Contribution from the School of Chemical Sciences and the Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801

Binuclear Dicyclopentadienyltitanium(III) Complexes: Magnetic Exchange Interactions Propagated by Unsaturated and Aromatic Dicarboxylate Dianions

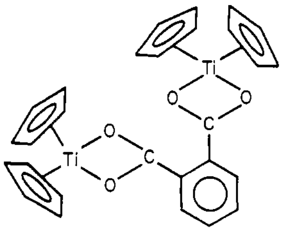
LYNN C. FRANCESCONI,[1] DAVID R. CORBIN,[2a] ARRIETTA W. CLAUSS,[1] DAVID N. HENDRICKSON,*[1,3]
and GALEN D. STUCKY*[2]

Received June 26, 1980

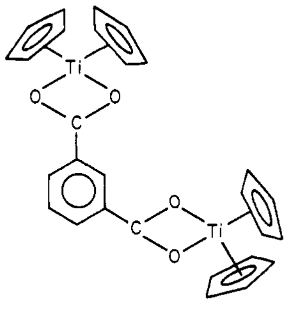
Antiferromagnetic exchange interactions are seen for binuclear bis(η^5-cyclopentadienyl)titanium(III) complexes bridged by the dianions of unsaturated and aromatic dicarboxylic acids. There is a monotonic decrease in the exchange interaction as the bridge is changed from the phthalate dianion ($J = -2.8$ cm^{-1}) to the isophthalate dianion ($J = -1.4$ cm^{-1}) and finally to the terephthalate dianion ($J = -0.7$ cm^{-1}). The magnitudes of the exchange parameters for these three phthalate-bridged complexes are intermediate between those of the corresponding cyclic and aliphatic complexes. The antiferromagnetic exchange interactions are propagated by σ-orbital overlaps. This is further substantiated by the fact that the exchange interaction seen for the fumarate-bridged complex is the same as that seen for the succinate-bridged complex. The ferrocene-1,1′-dicarboxylate-bridged complex exhibits an interaction with $J = -0.78$ cm^{-1}. Frozen toluene/benzene glass EPR spectra, taken at both X-band and Q-band frequencies, show triplet-state signals. The EPR spectra for the isophthalate- and terephthalate-bridged complexes can be computer simulated reasonably well. One curious observation is made. The magnetic susceptibility vs. temperature data for the supposedly monomeric benzoate complex $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5)$ are characteristic of the strongest antiferromagnetic interaction in all of the dicarboxylate-bridged complexes. The data can be fit to the theoretical susceptibility equation for a binuclear complex to give $J = -4.1$ cm^{-1}.

Introduction

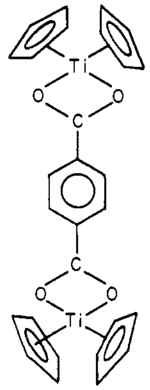
In the two preceding papers, a chain of methylene carbon atoms was shown to be a viable pathway for intramolecular magnetic exchange interactions in binuclear titanium(III) metallocenes. The two titanium(III) ions each have one unpaired electron that resides in a σ-type 3d orbital. The σ bonds of the methylene chain propagate the magnetic exchange interaction. The point of enquiry of the present paper is whether introduction of unsaturation into the bridging carbon chain will affect the magnitude of the magnetic exchange interaction. The dianions of 1,2-benzenedicarboxylic (phthalic) acid, 1,3-benzenedicarboxylic (isophthalic) acid, 1,4-benzenedicarboxylic (terephthalic) acid, 1,6-naphthalenedicarboxylic acid, fumaric acid, and 1,1′-ferrocenedicarboxylic acid were selected as bridging groups to examine this question. One mole of each dicarboxylic acid was oxidatively added to 2 mol of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ to give compounds I–IV and VI.



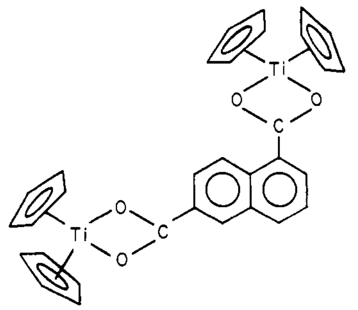
I



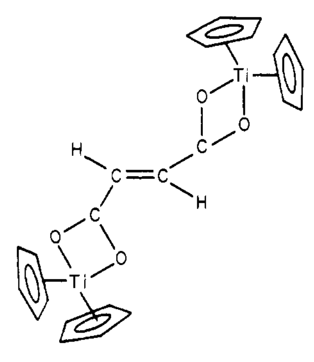
II



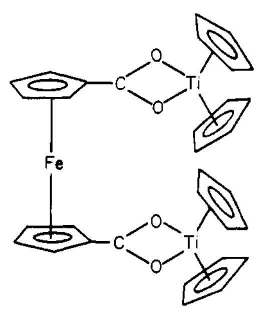
III



IV



V



VI

Results and Discussion

Magnetic Susceptibility. Data were collected from ca. 245 to 4.2 K for solid samples of the six binuclear complexes in this study; the data are given in Tables I–VI.[4] There is an antiferromagnetic exchange interaction present in these complexes. In the case of the phthalate-bridged complex, μ_{eff}/Ti is 1.78 μ_B at 224 K and drops to 1.26 μ_B at 4.2 K. These data were fit to the Bleaney–Bowers equation[5] to give $J = -2.8$ cm^{-1} and $g = 2.06$. The attenuation in μ_{eff}/Ti for the isophthalate-bridged complex is less than that for the phthalate complex; μ_{eff}/Ti varies from 1.77 μ_B at 245 K to 1.50 μ_B at 4.5 K to give fitting parameters of $J = -1.4$ cm^{-1} and $g = 1.99$. There is very little if any decrease in μ_{eff}/Ti for the terephthalate-bridged complex III where μ_{eff}/Ti is 1.77 μ_B at 224 K and decreases to 1.61 μ_B at 4.2 K. Fitting the data gives $-J \leq 0.72$ cm^{-1} and $g = 1.96$. The exchange parameters for the complexes studied in this paper are summarized in Table VII.

The successive addition of a carbon atom to the bridging chain interposed between the $(\eta^5\text{-}C_5H_5)_2Ti(O_2C)$ moieties in the benzenedicarboxylate-bridged complexes leads to a monotonic reduction in the magnitude of the exchange interaction. The same behavior was found for the binuclear complexes

---

(1) School of Chemical Sciences.

(2) (a) School of Chemical Sciences and the Materials Research Laboratory. (b) Address correspondence to Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, DE 19898.

(3) A. P. Sloan Foundation Fellowship, 1976–1978.

(4) Supplementary material.

(5) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

0020-1669/81/1320-2078$01.25/0

Table VII. Exchange Parameters

compd	J, cm^{-1}	compd	J, cm^{-1}
I	−2.8	IV	−1.4
II	−1.4	V	−1.6
III	−0.72	VI	−0.78

bridged by chains of aliphatic carbon atoms. The magnitudes of the exchange parameters found for the aromatic systems are roughly intermediate between those of the corresponding rigid and flexible aliphatic compounds. For example, in the cases where the number of noncarboxylate carbon atoms in the shortest pathway equals 4, the aromatic complex III has a J value of -0.72 cm^{-1}, which is intermediate between the J value for the adipate-bridged complex ($-J >$ ca. 0.3 cm^{-1}) and that for the cyclohexane-trans-1,4-dicarboxylate-bridged complex ($J = -1.1$ cm^{-1}). This could reflect the fact that the relative orientations and overlap properties of the σ orbitals in the bridge framework are more important than the availability of π orbitals. If the antiferromagnetic exchange interactions seen in the solid state are intramolecular in nature, it is clear that the magnetic exchange interactions observed for the three benzenedicarboxylate-bridged complexes are propagated largely by σ interactions.

The 1,6-naphthalenedicarboxylate dianion provides an even more extended aromatic bridge than is present in the phthalate series. In spite of the greater extension, there is indication of an antiferromagnetic interaction for the 1,6-naphthalenedicarboxylate-bridged complex. The data for this compound were fit to give $J = -1.4$ cm^{-1} and $g = 2.00$. The interaction is essentially the same as that found for the meta-substituted phthalate complex.

The fumarate-bridged complex V offers another opportunity to check whether the presence of π bonding affects the magnitude of the magnetic exchange interaction. The data for this compound are given in Table IV.[4] An antiferromagnetic interaction is present which is characterized by $J = -1.6$ cm^{-1} and $g = 1.98$. The value is the same as that observed in the preceding paper for the succinate-bridged complex, which indicates that the π bonding of the fumarate bridge does *not* affect the interaction.

It was fascinating to find that the ferrocene-1,1′-dicarboxylate-bridged complex VI also exhibits an antiferromagnetic exchange interaction. The value of μ_{eff}/Ti varies from 1.75 μ_B at 163 K to 1.62 μ_B at 4.2 K, and fitting the data gives $J = -0.78$ cm^{-1} and $g = 2.03$. A C–Fe–C fragment provides the interconnecting electron density between the two $(\eta^5\text{-}C_5H_5)_2TiO_2C$ moieties.

No signs of an antiferromagnetic exchange interaction were seen in the magnetic susceptibility data for the adipate-bridged complex or for the binuclear complexes bridged by aliphatic dicarboxylate dianions with six or ten methylene groups or for the mononuclear adamantane complex. Thus, it appears that those molecules with no possibility for an intramolecular interaction do not show an exchange interaction in the solid state. An exception to this general statement was found with the "mononuclear" benzoate complex $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5)$. The magnetic susceptibility data for this compound, illustrated in Figure 1 and given in Table VIII,[4] clearly show the presence of an antiferromagnetic interaction. The value of μ_{eff}/Ti varies from a spin-only value for one unpaired electron at high temperature to 0.83 μ_B at 4.2 K. This is the only compound in the three papers that exhibits a maximum in the χ_M vs. T curve. As can be seen by the solid lines in Figure 1, the data can be fit to the theoretical equation for a $S_1 = S_2 = {}^1/_2$ dimer with the parameters $J = -4.1$ cm^{-1} and $g = 2.00$. It is possible that there is a dimeric association present in the solid state for the benzoate complex. A structural investigation is currently in progress.

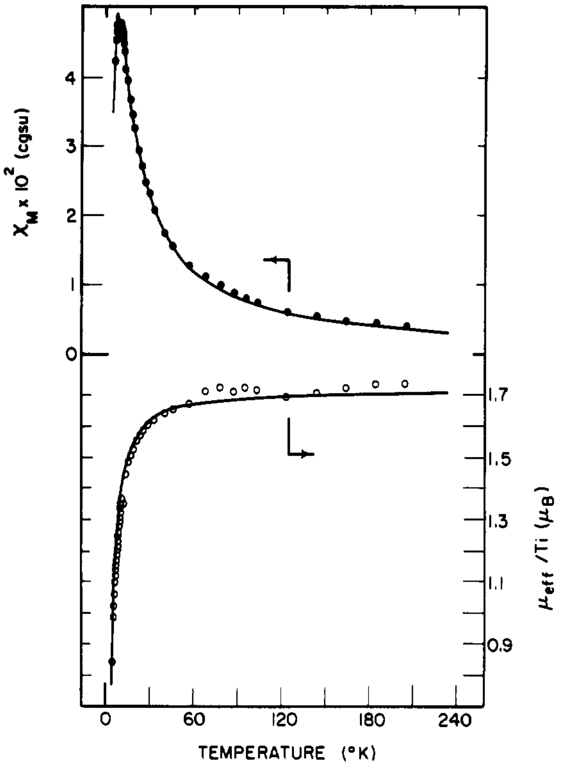


Figure 1. Plots of effective magnetic moment per titanium(III) ion, μ_{eff}/Ti, and molar paramagnetic susceptibility per binuclear complex, χ_M, vs. temperature for the associated complex of (benzoato)bis(η^5-cyclopentadienyl)titanium(III). The solid lines represent the least-squares fit of the data to the theoretical question.

Electron Paramagnetic Resonance. EPR spectra were recorded for liquid-nitrogen-temperature toluene/benzene (4:1) glasses of complexes I–IV and VI. The mononuclear benzoate complex VII was found to have the same g values and X-band and Q-band spectral appearance as we reported in the preceding papers for the mononuclear acetate and adamantane-1-carboxylate complexes. There is no evidence of a dimeric association of the benzoate complex in the glass media as seen for the benzoate in the solid state.

The aromatic dicarboxylate bridges provide a distinct advantage over the noncyclic and cyclic aliphatic dicarboxylates. Not only is the benzene unit rigid, but the carboxyl moieties would be expected to be conjugated with the benzene ring. The aromatic dicarboxylate dianions remain planar, which eliminates any problems involving more than one molecular conformation present in the glass media.

The X-band spectrum for a frozen glass of the terephthalate-bridged complex III is shown as the top tracing in Figure 2. The assignments of the spectral features are given in the figure. The derivatives marked Z_1 and Z_2 result from the zero-field splitting of the g_z signal. The spacing between these two features, 48 G, is equal to $2D$ (D is the axial zero-field splitting parameter) because this binuclear complex is centrosymmetric. The zero-field splitting of the g_x and g_y signals are also indicated and correspond to 22 and 21 G, respectively. It is clear that the rhombic zero-field splitting parameter E is very small for this complex, and, consequently, the splitting of the g_x and g_y signals is essentially equal to D. The Q-band spectrum for a frozen glass of this same compound is illustrated in Figure 3 (top tracing). In this case there is less overlap of signals compared to the X-band spectrum because the magnetic fields separating the components of the g tensor are greater than is present in the X-band case. Six signals are evident in the Q-band spectrum which has the classic appearance expected for a triplet-state molecule with

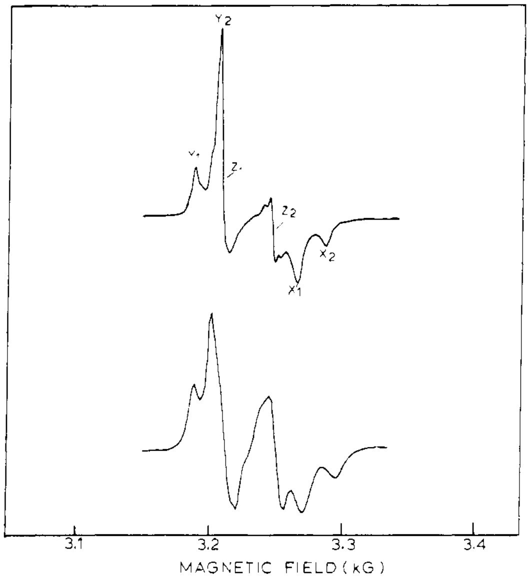


Figure 2. Experimental X-band spectrum for a liquid-nitrogen-temperature frozen toluene-benzene (4:1) glass of the terephthalate-bridged complex III (upper tracing) and the computer-simulated X-band spectrum (lower tracing).

Table IX. Least-Squares Fit of Frozen-Glass X-Band and Q-Band Data for the Isophthalate-Bridged Complex II and the Terephthalate-Bridged Complex III to the Theoretical Equations[a]

		field,[c] G		field,[d] G	
	peak[b]	obsd	calcd	obsd	calcd
X-band	Z1	3 231	3 238	3 249	3 268
	Y1	3 237	3 231	3 236	3 239
	X1	3 316	3 316	3 316	3 322
	Z2	3 300	3 308	3 297	3 315
	Y2	3 272	3 268	3 257	3 263
	X2	3 342	3 350	3 337	3 345
Q-band	Z1	12 556	12 555	12 712	12 708
	Y1	12 480	12 482	12 565	12564
	X1	12 808	12 806	12 885	12 883
	Z2	12 629	12 626	12 760	12 755
	Y2	12 518	12 519	12 590	12 588
	X2	12 842	12 840	12 907	12 906

[a] Wasserman et al.[6] derived equations for the resonance fields expected for the six $\Delta M_s = 1$ transitions of a $S = 1$ molecule. The fitting parameters are given in the text. [b] Compound II was fit to $D = 0.0033$ cm^{-1}, $E = 0.0001$ cm^{-1}, and $g_x = 1.9509$, $g_y = 2.0013$, and $g_z = 1.9869$. Compound III was fit to $D = 0.0022$ cm^{-1}, $E = 0.000\,04$ cm^{-1}, $g_x = 1.9516$, $g_y = 2.0010$, and $g_z = 1.9766$. [c] Compound II. [d] Compound III.

a rhombic **g** tensor. It can be seen that the zero-field splitting observed for a particular **g** tensor component is independent of the microwave frequency.

The theoretical equations for the resonance fields of the six ΔM_s signals of a centrosymmetric $S = 1$ molecule, as derived by Wasserman et al.,[6] are given in the first paper in this series. The magnetic field positions observed in both the X-band and Q-band spectra of the terephthalate-bridged complex were simultaneously least-squares fit to these equations to give $g_x = 1.951$, $g_y = 2.001$, $g_z = 1.987$, $D = 0.0022$ cm^{-1}, and $E = 0.0001$ cm^{-1}. The observed and calculated resonance fields are given in Table IX. As indicated before, the dipole–dipole zero-field splitting of the g_z component of a centrosymmetric binuclear complex is given as $D_{\mathrm{dd}} = 0.65 g_z^2/R^3$, where R is the Ti–Ti distance. A Ti–Ti distance of 10.55 Å is calculated by using the above values of g_z and D. This is in good agreement with a value of 10.6 Å that was estimated from a CPK space-filling model.

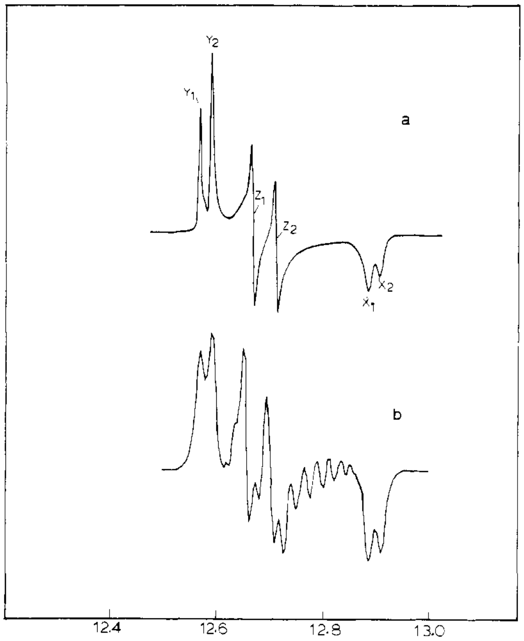
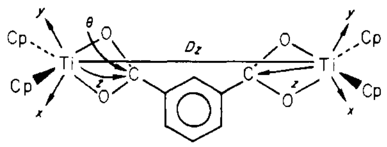


Figure 3. Experimental Q-band spectrum for a frozen toluene/benzene glass of the terephthalate-bridged complex III (upper tracing) and the computer-simulated Q-band spectrum (lower tracing).

The best check of the assignment of the spectra for the complex was afforded by computer simulating both the X-band and Q-band spectra with the same parameters. As implied above, the inter-titanium vector (z axis of **D** tensor) was taken as collinear with g_z. A Ti–Ti distance of 10.55 Å was assumed. The g values that were used to simulate the spectra were close to those found from fitting the resonance fields, and they are $g_x = 1.9516$, $g_y = 2.0010$, and $g_z = 1.9850$. The bottom tracings in Figures 2 and 3 give the computer simulations of the X-band and Q-band spectra, respectively. The simulations appear to be in good agreement with the experimental spectra. Some small "peaks" due to incomplete averaging are seen in the Q-band simulation.

The isophthalate-bridged complex II is similar to the glutarate-bridged complex described in our preceding paper in that both binuclear complexes have three-carbon-atom fragments interposed between the two $(\eta^5\text{-}C_5H_5)_2TiO_2C$ units. However, only one conformation of the isophthalate-bridged complex would be expected in the frozen-glass media. As indicated in



D_z and g_z are not collinear but are related by the angle θ. The X-band and Q-band spectra for this complex are illustrated in Figures 4 and 5 (top tracings) together with spectral assignments. The observed resonance fields were least-squares fit to the Wasserman equations (even though the complex is not strictly centrosymmetric). The resulting g, D, E, and observed and calculated resonance fields are given in Table IX. These parameters were varied slightly, then, to find that the X-band and Q-band EPR spectra can be simulated reasonably well with the parameters $g_x = 1.955$, $g_y = 2.002$, $g_z = 1.991$, a Ti–Ti distance of 9.2 Å, $E = 0.002$ cm^{-1}, and $\eta = \zeta = 0$ (collinearity of D_z and g_z). Close examination of the

---

(6) Waserman, E.; Synder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

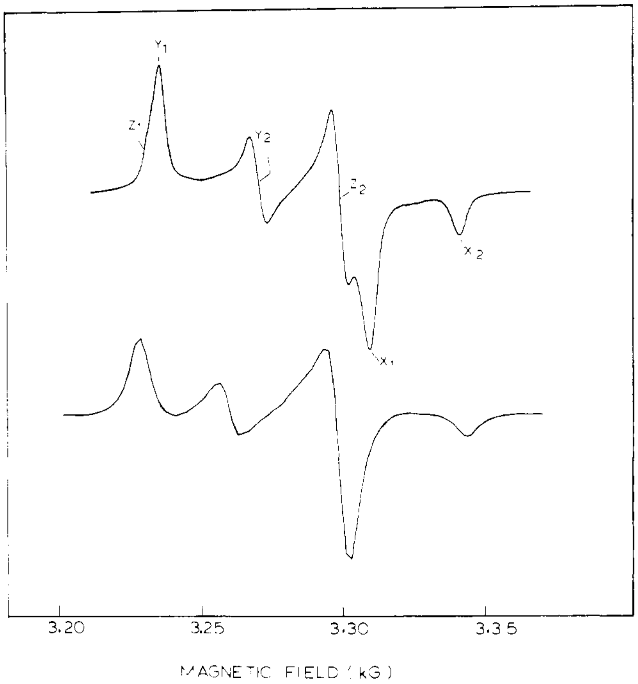


Figure 4. Experimental X-band spectrum for a frozen toluene/benzene glass of the isophthalate-bridged complex II (upper tracing) and the computer-simulated X-band spectrum (lower tracing).

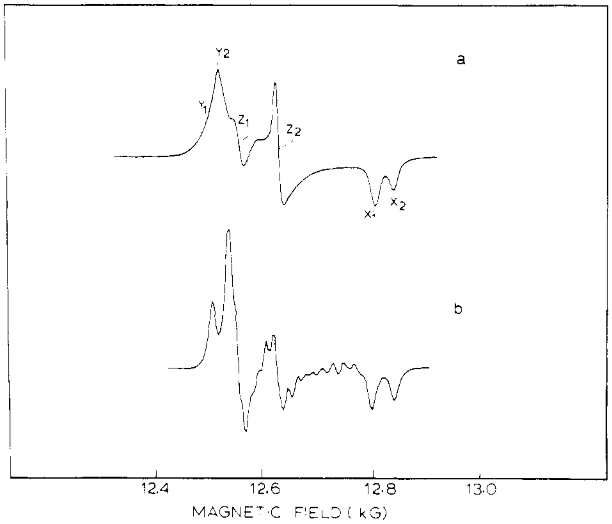


Figure 5. Experimental Q-band spectrum for a frozen toluene/benzene glass of the isophthalate-bridged complex II (upper tracing) and the computer-simulated Q-band spectrum (lower tracing).

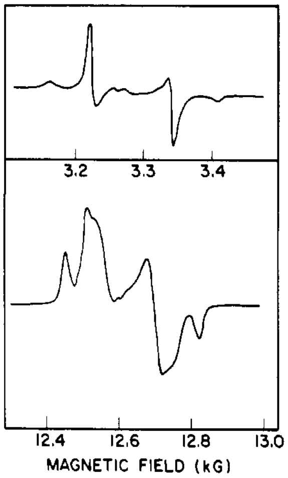


Figure 6. X-Band (upper) and Q-band (lower) spectra of a frozen toluene/benzene glass of the phthalate-bridged complex I.

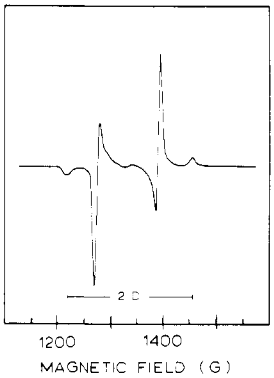


Figure 7. S-Band EPR spectrum of a frozen toluene/benzene glass of the phthalate-bridged complex I.

simulations in Figures 4 and 5 show that they are not as good as were obtained for the phthalate-bridged complex, but this is to be expected.

The phthalate-bridged complex I is far from centrosymmetric. The presence of a magnetic exchange in this complex would lead to an averaging of the different components of the **g** tensors of the two isolated $(\eta^5\text{-}C_5H_5)_2Ti$ moieties. This averaging would result in a **g** tensor for the triplet state of the binuclear complex that would not resemble the **g** tensors of a mononuclear complex. Neither the Wasserman equations nor the computer-simulation program can handle this situation. The X-band spectrum of a frozen toluene/benzene glass of complex I is shown in Figure 6. There is evidence of a weak signal in the center of the spectrum from mononuclear complexes. Only four $\Delta M_s = 1$ transitions are readily resolved in the X-band spectrum, whereas the Q-band spectrum shows six $\Delta M_s = 1$ signals. The **g**-tensor misalignment problem necessitates a decrease in the microwave frequency in order to deemphasize the Zeeman effect and **g**-tensor misalignment. The S-band (ca. 3.7 GHz) spectrum for complex I is shown in Figure 7. The spectrum is very axial in appearance, and the separation between the outermost turning points sets the magnitude of D as 123 G (=0.0115 cm^{-1}), which together with $g_z = 1.98$ gives a Ti–Ti distance of 6.05 Å. A CPK model gives a value of ca. 6.2 Å; a value of 6.17 Å can also be calculated from reasonable metal–ligand bond dimensions and the crystal structure[7] of a salt of the dianion of phthalic acid. It is interesting that, by a similar analysis of the EPR spectrum of a frozen solution of $TiCl_3$ and phthalic acid, a Ti–Ti distance of ca. 6.5 Å was estimated for a metal chelate complex.[8]

The X-ray structure[9] of naphthalene-1-carboxylic acid shows that the plane of the carboxyl group is twisted 11° from the plane of the naphthalene ring system due to steric interactions between one carboxyl oxygen atom and the proton at position 8. It is not surprising then that the EPR spectra for toluene/benzene glasses of the binuclear complex IV bridged by the naphthalene-1,6-dicarboxylate dianion reflect the presence of more than one molecular conformation frozen out in the glass, as the carboxyl group at the 1-position is not conjugated with the naphthalene unit.

Complex VI, which is bridged by the dianion of ferrocene-1,1′-dicarboxylic acid, would be expected to have misaligned **g** tensors. It is clear from the X-band and Q-band spectra (see Figure 8) for a frozen glass of complex VI that only one molecular conformation is present in the glass me-

---

(7) Smith, R. A. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1773.
(8) Smith, T. D.; Lund, T.; Pilbrow, J. R. *J. Chem. Soc. A* **1971**, 2786.
(9) Trotter, J. *Acta Crystallogr.* **1960**, 13, 732.

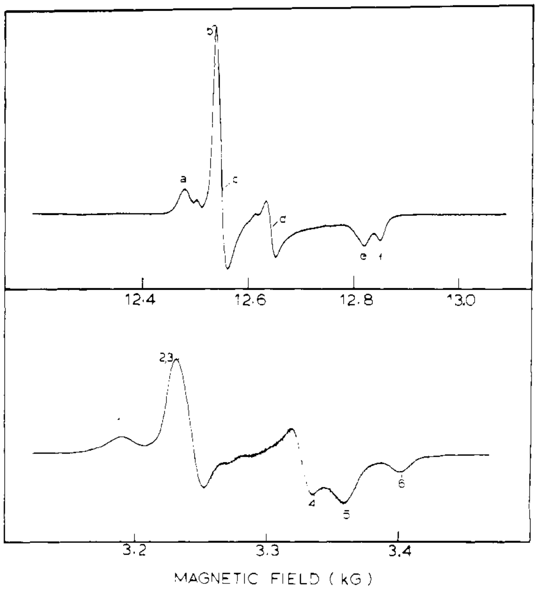


Figure 8. X-Band (lower) and Q-band (upper) EPR spectra for a frozen toluene-benzene glass of complex VI which is bridged by the dianion of ferrocene-1,1′-dicarboxylic acid.

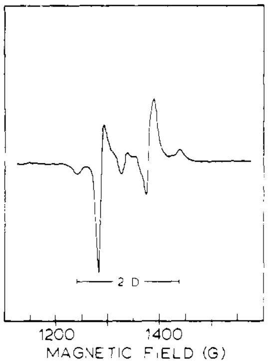


Figure 9. S-Band EPR spectrum of a frozen toluene/benzene glass of the ferrocene-1,1′-dicarboxylate-bridged complex VI.

dium. The S-band spectrum for complex VI, illustrated in Figure 9, gives a good estimate of the D value of this complex: 105 G = 0.0098 cm^{-1}. This D value corresponds to a Ti–Ti distance of 6.40 Å. If the cyclopentadienyl and carboxyl groups in binuclear complex VI were eclipsed, a Ti–Ti distance of ca. 3.3 Å (ring-to-ring distance) would result. Steric interactions between the cyclopentadienyl ligands on the two titanium ions preclude this eclipsed situation. If the two iron cyclopentadienyl ligands are eclipsed and the carboxyl groups are transoid, this centrosymmetric form of complex VI would have a Ti–Ti distance of ca. 10.6 Å. Obviously, the Ti–Ti distance calculated from the glass EPR data indicates an intermediate conformation. The crystal structure[10] of ferrocene-1,1′-dicarboxylic acid shows an eclipsed structure due apparently to intermolecular hydrogen-bonding interactions.

All of the binuclear titanium(III) metallocenes bridged by aromatic dicarboxylate dianions show well-developed $\Delta M_s = 2$ transitions in the X-band spectra for frozen glasses. The presence of *intra*molecular magnetic exchange interactions is also verified by the observation of ^{47}Ti and ^{49}Ti nuclear hyperfine in the X-band spectra for room-temperature solutions of these complexes. Figure 10 gives a comparison of the room-temperature spectra of the mononuclear benzoate complex and the isophthalate-bridged binuclear complex. The difference in interline spacing between the spectra of the mononuclear and binuclear complexes is characteristic of the presence of an *intra*molecular magnetic exchange interaction.

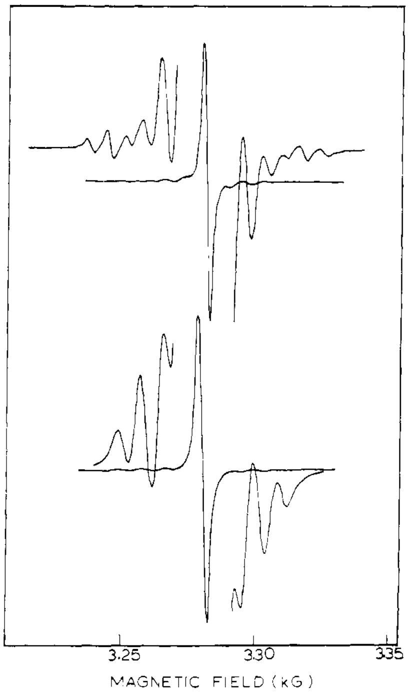


Figure 10. Room-temperature X-band EPR spectra of toluene/benzene (4:1) solutions of the mononuclear benzoate complex IV (lower tracing) and the isophthalate-bridged complex II (upper tracing). The insets are run at higher gains.

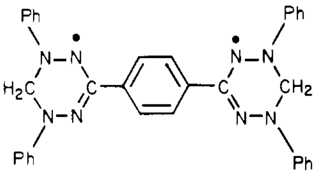
Comments and Comparison with Related Molecules. It was the goal of this series of three papers to establish if magnetic exchange interactions between two transition-metal ions could be propagated by chains of methylene carbon atoms. A comment on the level of success is appropriate at this point. Variable-temperature magnetic susceptibility data were presented for *solid* samples of most of the titanium(III) metallocenes prepared in this work. Antiferromagnetic exchange interactions are evident. The trends in the magnitudes of exchange parameters and the absence of signs of such interactions in monomers (except the benzoate) and binuclear complexes with very extended bridges suggest that these antiferromagnetic exchange interactions are *intra*molecular in nature. EPR spectra for frozen glasses of the complexes, in conjunction with mass spectral and infrared data, clearly indicate that the complexes are binuclear, where the dicarboxylate dianion most likely bridges in a bis-bidentate fashion, forming four-membered chelate rings. The presence of *intra*molecular antiferromagnetic exchange interactions in these binuclear titanium(III) metallocenes is definitely established via the titanium hyperfine structure that is seen in the EPR spectra for solution-state species. Furthermore, it is clear in the cases of the complexes bridged by the rigid polycyclic dicarboxylate dianions that the intramolecular exchange interaction is indeed propagated by chains of methylene carbon atoms.

A few biradicals (A–E) have been studied which have benzene units bridging two radical centers and these molecules are interesting to compare with the molecules in this paper. The two biradicals 1,4-bis(1,5-diphenyl-3-verdazyl)benzene-(*p*-verdazyl) and 1,3-bis(1,5-diphenyl-3-verdazyl)benzene(*m*-verdazyl) (A and B, respectively) have been studied in frozen glasses with EPR.[11] Both biradicals show triplet-state spectra

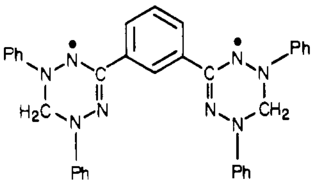
---

[10] Palenik, G. *Inorg. Chem.* **1969**, *8*, 2744.

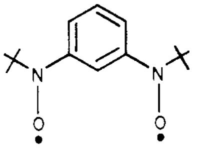
[11] Mukai, K.; Azuma, N.; Shikata, H.; Ishizu, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3958. Kopf, P.; Morokuma, K.; Kreilick, R. *J. Chem. Phys.* **1971**, *54*, 105.



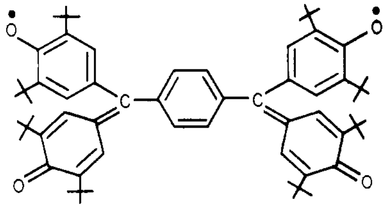
A



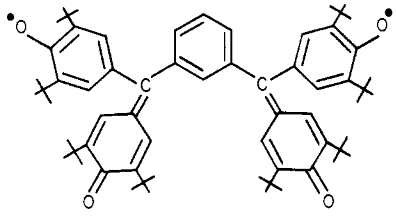
B



C



D



E

with zero-field splitting parameters ($2D$ values) of 43 and 53 G, respectively. These D values are close to those found for the analogous binuclear complexes II and III. Magnetic susceptibilities in the range of 1.8–300 K have been recently reported[12] for *solid* samples *p*-verdazyl and *m*-verdazyl to indicate that both of these biradicals have triplet-state ground states with $J \gg 200$ cm^{-1}. The *p*-verdazyl and *m*-verdazyl biradicals differ from our complexes in that these two organic biradicals have their unpaired electrons located in π-type orbitals. In fact, Hückel molecular orbital calculations[13] have predicted doubly degenerate highest occupied molecular orbitals, each half-filled, for the *p*-verdazyl and *m*-verdazyl biradicals. This would explain the apparent large ferromagnetic exchange interaction in these biradicals. The *N*,*N'*-di-*tert*-butyl-*m*-phenylenebinitroxide biradical C has also been found[14] to have a triplet ground state with $J \gg 100$ cm^{-1}.

There are clearly weak magnetic exchange interactions present in the *p*- and *m*-phenylenebis(galvinoxyl) biradicals (D and E, respectively). Biradicals D and E both show nine-line superhyperfine patterns due to the equivalent eight meta-ring protons in solution EPR spectra[15] which means that $J \gg 1.4$ G ($= 0.000\,13$ cm^{-1}). Very recently Mukai and Tamaki[16] determined the magnetic susceptibility of a solid sample of biradical D in the range of 55–290 K and found that $J \ll 19$ cm^{-1}. The magnitude of the magnetic exchange interaction in biradical D could be approximately the same as that found for the binuclear titanium(III) complex III. Additional work is needed on the organic biradicals.

Experimental Section

All of the binuclear complexes in this paper except one were prepared by reacting 1 mol of the dicarboxylic acid with 2 mol of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ in the manner described in the first paper in this series. The dicarboxylic acids were used as commercially available. Analytical data are given in Table X.

A sample of the fumarate-bridged complex V was prepared by reacting in an inert-atmosphre an aqueous solution of $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ with the sodium salt of fumaric acid.[17] This procedure was used because it was found that $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ catalyzes the hydrogenation of fumaric acid.[18]

All compounds were characterized by analytical data and mass spectra (intense parent peaks seen). Magnetic susceptibility and EPR measurements were carried out as indicated in the first paper in this series.

Acknowledgment. The support of NIH Grant HL 13652 (D.N.H.) is acknowledged as is the support of NSF Grants NSF-DMR-78-23999 and CHE-78-24964 (G.D.S.). The mass spectral data processing equipment was provided by NIH Grants CA 11388 and GM 16864. Professor R. L. Belford and J. R. Pilbrow are thanked for experimental assistance and helpful dicussions. The S-band EPR spectra were run at the National Biomedical ESR Center, Medical College of Wisconsin, Milwaukee, WI 53326. This center is supported by NIH Grant 5-P41-RR01008.

Registry No. I, 77071-32-0; II, 77071-33-1; III, 77071-34-2; IV, 77071-35-3; V, 12249-06-8; VI, 77097-66-6; VII, 51178-00-8.

Supplementary Material Available: Tables I–VI, VIII, and X (experimental and calculated magnetic susceptibility and analytical data) (15 pages). Ordering information is given on any current masthead page.

---

(12) Azuma, N.; Ishizu, K.; Mukai, K. *J. Chem. Phys.* **1974**, *61*, 2294.

(13) Fischer, P. H. H. *Tetrahedron* **1967**, *23*, 1939.

(14) Mukai, K.; Nagai, H.; Ishizu, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2381.

(15) Mukai, K.; Tamaki, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1239.

(16) Mukai, K.; Tamaki, T. *J. Chem. Phys.* **1978**, *68*, 2006.

(17) Coutts, R. S. P.; Wailes, P. C. *Aust. J. Chem.* **1967**, *20*, 1579.

(18) Corbin, D. R.; Stucky, G. D., manuscript in preparation.