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Synthesis, Electron Paramagnetic Resonance, and Magnetic Studies of Binuclear Bis(η^5-cyclopentadienyl)titanium(III) Compounds with Bridging Pyrazolate, Biimidazolate, and Bibenzimidazolate Anions

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The preparation and characterization of three binuclear Ti(III) complexes, $[(\eta^5\text{-}C_5H_5)_2Ti]_2(\text{BiIm})$, $[(\eta^5\text{-}C_5H_5)_2Ti]_2(\text{BiBzIm})$, and $[(\eta^5\text{-}C_5H_5)_2Ti(\text{pz})]_2$, where BiIm^{2-} is the dianion of 2,2′-biimidazole, BiBzIm^{2-} is the dianion of 2,2′-bibenzimidazole, and pz^- is the anion of pyrazole, are reported. The first two air-sensitive compounds are thermally quite stable due to the bis-bidentate nature of the bridging anions, BiIm^{2-} and BiBzIm^{2-}. Antiferromagnetic exchange interactions are present in the first two complexes where $J = -25.2$ cm^{-1} for the BiIm^{2-}-bridged Ti(III) complex and $J = -19.2$ cm^{-1} for the BiBzIm^{2-}-bridged complex, as indicated by magnetic susceptibility data taken from 270 to 4.2 K. In contrast, the bis(pyrazolate)-bridged dimer acts as a normal paramagnet down to 4.2 K with no signs of an antiferromagnetic interaction. An explanation for this difference is presented in terms of the structure of the two types of complexes. Frozen-glass EPR spectra of all three binuclear Ti(III) complexes are characteristic of triplet-state ($S = 1$) spectra with appreciable zero-field splittings. The triplet-state spectra of the three complexes are fit to theoretical equations to give the zero-field splitting parameters D (axial) and E (nonaxial), e.g., for $[(\eta^5\text{-}C_5H_5)_2Ti]_2(\text{BiIm})$ it is found that $|D| = 0.0214$ cm^{-1} and $|E| = 0.0018$ cm^{-1}. Excellent agreement between actual Ti–Ti distances from crystal structures and the calculated distances based on the observed D values is obtained. The 77 K X-band EPR glass (toluene–benzene, 4:1) spectrum of the analogous monomeric complex (*N*-methylbibenzimidazolato)bis(η^5-cyclopentadienyl)titanium(III) shows both titanium hyperfine ($A = 11.0$ G) and nitrogen superhyperfine ($A = 2.2$ G) structure. The nitrogen superhyperfine structure indicates that the two coordinated nitrogen atoms of the *N*-methylbibenzimidazolate are essentially equivalent and demonstrates that appreciable unpaired electron density is found on these two nitrogen atoms in agreement with the observed superexchange interaction in the BiIm^{2-} and BiBzIm^{2-} complexes.

Introduction

The large number of readily available metallic compounds of d^3–d^9 transition metals has greatly encouraged physical and spectral studies of these complexes. In contrast, work with paramagnetic dimers of the early transition metals has lagged, except for those involving the stable vanadyl ion (VO^{2+}), largely because of the air-sensitive nature of many of these compounds.[3]

Recently, we have investigated the structural and electronic properties of a number of paramagnetic bi- and trimetallic organometallic complexes of d^1 metal ions. The structures and antiferromagnetic exchange properties of halide-bridged $[(\eta^5\text{-}C_5H_4CH_3)_2TiX]_2$ (X = Cl or Br) have been reported.[4] The MX_4^{2-} [M = Be(II), Mn(II), or Zn(II)] bridge in $[(\eta^5\text{-}C_5H_5)_2Ti]_2MX_4$ has also been shown to propagate a weak antiferromagnetic interaction.[5] Magnetic and EPR studies have been described for the bimetallic Ti(III) compound $[(\eta^5\text{-}C_5H_4CH_3)_2Ti]_2$(uracil)[6] as well as the analogous trimetallic cyanurate derivative, $[(\eta^5\text{-}C_5H_4CH_3)_2Ti]_3$(cyanurate).

The above and earlier synthetic and theoretical studies of low-valent organotitanium compounds[7] suggested that new bimetallic titanium(III) compounds could be prepared with a variety of bridging organic ligands. The dianions of both biimidazole (BiIm) and bibenzimidazole (BiBzIm) have the potential to function as bis-bidentate nitrogen ligands, bridging between two metal centers, and were selected in an attempt to prepare binuclear Ti(III) complexes. During the course of the research reported here, the X-ray structure of two rhodium complexes with BiIm^{2-} bridges were reported.[9] In particular, the diamagnetic molecule $Rh_2(\text{COD})_2(\text{BiIm})$ was found to be dimeric by virtue of a bridging BiIm^{2-}.

At the outset of this work, it was also anticipated that, in addition to BiIm^{2-} and BiBzIm^{2-}, two pyrazolate (pz) monoanions might bridge two $(\eta^5\text{-}C_5H_5)_2Ti^{III}$ moieties. In this respect, it is relevant to note that Manzer[10] has reported the synthesis of $[(\eta^5\text{-}C_5H_5)_2Ti((\text{pz})_2B(\text{pz})_2)Ti(\eta^5\text{-}C_5H_5)_2](BPh_4)$, where the pyrazoylborate $(\text{pz})_2B(\text{pz})_2^-$ bridges two $(\eta^5\text{-}C_5H_5)_2Ti^{III}$ moieties.

In this paper we report the preparation, EPR, and variable-temperature magnetic susceptibility charactertistics of $[(\eta^5\text{-}C_5H_5)Ti]_2(\text{BiIm})$, $[(\eta^5\text{-}C_5H_5)_2Ti]_2(\text{BiBzIm})$, and $[(\eta^5\text{-}C_5H_5)_2Ti(\text{pz})]_2$. These results are compared with recent theoretical models for bis(cyclopentadienyl)metal complexes.[11,12] In the preceding paper[13] we presented the X-ray crystal structure of $[(\eta^5\text{-}C_5H_5)_2Ti(\text{pz})]_2$, a compound which shows interesting magnetic properties.

Experimental Section

Spectroscopy. EPR studies were carried out on a Varian E-9 X-band spectrometer fitted with a variable-temperature apparatus. Solution samples were run in a toluene–benzene solution (4:1) using sealed quartz sample tubes. Triplet-state EPR spectra were fit to theoretical expressions with an iterative computer program.[14] A polycrystalline sample of diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) in a sealed capillary tube was used as an internal standard for powder samples.

NMR spectra were run on a Varian A60 spectrometer using tetramethylsilane (Me_4Si) as an internal standard. Mass spectra were run on a MAT-Varian CH-5 spectrometer by the staff of the mass spectrometry laboratory of the School of Chemical Sciences.

Magnetic Susceptibility. Variable-temperature (4.2–270 K) magnetic susceptibility measurements were made using a Princeton Applied Research Model 150A vibrating-sample magnetometer that was run at 12.7 kG with $CuSO_4 \cdot 5H_2O$ as the standard. The procedure for data collection has been previously outlined.[15] The magnetic susceptibility as a function of temperature was fit by an iterative computer program to the appropriate form of the Bleaney–Bowers equation (vide infra).[16] Diamagnetic corrections were taken from published tables.[17]

Compound Preparation. Work with air-sensitive organolithium compounds was performed in Schlenk glassware. Synthetic work with titanium compounds was carried out in a Vacuum Atmospheres drybox employing a helium atmosphere. Unless otherwise indicated all reagents and solvents were purchased from Aldrich. Solvents were distilled from sodium and benzophenone. *n*-Butyllithium was used as purchased from Alfa as a 2.4 M solution in hexane, and sodium methoxide was obtained from Matheson. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDT) was bought from Eastman and used with no further purification. Bis(cyclopentadienyl)titanium monochloride was prepared from bis(cyclopentadienyl)titanium dichloride by published procedures.[8] Elemental analyses were performed in the microanalytical laboratory of the School of Chemical Sciences at the University of Illinois.

2,2′-Biimidazole (BiIm). Anhydrous ammonia was slowly bubbled into 250 mL of a 20% solution of glyoxal at such a rate that the temperature was maintained between 40 and 50 °C. After 10 h, the

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solution was filtered and washed with water to give 19.2 g of crude brown product for a yield of 33%. Four grams of the crude product was dissolved in a solution of 4 L of water and 4 g of sodium hydroxide, and on slow cooling, a light brown, fibrous material was recovered in 70% yield. The product was purified to a slightly yellow, fibrous material by nearly quantitative sublimation at 180 °C under a high vacuum. Anal. Calcd for $C_6H_6N_4$: C, 53.72; H, 4.51; N, 41.77. Found: C, 53.87; H, 4.44; N, 41.84. Mass spectrum: calcd, 134; found, 134.

Bis((1,1,4,7,7-pentamethyldiethylenetriamine)lithium) Biimidazole. In 25 mL of distilled tetrahydrofuran (THF) 1.5 g (11 mmol) of biimidazole and 3.89 g (22 mmol) of pentamethyldiethylenetriamine (PMDT) were mixed under a nitrogen atmosphere. On cooling of the mixture to 0 °C, 9.3 mL of 2.4 M *n*-butyllithium (2.2 mmol) was slowly added. After 45 min of stirring at room temperature, the yellow solution was cooled to −78 °C and a white powder precipitated. Upon filtering with Schlenk vessels, 3.11 g of slightly hygroscopic powder was recovered after washing with cold THF for a yield of 58%. The product was sufficiently pure for use in the next reaction step. Anal. Calcd for $C_{24}H_{50}N_{10}Li_2$: C, 52.52; H, 10.23; N, 28.43. Found: C, 58.27; H, 9.33; N, 28.91. ^{1}H NMR (THF-d_8): δ 6.80 (s, 4, bimidazole), 2.5–2.4 (m, 16, methylene of PMDT), 2.35 (s, 6, 4-CH_3 of PMDT), 2.15 (s, 24, terminal CH_3 of PMDT).

Bis(bis(η^5-cyclopentadienyl)titanium) Biimidazole (I). In a drybox 1.2 g of $(LiPMDT)(BiIm)_{1/2}$ (2.4 mmol) and 1.1 g of bis(cyclopentadienyl)titanium monochloride (5.1 mmol) were mixed in 20 mL of THF. Immediately a green precipitate formed and after 3 h of stirring, the solvent was removed at reduced pressure to give a pyrophoric green powder. The powder was extracted in a small Soxhlet extractor under a helium atmosphere for 2 days until the thimble was free of product with a total of 40 mL of toluene. Green microcrystals formed in the solvent during the extraction and were collected by filtration. A total of 0.45 g of bright green air-sensitive crystals was recovered for a yield of 39%. Anal. Calcd for $C_{26}H_{24}N_4Ti_2$: C, 63.95; H, 4.95; N, 11.47; Ti, 19.62. Found: C, 63.39; H, 4.97; N, 11.42; Ti, 19.52. The mass spectrum showed a strong parent ion peak at mass number 488 (calcd 488).

2,2′-Bibenzimidazole (BiBzIm). This ligand was prepared by a modification of the method of Lane.[18] In 40 mL of ethylene glycol 17.6 g (0.20 mol) of oxamide and 45 g (0.40 mol) of *o*-phenylenediamine were mixed and refluxed with stirring for 24 h. After the solution was cooled, it was added to 800 mL of refluxing water and was filtered while hot to give 27 g of water-insoluble yellow product. The crude product was recrystallized from ethylene glycol (1 g/85 mL) using charcoal and produced a fluffy yellow microcrystalline product for a final yield of 53%. Anal. Calcd for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.91. Found: C, 71.50; H, 4.33; N, 23.96. The NMR spectrum taken in trifluoroacetic acid showed a complicated multiplet at δ 7.85–8.10. The nitrogen hydrogens rapidly exchange with the solvent and were not detected.

Bis((1,1,4,7,7-pentamethyldiethylenetriamine)lithium) Bibenzimidazole. Four grams (17.3 mmol) of bibenzimidazole and 6.0 g (34.7 mmol) of 1,1,4,7,7-pentamethyldiethylenetriamine (PMDT) were mixed in 40 mL of distilled THF in a nitrogen atmosphere. With the reaction mixture cooled to 0 °C, 14.4 mL (34.6 mmol) of *n*-butyllithium in hexane (2.4 M) was added. After being stirred for 2 h at room temperature, the green solution was cooled to −78 °C and filtered using Schlenk glassware. After the product was washed with THF at 0 °C, 9.05 g of light green, air-stable product $(LiPMDT)_2(BiBzIm)$ was recovered for a yield of 89%. Anal. Calcd for $C_{34}H_{28}N_4Li_2$: C, 64.84; H, 9.18; N, 23.63. Found: C, 64.72; H, 8.93; N, 23.72.

Bis(bis(η^5-cyclopentadienyl)titanium) Bibenzimidazole (II). In a drybox 1 g (1.69 mmol) of $(LiPMDT)_2(BiBzIm)$ and 0.75 g (3.51 mmol) of bis(cyclopentadienyl)titanium monochloride were mixed in 15 mL of THF. Immediately the solution turned dark green, and a green powder precipitated. Stirring was continued for 1 h and then the solvent was removed under reduced pressure. The product was extracted free of sodium chloride by stirring the green residue repeatedly in 10-mL portions of refluxing toluene until the solvent was saturated and then filtering the solution while hot. On slow cooling, 0.55 g of dark green, air-sensitive microcrystalline product $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiBzIm)$ was recovered for a yield of 53%. Anal. Calcd for $C_{34}H_{28}N_4Ti_2$: C, 69.40; H, 4.80; N, 9.52; Ti, 16.28. Found: C, 69.51; H, 4.54; N, 9.49; Ti, 16.01. The low-resolution mass spectrum showed a strong parent ion at mass number 588 (calcd 588).

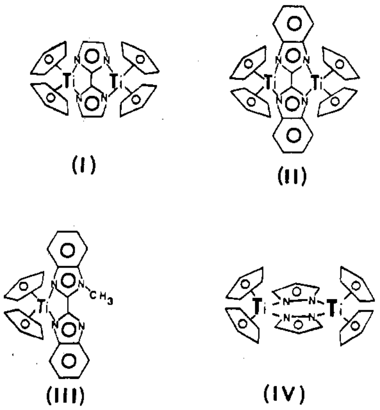


Figure 1. Molecular structures of the compounds: (I) $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiIm)$; (II) $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiBzIm)$; (III) $[(\eta^5\text{-}C_5H_5)_2Ti](N\text{-}CH_3\text{-}BiBzIm)$; (IV) $[(\eta^5\text{-}C_5H_5)_2Ti(pz)]_2$.

***N*-Methyl-2,2′-bibenzimidazole.** One and a half grams of bibenzimidazole (6.4 mmol) was stirred with 0.44 g (8.3 mmol) of sodium methoxide in 400 mL of THF for 1 h with a nitrogen atmosphere. After the addition of 1.3 g (8.3 mmol) of methyl iodide, the solution was sealed in a glass pressure bottle and heated at 95 °C (4 atm) for 2 days with stirring. The solvent was removed under reduced pressure and the residue was sublimed at 150 °C (10^{-3} Torr) to give 0.95 g of crude product consisting of both the mono- and dimethylated products. The more volatile monomethylated product Me-BiBzIm was recovered as a yellow powder by sublimation at 120 °C for a yield of 39% (0.61 g). Anal. Calcd for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57. Found: C, 72.36; H, 4.79; N, 22.85. ^{1}H NMR (F_3CCOOH): δ 8.05–7.90 (m, 8, phenyl), 4.52 (s, 3, Me).

Bis(η^5-cyclopentadienyl)titanium *N*-Methylbibenzimidazole (III). In a drybox 0.25 g of Me-BiBzIm (1.0 mmol) was mixed with 0.174 g (1.0 mmol) of PMDT. *n*-Butyllithium (0.42 mL of a 2.4 M solution in hexane, 1.0 mmol) was added and the solution was stirred for 2 h. Bis(cyclopentadienyl)titanium monochloride was added (0.22 g, 1.0 mmol) and the solution was stirred for 2 h; the solvent was removed under reduced pressure to give an oil, which turned to a brown powder when washed with hexane. The brown powder was extracted with boiling heptane and filtered while hot through a glass frit to give 0.10 g of brown needles for a yield of 24%. Anal. Calcd for $C_{25}H_{21}N_4Ti$: C, 70.59; H, 4.97; N, 13.17; Ti, 11.26. Found: C, 70.02; H, 5.06; N, 12.90; Ti, 11.23. The mass spectrum had a strong parent ion peak at mass number 425 (calcd 425).

Bis(bis(η^5-cyclopentadienyl)titanium pyrazole) (IV). This dimer was prepared by the method presented in the preceding paper.[13]

Bis(η^5-cyclopentadienyl)titanium Bipyridyl Hexafluorophosphate (V). This compound was prepared by the method of Green and Lucas.[19] Anal. Calcd for $C_{20}H_{18}N_2PF_6Ti$: C, 50.13; H, 3.79; N, 5.85; Ti, 9.99. Found: C, 50.26; H, 3.93; N, 5.86; Ti, 9.97.

Results and Discussion

Synthesis and Structure. One of the factors that has limited studies of low-valent titanium compounds is the lack of a general synthetic method for removing protons from strongly basic ligands ($pK_a > 11$) so that titanium atoms can be complexed. Three binuclear Ti(III) metallocenes were prepared in this work; see Figure 1. In the syntheses of the biimidazolate (BiIm) complex, I, and the bibenzimidazolate (BiBzIm) complex, II, the preparation and isolation of the dilithium salt of the basic ligand, stabilized with two molecules of the chelating amine 1,1,4,7,7-pentamethyldiethylenetriamine (PMDT), proved to be a convenient pathway which should be applicable to other transition-metal syntheses.[20] The lithium salt can be synthesized and reacted with the appropriate metal halide to give the metal complex and lithium chloride as indicated

$$H_2B + 2n\text{-BuLi} \xrightarrow[\text{THF}]{\text{PMDT}} [LiPMDT]_2B + 2C_4H_{10}$$

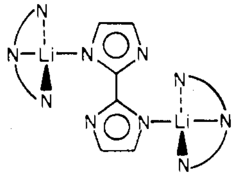
$$[LiPMDT]_2B + [Cp_2TiCl]_2 \xrightarrow[\text{THF}]{} 2[LiPMDT]Cl + [Cp_2Ti]_2B$$

Table III. Magnetic Susceptibility Data for $[Cp_2Ti(pz)]_2$[a]

T, K	$10^3\chi_M$, cgsu	μ_{eff}/Ti, μ_B	T, K	$10^3\chi_M$, cgsu	μ_{eff}/Ti, μ_B
269.6	3.097	1.83	35.8	22.39	1.79
248.6	3.413	1.84	27.4	29.52	1.80
220.8	3.914	1.86	23.2	35.18	1.81
196.9	4.343	1.85	20.8	39.51	1.81
169.5	4.842	1.81	18.3	45.10	1.82
140.5	5.627	1.78	15.7	53.82	1.84
120.7	6.536	1.78	14.2	59.45	1.84
102.7	7.647	1.77	12.7	66.23	1.83
81.6	9.499	1.76	11.2	75.51	1.84
70.0	10.97	1.75	9.5	87.32	1.82
58.1	13.19	1.75	7.9	105.9	1.83
47.7	16.32	1.76	7.1	117.6	1.82
41.3	18.79	1.76			

[a] Diamagnetic correction: -0.274×10^{-3} cgsu/mol of dimer.

where B is the anion of the base biimidazole or bibenzimidazole. A probable structure of the lithium salt intermediate is that presented below where the normal tetrahedral



coordination sphere of each lithium ion is filled by the three nitrogens of PMDT and one nitrogen of the biimidazole compound. The small ionic radius of the lithium ion (0.60 Å) makes chelation to the two biimidazolate nitrogen atoms unlikely. Attempts to prepare the lithium salt of biimidazole stabilized with the bidentate ligand 1,1,4,4-tetramethylethylenediamine (TMED) were unsuccessful. We believe that it is not possible to achieve tetrahedral coordination about the lithium ion utilizing the two nitrogen atoms from the TMED molecule and two nitrogen atoms from the biimidazole.

The bimetallic compounds I and II show remarkable thermal stability. In sealed capillary tubes, both I and II are stable as green solids on heating to 300 °C and show no signs of decomposing. A strong parent ion peak is observed in the mass spectra which is an indication of the stability of the compounds and confirms the bimetallic structure. As crystals, the two compounds are stable in air for up to 1 h before they exhibit any signs of decomposition. The stability probably arises from the chelation of the titanium ion by the biimidazolate and bibenzimidazolate and the bulky cyclopentadienide rings which sterically block attack on the metal ion and electronically stabilize the reduced titanium metal center. One indication of the importance of the chelate in stabilizing the biimidazolate compounds is that all attempts to isolate a product of the reaction of sodium imidazolate with $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ were unsuccessful. This is surprising in light of the fact that several other transition metals form polymeric bis(imidazolato)–metal complexes.[21]

Magnetic Susceptibility. Variable-temperature magnetic susceptibility data were obtained for compounds I, II, and IV; these data are collected in Tables I, II, and III, respectively (Tables I and II are supplementary material). As can be seen in Figure 2, compounds I and II both exhibit susceptibility data that are characteristic of an antiferromagnetic exchange interaction. The biimidazolate-bridged compound shows a maximum in the corrected molar paramagnetic susceptibility, χ_M, at ca. 45 K, whereas, the maximum occurs at ca. 39 K for the bibenzimidazolate-bridged compound. The χ_M values are corrected for diamagnetism; the diamagnetic corrections are listed at the bottom of Tables I and II.

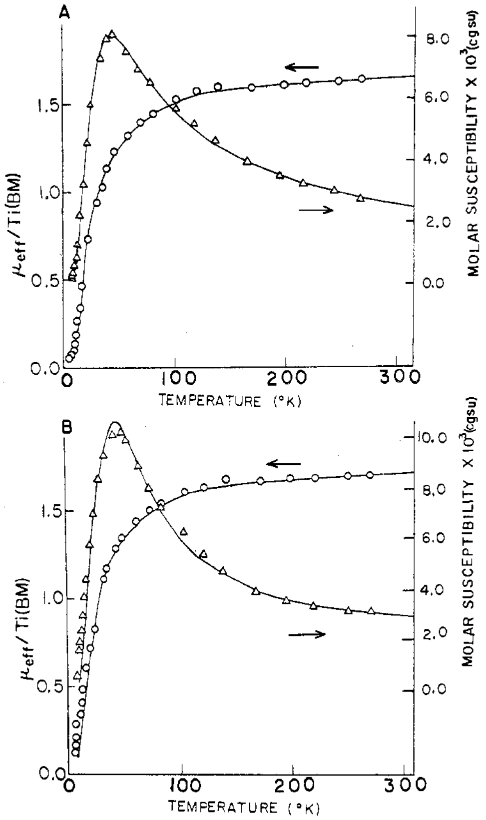


Figure 2. Corrected molar paramagnetic susceptibility (in cgsu per binuclear complex) and μ_{eff}/Ti vs. temperature curves for $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiIm)$ (A) and $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiBzIm)$ (B). The solid lines represent least-squares fits of the data to the theoretical equations. Fitting parameters are given in the text.

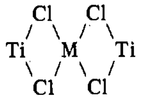
These binuclear Ti(III) complexes are, of course, $S_1 = S_2 = {}^1/_2$ exchange interacting species and the variation in magnetic susceptibility as a function of temperature is represented by the Bleaney–Bowers equation (1).[16] In this

$$\chi_M = \frac{Ng^2\beta^2}{k(T-\Theta)}\left[\frac{2}{3+\exp(-2J/kt)}\right] + N\alpha \qquad (1)$$

equation, N is Avogadro's number, g is the average electronic g factor, β is the Bohr magneton, k is the Boltzmann constant, T is the temperature, Θ is the Weiss constant, J is the parameter which gauges the magnitude of the exchange interaction, and $N\alpha$ is the TIP correction. The data for compounds I and II were least-squares fit to eq 1. In order to limit the available parameters, the TIP was taken as zero. This left three parameters for each least-squares fitting. In the case of compound I, fitting to eq 1 gave $J = -25.2$ cm^{-1}, $g = 1.92$, and $\Theta = 1.27$ K. The Weiss constant, Θ, has been shown to be a gauge of intermolecular interactions,[22] but it is small for this compound. Fitting the data for compound II gives $J = -19.0$ cm^{-1}, $g = 1.95$, and $\Theta = 0.55$ K. These two fits to the susceptibility data are illustrated by the solid lines in Figure 2. Figure 2 also gives the appearance of the μ_{eff}/Ti^{III} curves where it can be seen that the effective magnetic moments of these two compounds do drop to very small values at 4.2 K.

The susceptibility data for the biimidazolate- and bibenzimidazolate-bridged compounds clearly demonstrate that antiferromagnetic interactions between two Ti(III) ions can be propagated by extended organic bridges. As expected, the antiferromagnetic interactions are considerably weaker than were observed for the halide-bridged compounds $[(\eta^5\text{-}C_5H_4CH_3)_2TiX]_2$, where J is -160 cm^{-1} for X = Cl and -138

cm^{-1} for X = Br. The available magnetic and structural data for these halide-bridged dimers suggest the presence of direct Ti–Ti interactions.[7] On the other hand, the antiferromagnetic interactions in the present complexes are greater than was found for the bridged complexes of the composition $[(\eta^5\text{-}C_5H_5)_2Ti]MCl_4$, where J is -8.9 cm^{-1} for M = Zn and -6.9 cm^{-1} for M = Be.[8]



Preliminary X-ray structural work[23] on compound I has confirmed the bimetallic structure of the compound and the fact that the biimidazole dianion is functioning as a bis-bidentate ligand. The BiIm^{2-} bridge is indicated to be essentially planar with a small dihedral angle of ca. 3.3° between the two imidazole rings. The titanium atoms are separated by a distance of ca. 6.02 Å. At the present stage of refinement, the two Ti–N bonds to each titanium atom are found to be unequal, indicating perhaps that the bite of the BiIm^{2-} ligand may be large for a first-row early transition-metal ion.

The antiferromagnetic exchange interactions observed for compounds I and II are almost of comparable magnitude. There are several factors that could result in this situation. The potential exists for further studies into the substituent effects of the BiIm^{2-} bridge on the magnetic exchange interaction. Numerous substituted biimidazoles have been prepared where one or more hydrogen atoms are replaced by methyl, phenyl, nitro, chloro, bromo, or other substituents.[24]

The pyrazolate-bridged Ti(III) dimer, compound IV, is a clear example that several factors, in addition to metal–metal distance, are important in determining the magnitude of the magnetic exchange interaction. Even though compound IV has a relatively short Ti–Ti distance of 4.339 (3) Å, which approaches the intermetallic distances of 3.943 (2) and 3.968 (2) Å observed in the two crystallographically unique dimers of the strongly interacting compound $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$, the pyrazolate-bridged dimer shows no signs of a magnetic exchange interaction down to low temperatures. As can be seen in Table III, the value of μ_{eff}/Ti is in the range of 1.80 ± 0.05 μ_B from 269.6 to 7.1 K for $[(\eta^5\text{-}C_5H_5)_2Ti(pz)]_2$. Because there is no indication of a decrease in μ_{eff}/Ti down to 7.1 K, the absolute value of the exchange parameter J is less than ca. 0.5 cm^{-1}. In the following EPR section it will be demonstrated, however, that there is a weak magnetic exchange interaction in this compound.

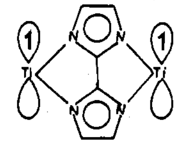


Figure 3. Relative orientation of the two unpaired-electron metal orbitals in $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiIm)$. The cyclopentadienyl rings have been omitted for clarity.

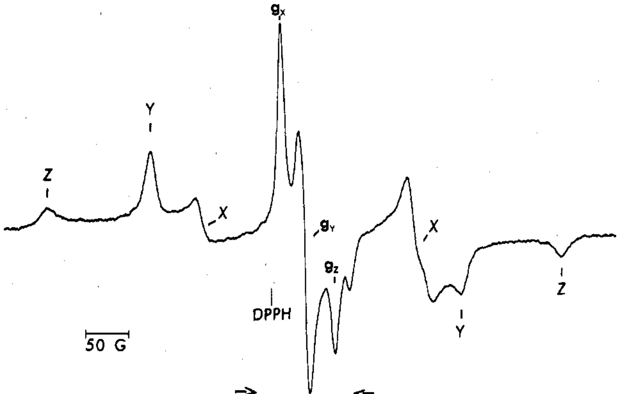
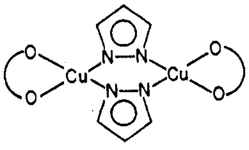


Figure 4. Frozen-glass (toluene–benzene, 4:1) EPR spectrum of $[(\eta^5\text{-}C_5H_5)_2Ti(pz)]_2$ taken at ca. 7 K. The features labeled X, Y, and Z are due to the binuclear complex, whereas those labeled g_x, g_y, and g_z result from a monomeric complex; see text.

It is important to explain why the antiferromagnetic interaction is so very weak in $[(\eta^5\text{-}C_5H_5)_2Ti(pz)]_2$, whereas the interaction in $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiIm)$ is appreciable. In molecular orbital terms, the molecular orbitals of the bridge interact with the metal orbitals in which the unpaired electrons reside.[25] It is the magnitude of this interaction that determines the antiferromagnetic contribution to the magnetic exchange interaction. In these two binuclear Ti(III) complexes, each Ti(III) ion has one unpaired electron. Dahl et al.[12] have recently demonstrated with single-crystal EPR experiments and photoelectron spectroscopy that the unpaired electron in the d^1 system $(\eta^5\text{-}C_5H_5)_2VCl_2$ is primarily in a molecular orbital of a$_1$ symmetry (C_{2v} point group). The unpaired electron density is in a nonbonding metal orbital which is perpendicular to the twofold symmetry axis of the molecule and is in the plane of the VCl$_2$ group. As indicated above, the Ti(III) ions and BiIm^{2-} bridge are indicated[23] to be coplanar in $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiIm)$. Figure 3 illustrates the relative orientation, compared to the bridge, of the two Ti(III) orbitals containing the unpaired electrons. Because the unpaired-electron Ti(III) orbitals are in the BiIm^{2-} plane, it is the σ orbitals of the BiIm^{2-} bridge that are important in $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiIm)$. To picture the interaction in $[(\eta^5\text{-}C_5H_5)_2Ti(pz)]_2$, we need only replace the BiIm^{2-} bridge in Figure 3 by two pyrazolate monoanions. There is also one important difference. In the pyrazolate-bridged complex, the Ti(III) ions are not in the plane formed by the two pyrazolate anions.[13] One Ti(III) ion is 0.40 Å above and the other Ti(III) ion is 0.40 Å below the bridge plane. If a σ exchange pathway is important, the fact that the Ti(III) ions are not in the bridge plane in $[(\eta^5\text{-}C_5H_5)_2Ti(pz)]_2$ provides an explanation for why the antiferromagnetic interaction is so relatively weak in this complex.

Barraclough et al.[26] have reported on the magnetic properties of $[Cu(acac)(pz)]_2$. The complex was assumed to have the planar structure It is interesting that magnetic susceptibility measurements taken down to 92 K indicated the presence of an antiferromagnetic interaction with $J = -35$ cm^{-1}.



EPR Studies. Electron paramagnetic resonance spectra were obtained for the four compounds illustrated in Figure 1 and for $[(\eta^5\text{-}C_5H_5)_2Ti(bpy)]PF_6$, compound V. As powders, compounds I–V each give single-derivative EPR signals. The g values of these signals are all approximately the same and are relatively close to the free-electron value of 2.0023; see summary in Table IV. The closeness in g values demonstrates that the unpaired electrons in these five compounds are located in similar orbitals. Room-temperature solution (toluene–benzene, 4:1) spectra of the binuclear compounds I, II, and IV are very much like the signals from the powdered samples, but upon cooling of the solution samples to −150 °C to form a glass, multiline spectra as illustrated in Figures 4 and 5 were observed. These glass EPR spectra can be recognized as basically typical rhombic triplet-state ($S = 1$) spectra appropriate for magnetic exchange interacting binuclear Ti(III)

Table IV. Summary of Observed Magnetic Susceptibility and EPR Parameters for Monomeric and Dimeric Titanium(III) Compounds

no.	compd	J, cm^{-1}	g_{av}[a]	g_x, g_y, g_z[b]	$\lvert D\rvert$,[c] cm^{-1}	$\lvert E\rvert$,[c] cm^{-1}	A, G
I	$[Cp_2Ti]_2(BiIm)$	−25.2	1.984 (3) (80 G)	1.969 (2) 1.984 (2) 1.992 (2)	0.0124 (3)	0.0018 (2)	
II	$[Cp_2Ti]_2(BiBzIm)$	−19.2	1.985 (3) (80 G)	1.969 (2) 1.984 (2) 1.992 (2)	0.0122 (3)	0.0019 (2)	
III	$[Cp_2Ti](Me\text{-}BiBzIm)$		1.983 (3) (65 G)				(Ti)[d] 11.0 (2) (N) 2.3 (1)
IV	$[Cp_2Ti(pz)]_2$	−0.5 to −0.001	1.982 (3) (750 G)	1.974 (2) 1.977 (2) 1.981 (2)	0.0271 (3)	0.0017 (2)	
V	$[Cp_2Ti(bpy)]PF_6$		1.980 (3) (80 G)				(Ti)[e] 8.1

[a] EPR spectra taken as a powder at room temperature with DPPH as a standard. The second number in parentheses is the half-width of the signal in gauss. [b] EPR spectra taken as glasses (toluene–benzene, 4:1) at −140 to −160 °C. [c] Values calculated by computer fitting of spectral features. [d] Room-temperature spectrum taken in toluene–benzene (4:1). [e] Room-temperature spectrum taken in acetone–ethanol (1:1).

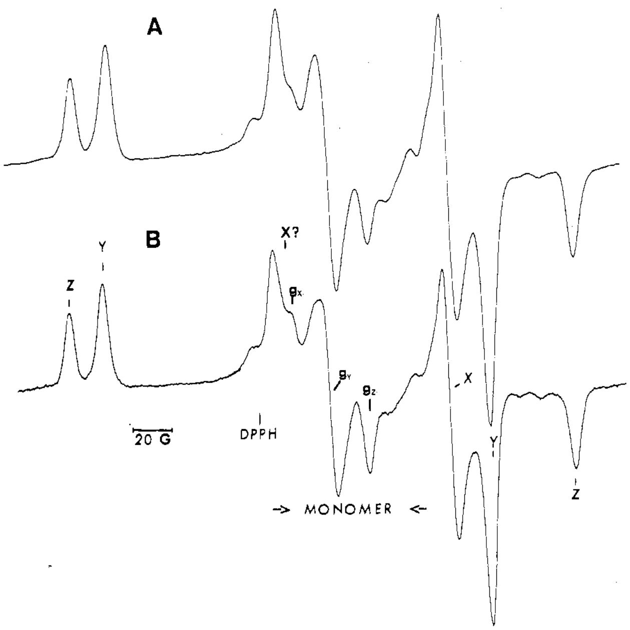


Figure 5. EPR spectra of glasses (toluene–benzene, 4:1) taken at 77 K for $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiIm)$ (A) and $[(\eta^5\text{-}C_5H_5)_2Ti]_2(BiIm)$ (B).

complexes. Such triplet-state spectra have been reported by several workers for organic diradical species and triplet excited states.[27-30] We have observed similar spectra for frozen glasses of triplet-state titanium compounds such as the monomeric Ti(II) species $[(\eta^5\text{-}C_5H_5)_2Ti](bpy)$[7] and the binuclear complex $[(\eta^5\text{-}C_5H_4CH_3)_2Ti]_2(uracil)$.[6]

As indicated in Figures 4 and 5, the triplet-state spectrum consists of a basic six-line pattern labeled X, Y, and Z. Thus, the three signals resulting from the rhombic **g** tensor of the $S = 1$ state are each split into two signals by *inter*ion zero-field splitting. The features in the central region of each spectrum labeled g_x, g_y, and g_z are assignable as the doublet ($S = {}^1/_2$) signal from a *monomeric* Ti(III) species. This monomeric species could be due to a monomeric impurity in the compound, or more probably the monomeric species results from a dissociative equilibrium established when the binuclear complex is dissolved. The three g values observed are very characteristic of such a monomeric Ti(III) complex.

Triplet-state spectra can be described by the Hamiltonian expression

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

where the second and third terms are for axial and nonaxial zero-field interactions. Wassermann derived the six equations for the resonance fields of the six $\Delta M_s = 1$ transitions.[27] In terms of H_0, the magnetic field expected for a free electron, and the zero-field parameters D and E expressed in gauss, the six resonance fields are[28,29]

Table V. Computer Fit to Theoretical $S = 1$ Expressions of the Features of the Glass-Phase (Toluene–Benzene, 4:1) EPR Spectra at 130 K for Three Titanium Dimers[a]

	$[Cp_2Ti]_2(BiIm)$ field, G		$[Cp_2Ti]_2(BiBzIm)$ field, G		$[Cp_2Ti(pz)]_2$ field, G	
peak[b]	obsd	calcd	obsd	calcd	obsd	calcd
Z	3146	3143	3146	3144	2976	2974
Y	3164	3167	3164	3166	3094	3096
X	3260	3263	3263	3265	3153	3155
X	3341	3338	3338	3336	3396	3394
Y	3363	3360	3360	3358	3447	3445
Z	3406	3409	3404	3406	3558	3560

[a] The values of g_x, g_y, g_z, $\lvert D\rvert$, and $\lvert E\rvert$ which were obtained from the fit of the data are given in Table IV. [b] Peaks are labeled from low field to high field as shown in Figures 5 and 6.

$$\begin{aligned}
H_{x_1} &= \frac{2.0023}{g_x}[(H_0 - D + E)(H_0 + 2E)]^{1/2} \\
H_{y_1} &= \frac{2.0023}{g_y}[(H_0 - D - E)(H_0 - 2E)]^{1/2} \\
H_{z_1} &= \frac{2.0023}{g_z}[(H_0 - D)^2 - E^2]^{1/2} \\
H_{x_2} &= \frac{2.0023}{g_x}[(H_0 + D - E)(H_0 - 2E)]^{1/2} \\
H_{y_2} &= \frac{2.0023}{g_y}[(H_0 + D + E)(H_0 + 2E)]^{1/2} \\
H_{z_2} &= \frac{2.0023}{g_z}[(H_0 + D)^2 - E^2]^{1/2}
\end{aligned} \qquad (3)$$

The equations were incorporated into an iterative least-squares computer program[14] to fit the spectra for values of $\lvert D\rvert$ and $\lvert E\rvert$. The procedure does not allow the calculation of the sign of D or E. As shown in Table V, there is a good fit of the triplet-state spectral features for compounds I, II, and IV and the nonzero values of E confirm that the Ti centers are in rhombic environments. As anticipated, the structurally similar compounds I and II gave almost superimposable EPR spectra which yielded essentially the same $\lvert D\rvert$ values of 0.0124 (3) and 0.0122 (3) cm^{-1} and $\lvert E\rvert$ values of 0.0018 (2) and 0.0019 (2) cm^{-1}, respectively. The larger $\lvert D\rvert$ value of 0.0271 (3) cm^{-1} for compound IV reflects the presence of the smaller Ti–Ti distance; the same $\lvert E\rvert$, 0.0017 (2) cm^{-1}, was obtained for this compound.

Table VI. Estimates of Ti–Ti Bond Distances from Observed Zero-Field Splittings

			distance, Å	
no.	compd	$\|D\|$,[a] cm^{-1}	calcd	obsd
I	$[Cp_2Ti]_2(BiIm)$	0.0124 (3)	5.91	6.02 (2)[b]
II	$[Cp_2Ti]_2(BiBzIm)$	0.0122 (3)	5.91	6.02[c]
IV	$[Cp_2Ti(pz)]_2$	0.0271 (3)	4.55	4.339 (3)[d]

[a] See text for details of how $|D|$ was determined. [b] See ref 23. [c] It is assumed the compounds I and II have similar Ti–Ti distances. [d] See ref 13.

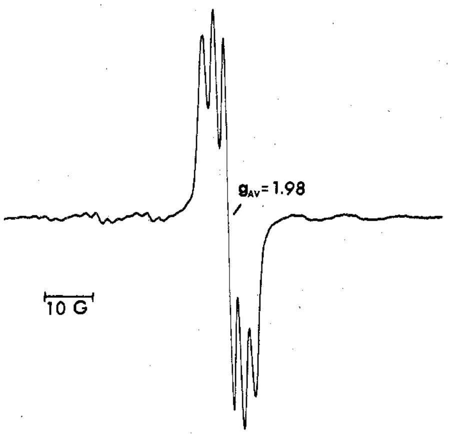


Figure 6. EPR spectrum taken at 24 °C for a toluene–benzene (4:1) solution of $[(\eta^5\text{-}C_5H_5)_2Ti](N\text{-}CH_3\text{-}BiBzIm)$ showing titanium hyperfine and nitrogen superhyperfine splitting.

It is possible to relate the distance R between two paramagnetic metal centers to the value of D, the axial *inter*ion zero-field splitting, using the equation[30]

$$R = (0.650g^2/D_{dd})^{1/3} \tag{4}$$

The observed D has contributions from both dipolar–dipolar (D_{dd}) and pseudo-dipolar (D_{ls}) terms. The pseudo-dipolar term arises from spin–orbital admixture of excited states into the triplet state and is directly proportional to the exchange parameter J. Because the exchange parameters for compounds I, II, and IV are small, it is usually acceptable to disregard D_{ls} and to assume that $D = D_{dd}$. Table VI indicates the good agreement between the calculated Ti–Ti distances and those observed from crystallographic studies. Compound I has an observed metal–metal separation of 6.02 (2) Å, which is in good agreement with a value of 5.91 Å calculated from eq 4. Similarly, compound IV has an observed Ti–Ti distance of 4.339 (3) Å, which is in accord with the calculated value of 4.55 Å.

The dipole–dipole interaction observed in the triplet-state spectra broadens the signal and obscures all hyperfine structure. In an effort to see titanium hyperfine structure, we prepared a monomeric Ti(III) compound directly analogous to compound II. After experiencing difficulty in preparing an N-methylated derivative of biimidazole, we were able to synthesize *N*-methylbibenzimidazole from which compound III could be prepared. At 24 °C in a toluene–benzene (4:1) solution, the EPR spectrum shown in Figure 6 was observed. The predominant feature in this spectrum is the isotropic signal centered at $g = 1.980$. This is the signal for the molecules with titanium isotopes having a zero value of nuclear spin; it is split into five lines due to nitrogen superhyperfine from the equivalent nitrogen atoms. At either higher or lower field of this signal there are weaker features (six are visible) resulting from titanium hyperfine splitting for ^{47}Ti ($I = ^5/_2$, 7.75% abundance) and ^{49}Ti ($I = ^7/_2$, 5.51%). The hyperfine splitting is essentially the same for these two isotopes and only one superimposed pattern is seen. Examination of one of the low-field titanium hyperfine signals shows that there is also a five-line nitrogen superhyperfine pattern imposed on each titanium hyperfine feature. The five-line nitrogen superhyperfine pattern results from the unpaired electron interacting with two equivalent nitrogen atoms from the *N*-methylbibenzimidazole ligand. The titanium A value is 11.0 (2) G for both isotopes and the nitrogen A value is 2.3 (1) G.

A similar monomeric bis(cyclopentadienyl)titanium(III) compound, $[(\eta^5\text{-}C_5H_5)_2Ti(bpy)]PF_6$, was prepared for comparison with compound III. Compound V gives a solution spectrum with titanium hyperfine splitting of $A = 8.1$ (2) G, which is slightly smaller than that found for III. No nitrogen superhyperfine splitting is observed for this compound (V) which could reflect the fact that bibenzimidazole is expected to have a larger bite angle than bipyridine. The nitrogen bases would thus interact somewhat differently with the titanium metal center and with the titanium orbital in which the unpaired electron occupies.

The nitrogen hyperfine structure in the EPR spectrum of compound III demonstrates that in solution the titanium unpaired electron density is delocalized equally onto the two immediate nitrogen atoms of the bridging bibenzimidazole group.

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Registry No. I, 66652-58-2; II, 66652-57-1; III, 66652-63-9; IV, 66652-62-8; V, 12701-37-0; BiIm, 492-98-8; (LiPMDT)(BiIm)$_2$, 66687-77-2; BiBzIm, 6965-02-2; (LiPMDT)$_2$(BiBzIm), 66652-61-7; Me-BiBzIm, 62627-68-3.

Supplementary Material Available: Tables I and II listing magnetic susceptibility data (2 pages). Ordering information is given on any current masthead page.

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Tetrakis(2-methoxy-5-methylphenyl)dichromium

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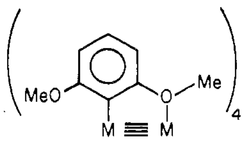
The title compound has been prepared from $Cr_2(O_2CCH_3)_4$ and 2-methoxy-5-methylphenyllithium. Small single crystals, obtained under special conditions, were used to determine the structure. The solid consists of a van der Waals packing of discrete $Cr_2[C_6H_3Me(OMe)]_4$ molecules, in which the Cr–Cr distance is 1.828 (2) Å. The molecules lie on crystallographic centers of symmetry and have virtual symmetry C_{2h}. The extreme insolubility of this compound and the previously reported $Cr_2(C_6H_4OMe)_4$ are evidently due to factors other than polymerization. The crystals belong to the monoclinic system, space group $P2_1/c$, with a = 8.799 (2) Å, b = 14.294 (3) Å, c = 11.372 (2) Å, β = 89.89 (2)°, V = 1430.3 (9) Å^3, and Z = 2.

Introduction

We have now reported the preparation and characterization of several compounds containing exceedingly short Cr–Cr quadruple bonds, viz., **1a**,[1] **2**,[2] **3**,[3] and **4a**[4] as well as several of their molybdenum analogues, **1b**[1] and **4b**.[4] We have also noted that the one earlier compound of this general type, **5**, which has twice been reported[5,6] but never structurally characterized, can indeed be prepared as directed and is so insoluble as to be intractable from the crystallographic point of view. It has been suggested,[6] because of "its extreme insolubility, ...that it is a polymeric species with metal–metal bonds and bridging *o*-anisyl groups." However, those who originally prepared it[5] suggested a binuclear, molecular structure.



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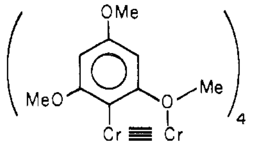
b, M = Mo



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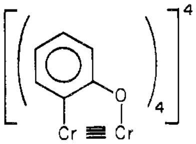

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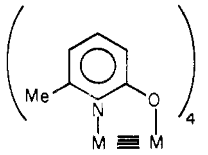
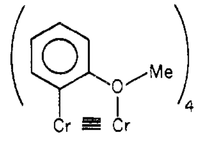


4a, M = Cr
b, M = Mo



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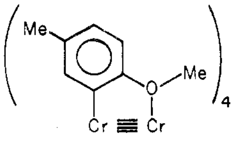

6

Our efforts to resolve this question by means of X-ray crystallography were frustrated by the impossibility of growing crystals. We therefore decided to examine a substance in which a ring substituent was added *in such a way as not to interfere with the type of polymerization previously proposed.* Our rationale in doing this was to try to increase solubility without destroying the suggested type of polymeric structure, *if there was in fact the suggested type of polymeric structure*, which we doubted. The compound we have made is **6**, in which a methyl group has been placed at the 5-position of the ring, where it does not seem possible that it could interfere with the type of polymerization suggested. The introduction of this substituent does not change the color of the compound nor does it increase its solubility very much, if at all. However, it has been possible to obtain useable single crystals, and we are therefore able to report the structure of **6**, which, we believe, gives a fairly good clue as to the structural nature of **5** as well.

Procedures

All manipulations were conducted in an atmosphere of nitrogen and solvents were carefully dried and degassed.

Preparation of 2-Methoxy-5-methylphenyllithium. 4-Methylanisole (40.0 g, 0.33 mol) and 205 mL of *n*-butyllithium (1.6 M in hexane) were refluxed in 150 mL of diethyl ether for 48 h. The solvent was removed under vacuum and replaced with 100 mL of hexane. After filtration, the solid was washed with 200 mL of hexane to give 25 g of white microcrystalline product. That this product is the one desired is ensured by the work of Letsinger and Schnizer,[7] who showed that lithiation under these conditions is essentially 100% stereospecific. The yield of ca. 60% is far greater than the 16% stated by Wakefield.[8]

Preparation of Tetrakis(2-methoxy-5-methylphenyl)dichromium. A solution of 2-methoxy-5-methylphenyllithium (3.0 g, 23.5 mmol) in 100 mL of THF was added to $Cr_2(OAc)_4$ (2.0 g, 5.9 mmol) in 100 mL of THF. An immediate reaction ensued and a yellow microcrystalline compound separated. Filtering and drying under vacuum gave 2.0 g (58% yield) of product.

Preparation of Crystals of Tetrakis(2-methoxy-5-methylphenyl)dichromium. Into a flat-bottomed flask containing 1.0 g (2.9 mmol) of $Cr_2(OAc)_4$ was added 50 mL of cold (−78 °C) THF. A solution of 2-methoxy-5-methylphenyllithium (2.0 g, 15.6 mmol) dissolved in 50 mL of cold (−78 °C) THF was gently layered on top of the $Cr_2(OAc)_4$/THF mixture. The flask was then allowed to stand undisturbed at room temperature for 6 days.

X-ray Structure Determination. A rectangular crystal with approximate dimensions 0.10 × 0.10 × 0.15 mm was embedded in epoxy cement in a thin-walled glass capillary. Preliminary rotation photographs showed that so small a crystal did not diffract Mo Kα radiation well enough to give sufficient data. It was therefore necessary to use Cu Kα radiation from a more intense source for the intensity data.

The crystal was mounted on a Syntex $P\bar{1}$ diffractometer. General procedures for data collection[9] and interpretation[10] have been described