–Ti distance of 10.8 Å, which is in agreement with the distance of 10.5 Å calculated from a molecular model. Additional work, perhaps on various substituted forms of complex V, is needed to explain the features in the spectra. In particular, attention is drawn to the Q-band signals (insets) at ca. 12.4 and 13.0 kG. If these two signals are attributable to one zero-field split signal, a Ti–Ti distance of ca. 4.5 Å is calculated.

Table IX. Fit of Selected X-Band and Q-Band Resonance Fields to Theoretical Equations for (μ-(Cyclohexane-*trans*-1,4-dicarboxylato))-bis[bis(η^5-cyclopentadienyl)titanium(III)][a]

		field, G	
	peak	obsd	calcd
X-band	Z1	3 256.0	3 256.1
	Y1	3 293.0	3 292.1
	X1	3 238.7	3 240.4
	Z2	3 298.9	3 299.3
	Y2	3 314.0	3 315.4
	X2	3 261.5	3 260.3
Q-band	Z1	12 620	12 620
	Y1	12 724	12 722
	X1		12 490
	Z2	12 670	12 666
	Y2	12 749	12 747
	X2		12 510

[a] Wasserman's theoretical equations are given in the preceding paper. The present data were fit to $D = 0.0020$ cm^{-1}, $E = 0.000\,05$ cm^{-1}, $g_x = 2.001$, $g_y = 1.969$, and $g_z = 1.984$.

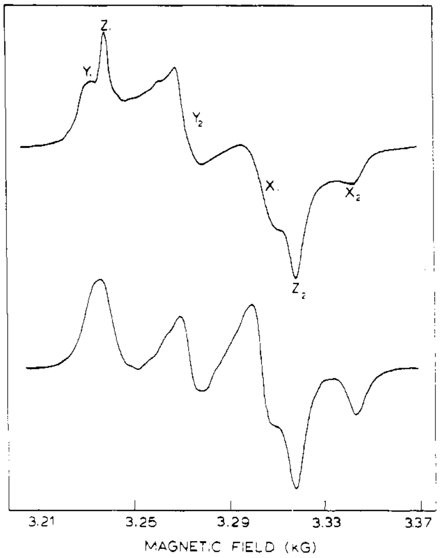


Figure 11. X-Band EPR spectrum (upper tracing) for a liquid-nitrogen-temperature toluene/benzene (4:1) glass of the 3-methylcyclopropane-*trans*-1,2-dicarboxylate bridged complex VII. The computer-simulated spectrum is shown in the lower tracing; see text for parameters.

The titanium ions of compound VII, which is bridged by the 3-methylcyclopropane-*trans*-1,2-dicarboxylate dianion, are expected to be separated by a greater distance than is present in compound IV. This expectation is borne out by the EPR spectra shown in Figures 11 and 12. Both the X- and Q-band spectra span a smaller range of magnetic field values than the corresponding spectra of compound IV, which indicates a decrease in the zero-field interaction and increase in the Ti–Ti distance. The six-line patterns found in both the X- and Q-band spectra suggest that only one conformation is present

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(14) Benedentti, E.; Corradini, P.; Pedone, C. *J. Am. Chem. Soc.* **1969**, *91*, 4075.

(15) Winstein, S.; Holness, X. X. *J. Am. Chem. Soc.* **1955**, *77*, 5562.

(16) Ellel, E. L. *Angew. Chem., Int. Ed. Engl.* **1973**, *29*, 2959. Orloff, H. D. *Chem. Rev.* **1954**, *54*, 347.

(17) Luger, P.; Plieth, K.; Ruban, G. *Acta Crystallogr., Sec. B* **1972**, *B28*, 706.

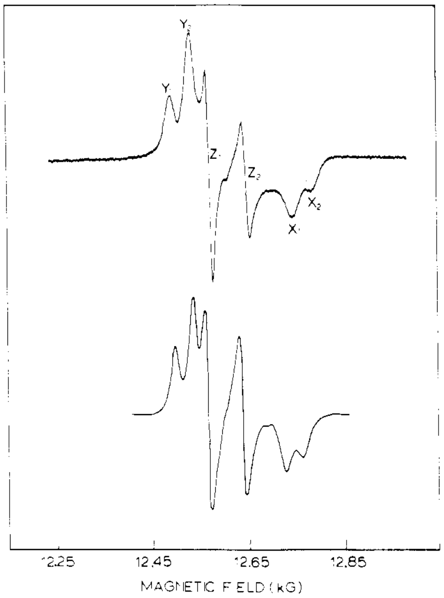

Figure 12. Q-Band EPR spectrum (upper tracing) for a liquid-nitrogen-temperature toluene/benzene (4:1) glass of the 3-methylcyclopropane-*trans*-1,2-dicarboxylate-bridged complex VII. The computer-simulated spectrum is shown in the lower tracing; see text for parameters.

in the glass. The **g** and **D** tensors in this complex are not collinear, but the deviation from collinearity is expected to be small, permitting computer simulations to be carried out. The X- and Q-band spectra were simulated with the parameters $g_x = 1.96$, $g_y = 1.99$, $g_z = 1.98$, a Ti–Ti distance of 8.85 Å, $E = 0.0$ cm^{-1}, and $\eta = \zeta = 0$ (collinearity of D_z and g_z). The Ti–Ti distance from the EPR simulation agrees with the value of 8.7 Å calculated with use of reasonable estimates of bond distances and bond angles.

The EPR spectra for compound VI, which is bridged by cyclobutane-*trans*-1,2-dicarboxylate dianion, are disappointing. Instead of the resolved signals of the previous compound, the EPR features of this compound were broad and poorly resolved. A crystal structure[18] of the parent diacid showed that the four-membered ring is not planar but has a dihedral angle of 149 ± 2°. The potential barrier between the puckered and planar conformations of the ring in the gas phase was estimated to be 1 kcal mol^{-1}. The broadness of the EPR spectra of the corresponding binuclear titanium compound may result from the presence of more than one conformation in the glass due to the flexibility of the ring.

EPR of Toluene/Benzene Solutions. There are two isotopes of titanium which have a nonzero nuclear spin. The hyperfine structure from these two isotopes can be used to ascertain whether a magnetic exchange interaction is present in a particular binuclear complex. The two isotopes are ^{47}Ti with $I = {}^5/_2$ in 7.28% natural abundance and ^{49}Ti with $I = {}^7/_2$ in 5.51% natural abundance. The gyromagnetic ratios for these two isotopes are almost equal, and, consequently, the magnitude of hyperfine interaction is the same.

In solution, a mononuclear titanium(III) metallocene will show a simple EPR spectrum consisting of a single derivative for the 87.21% of molecules possessing metal ions with $I = 0$. The bottom tracing in Figure 13 illustrates the room-temperature X-band spectrum for a toluene/benzene (4:1) solution of the mononuclear adamantane complex I. At low gain it can be seen that there is essentially only a single derivative. Weak signals, seen on either side of the derivative are due to the molecules that have either ^{47}Ti or ^{49}Ti ions. A pattern of six equally intense (and to first order equally spaced) lines will be seen for the ^{47}Ti molecules, while the ^{49}Ti molecules will exhibit a pattern of eight equally intense (and equally spaced) lines. The six-line pattern from the ^{47}Ti molecules will superimpose on the central six lines of the eight-line pattern of the ^{49}Ti molecules to give one eight-line pattern with the inner six lines having equal intensities and the outer two lines with approximately half the intensity of the inner lines. If all lines could be resolved, the spectrum of a solution of a mononuclear complex would consist of nine lines with the approximate relative intensities of 1:2.3:2.3:2.3:15.8:2.3:2.3:2.3:1. In practice, the intense central derivative masks two of the lines from the $I \neq 0$ molecules. Thus, three hyperfine lines are seen on either side of the central intense signal in the spectrum for the mononuclear adamantane complex. It can also be seen that one of the three signals in each grouping is weaker than the other two. The average titanium hyperfine splitting in this eight-line pattern is 8.5 G, which is in agreement with reported

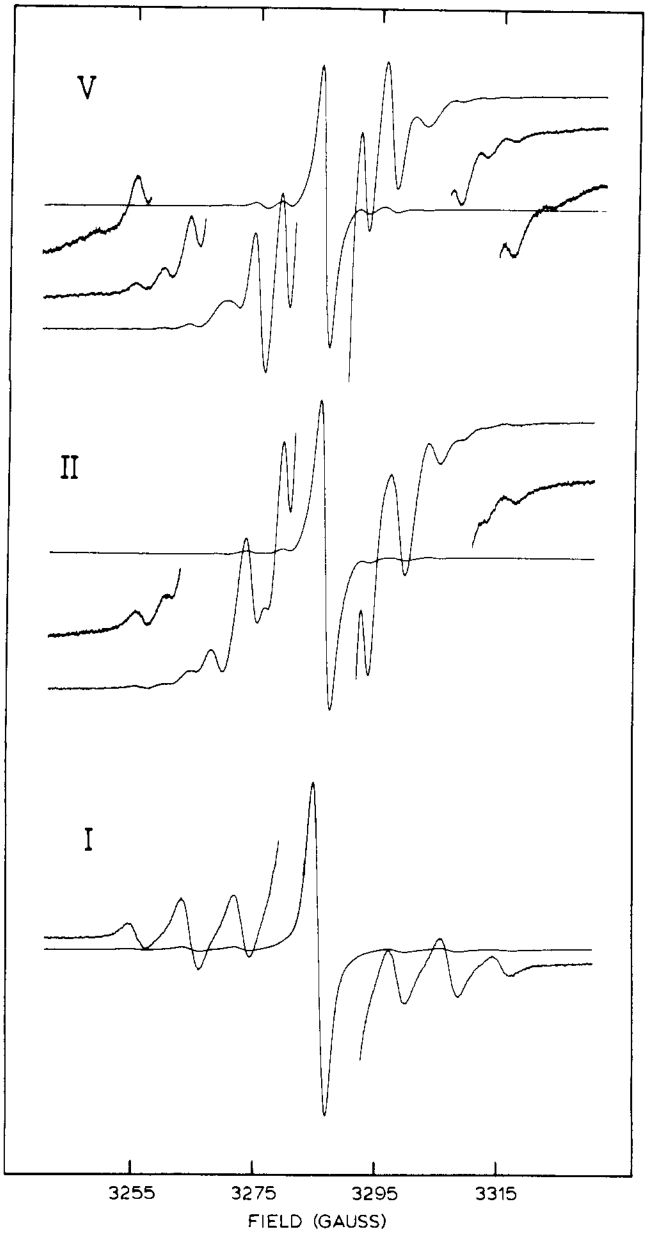

Figure 13. X-Band EPR spectra for room-temperature toluene/benzene (4:1) solutions of complex I (adamantane-1-carboxylate, bottom tracing), complex II (adamantane-1,3-dicarboxylate, middle tracing), and complex V (cyclohexane-*trans*-1,4-dicarboxylate, top tracing).

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[18] Benedetti, E.; Corradini, P.; Pedone, C. *Acta Crystallogr., Sect. B* **1970**, *B26*, 493.

average hyperfine splittings for titanium(III) ions in other metallocenes. The mononuclear titanium(III) compounds $[(\eta^5\text{-}C_5H_5)_2Ti(bpy)]PF_6$,[19] where bpy is 2,2′-bipyridine, $(\eta^5\text{-}C_5H_5)_2Ti(N\text{-}CH_3BiIm)$,[19] where N-CH_3BiIm is the anion of *N*-methylbiimidazole, and $(\eta^5\text{-}C_5H_5)$ TiL,[20] where L is the anion of 2-hydroxypyridine, each exhibit an eight-line hyperfine pattern with average hyperfine coupling constants of 10, 11, and 8.6 G, respectively.

The room-temperature EPR spectrum of a binuclear titanium(III) complex can be different from that of a mononuclear complex. Zero-field splitting is averaged to zero by virtue of the complex tumbling in solution.[21] If the magnetic exchange interaction is weaker than the titanium hyperfine ($J \ll a$), each of the two unpaired electrons of the binuclear complex will each be localized on one titanium(III) ion and the spectrum will look like that of a mononuclear complex. If $J \simeq a$, a second-order EPR spectrum will be seen from which J and a can be evaluated. If the magnetic exchange interaction exceeds the hyperfine interaction, $J \gg a$, then the two unpaired electrons are exchanging between the two titanium(III) ions rapidly on the EPR timescale; i.e., the rate of electron exchange is greater than ca. 10^{10} s^{-1}. In this last case the hyperfine structure will be different than that of a mononuclear complex and will reflect the presence of the following binuclear complexes: 76.06% Ti ($I = 0$)–Ti ($I = 0$); 12.70% Ti ($I = 0$)–^{47}Ti ($I = {}^5/_2$); 9.61% Ti ($I = 0$)–^{49}Ti ($I = {}^7/_2$); 0.53% ^{47}Ti ($I = {}^5/_2$)–^{47}Ti ($I = {}^5/_2$); 0.30% ^{49}Ti ($I = {}^7/_2$)–^{49}Ti ($I = {}^7/_2$); 0.80% ^{49}Ti ($I = {}^7/_2$)–^{47}Ti ($I = {}^5/_2$). The binuclear complex with two $I = 0$ ions, will give a single, centrally located, intense derivative signal. The Ti ($I = 0$)–^{47}Ti ($I = {}^5/_2$) complex will exhibit a six-line pattern in which all lines are equally intense and the average hyperfine (approximately the interline spacing) is half that of the corresponding mononuclear complex. The same magnitude of titanium hyperfine will be exhibited by the Ti ($I = 0$)–^{49}Ti ($I = {}^7/_2$) complexes with eight equally intense lines. Low-intensity 11-line, 15-line, and 13-line patterns will be exhibited by the ^{47}Ti–^{47}Ti, ^{49}Ti–^{49}Ti, and ^{47}Ti–^{49}Ti complexes, respectively, because of the lower relative abundance of these complexes. Thus, the hyperfine structure for the binuclear complex will look similar to that for the mononuclear complex, except the interline spacing will be halved and there will be some weak features seen for the complexes where both ions have $I \neq 0$.

The EPR spectra for room-temperature toluene/benzene solutions of the binuclear complexes V (cyclohexane-*trans*-1,4-dicarboxylate) and II (adamantane-1,3-dicarboxylate) are shown in Figure 13. The hyperfine structure is different from that seen for the monomer and is as expected for a binuclear complex with $J \gg a$. The interline spacings between the more intense features are in the range of 4–5 G, which is half the value for the mononuclear complex. A pattern of weaker signals is also seen in each case. The same type of spectrum was seen for binuclear complex II bridged by the bicyclo[1.1.1]pentane-1,3-dicarboxylate dianion. The observation of such spectra substantiates the fact that there are *intra*molecular magnetic exchange interactions present in these three binuclear complexes.

The spectrum for binuclear complex IV bridged by the cyclohexane-*trans*-1,2-dicarboxylate dianion is not as well resolved as those for the above binuclear complexes. Eight poorly resolved hyperfine peaks and a central derivative which is much broader than seen for the above complexes are found for complex IV. The broadness and resultant poor resolution are due to the fact that complex IV is less symmetric than the other complexes and consequently will tumble more slowly in solution. The dipole–dipole interactions (zero-field splitting) are not completely averaged to zero by the slower tumbling of complex IV. Finally, it should be noted that most of the binuclear complexes bridged by aliphatic dicarboxylate dianions, which were described in the preceding paper, do ***not*** show resolved hyperfine in their room-temperature solution spectra but show only broad single derivatives. These binuclear complexes are more flexible than the cyclic aliphatic species and, consequently, do not tumble readily in solution. It was possible to heat toluene/benzene (4:1) solutions of five of the straight-chain compounds and resolve hyperfine features that are characteristic of an exchange interacting binuclear complex. Solutions of the binuclear complexes bridged by the oxalate, succinate, 2-methyl-2-ethylsuccinate, 3,3-diethylglutarate, and adipate dianions were examined at 90 °C. In all cases four of the expected eight intense hyperfine features were seen and interline spacings of 4–5 G were measured.

Comments and Comparison with Related Systems. The magnetic susceptibility and EPR data for the complexes in the present paper further support the suggestion from the preceding paper that magnetic exchange interactions between two titanium(III) metallocene units can be propagated by chains of methylene carbon atoms. From the EPR spectra for solutions it can be concluded that there is an intramolecular antiferromagnetic interaction present in these binuclear complexes and $|J| \gg 10^{-3}$ cm^{-1}. With the susceptibility data for the solids it is difficult to conclude that all of the observed antiferromagnetic interaction is intramolecular. Some of the interaction might be intermolecular in nature. The rigid saturated frameworks of the adamantane, bicyclo[1.1.1]pentane, cyclobutane, and cyclopropane units ensure that the *intra*molecular magnetic exchange interactions are not occurring by virtue of two $(\eta^5\text{-}C_5H_5)_2Ti$ moieties coming into contact in a binuclear complex. Although the solid-state structures are not known, it is interesting that the antiferromagnetic exchange interaction is greater in the adamantane-1,3-dicarboxylate ($J = -2.3$ cm^{-1}) and bicyclo[1.1.1]pentane-1,3-dicarboxylate ($J = -1.4$ cm^{-1}) bridged complexes than in the glutarate-bridged complex ($J = -0.82$ cm^{-1}). In all three of these complexes there is a three-methylene-carbon bridge between the two $(\eta^5\text{-}C_5H_5)_2TiO_2C$ moieties. Likewise, the cyclobutane-*trans*-1,2-dicarboxylate bridged complex ($J = -2.2$ cm^{-1}) exhibits a greater exchange interaction than the succinate-bridged complex ($J = -1.6$ cm^{-1}), the corresponding linear-chain molecule. The σ orbitals of the three rigid systems may be poised for better overlap and spin polarization which could enhance the antiferromagnetic exchange interaction relative to the open-chain molecule. The 3-methylcyclopropane-*trans*-1,2-dicarboxylate complex ($J = -1.3$ cm^{-1}), on the other hand, exhibits a weaker exchange interaction than the succinate-bridged complex. This result may be attributable to poor orbital overlap in the strained cyclopropane ring which would decrease the antiferromagnetic exchange interaction relative to the open-chain analogue. No effect from a through-space interaction in the bicyclo[1.1.1]pentane complex seems to be evident. It is clear that there is some orientation effect in operation, for the cyclohexane-*trans*-1,4-dicarboxylate-bridged complex exhibits a greater interaction than observed for the cyclohexane-*trans*-1,2-dicarboxylate-bridged complex. It would be interesting to use the dianion of cyclohexane-*cis*-1,2-dicarboxylic acid as a bridge.

Data have been reported in the literature for two organic biradicals that are related to the biradicals described in this paper. The molecules 1,4-bis(4,4′-dimethyloxagolidine-3′-oxyl)cyclohexane (A) and *N*,*N*′-dioxy-2,6-diazadamantane (B)

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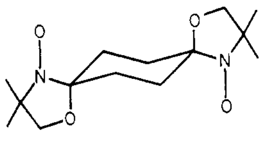
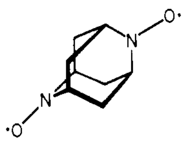
(19) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2078.

(20) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 1841.

(21) Abragam, A.; Bleaney, B. "Electron Paramagnetic Resonance of Transition Ions"; Clarendon Press: Oxford, 1970; p 494. Weissman, S. I. *J. Chem. Phys.* **1958**, *29*, 1189.



A



B

have been studied recently by EPR. In the solid state the biradical B is diamagnetic, whereas in a frozen glass a triplet-state EPR spectrum is seen.[22] *Inter*molecular interactions are believed to be present in the solid state as found for other organic biradicals.[23] The temperature dependence of the $\Delta M_s = 2$ transition was monitored for the glass-state complex, and it was concluded that biradical B is a ground-state triplet with $J = +220$ cm^{-1}.

The cyclohexane biradical A has been studied in solution by various techniques[24] and in a diamagnetic host lattice with EPR.[25] These studies indicate that the biradical has the chair diequatorial conformation both in solution and in the solid state. This has been confirmed by an X-ray structure.[26] The activation energy for interconversion to a chair diaxial conformation was determined to be ca. 11 kcal mol^{-1}.[24] It will be recalled that we found evidence for only the chair diequatorial conformation of the cyclohexane-*trans*-1,2-dicarboxylate-bridged titanium(III) complex and for a predominance of the chair diequatorial form of the cyclohexane-*trans*-1,4-dicarboxylate-bridged complex. The temperature dependence of the $\Delta M_s = 2$ transition was used[24] to provide a limiting value for the magnetic exchange parameter of $J = 0 \pm 1.4$ cm^{-1} for biradical B. The cyclohexane-*trans*-1,4-dicarboxylate-bridged titanium(III) metallocene has about the same order of J value ($=-1.1$ cm^{-1}), which could reflect the fact that both biradicals have an equal number of σ bonds through which the magnetic exchange interaction must be transmitted.

Experimental Section

Compound Preparation. Samples of cyclohexane-*trans*-1,2-dicarboxylic acid, cyclohexane-*trans*-1,4-dicarboxylic acid, cyclobutane-*trans*-1,2-dicarboxylic acid, 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid, and adamantane-1-carboxylic acid were used as received from Aldrich. Adamantane-1-carboxylic acid was converted to adamantane-1,3-dicarboxylic acid with use of the reported procedure.[27] A sample of bicyclo[1.1.1]pentane-1,3-dicarboxylic acid was kindly supplied by Terry L. Renken.[28] Analytical data are given in Table VIII. All of the compounds gave a strong parent peak in a mass spectrum.

The mononuclear and binuclear titanium(III) metallocenes were prepared in the manner described in the preceding paper.

Physical Measurements. The details of physical measurements can be gleaned from the preceding paper.

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Registry No. I, 77071-25-1; II, 77071-26-2; III, 77071-27-3; IV, 77071-28-4; V, 77071-29-5; VI, 77071-30-8; VII, 77071-31-9.

Supplementary Material Available: Tables I–VII (experimental and calculated magnetic susceptibility data) and Figures 2–5 (plots of χ_M and μ_{eff} vs. temperature) (17 pages). Ordering information is given on any current masthead page.

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(22) Dupeyre, R.-M.; Rassat, A.; Ronzaud, J. *J. Am. Chem. Soc.* **1974**, *96*, 6559.

(23) Parmon, V. N.; Kokorin, A. I.; Zhidomirov, G. M. *Zh. Strukt. Khim.* **1977**, *18*, 132.

(24) Michon, P.; Rassat, A. *J. Am. Chem. Soc.* **1975**, *97*, 696.

(25) Rohde, O.; Van, S. P.; Kester, W. R.; Griffith, O. H. *J. Am. Chem. Soc.* **1974**, *96*, 5311.

(26) Gleason, W. B. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2959.

(27) Butenko, L. N.; Derbisher, V. E.; Khardin, A. P.; Shreibert, A. I. *Zh. Org. Khim.* **1973**, *9(4)*, 728.

(28) Renken, T. L., unpublished results.