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Electronic Properties of Bis(η^5-cyclopentadienyl)titanium 2,2′-Bipyridyl. A Singlet Molecule with a Low-Lying Triplet Excited State[1]

Arlene Mootz McPherson,[2a] Benjamin F. Fieselmann,[2a] Dennis L. Lichtenberger,[2c] Gary L. McPherson,*[2b] and Galen D. Stucky*[2a]

Contribution from the School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801, and the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118. *Received October 11, 1978*

Abstract: Magnetic susceptibility and EPR studies show that (η^5-C_5H_5)$_2$Ti(bpy) has a triplet excited state which is thermally accessible from the ground-state singlet. The temperature dependence of the magnetic susceptibility and the EPR spectra was measured and confirms that the singlet and triplet states are separated by approximately 600 cm^{-1} in toluene solution and 750 cm^{-1} in the solid state. In both solution and solid state (η^5-C_5H_5)$_2$Ti(bpy) is monomeric so that the presence of extended Ti-Ti interactions is unlikely. The low-lying triplet most likely corresponds to a state in which one unpaired electron formally occupies a molecular orbital which is localized on (η^5-C_5H_5)$_2$Ti while a second unpaired electron resides in the lowest energy π^* orbital of the bipyridyl group. This conclusion is supported by Fenske-Hall molecular orbital calculations. The calculations and single crystal X-ray data also suggest that the preferred molecular geometries of the singlet and triplet states are not the same. The cationic complex formed by the one-electron oxidation of (η^5-C_5H_5)$_2$Ti(bpy) has been isolated as a hexafluorophosphate salt. The magnetic susceptibility and EPR spectrum of this material are characteristic of a d^1 complex.

Introduction

Reactive low-valent titanium compounds (Ti(II) and Ti(III)) have been the subject of an increasing number of studies because of the potential applications of these compounds in isomerization, polymerization, and hydrogenation reactions. Reduced titanium compounds can convert dinitrogen to ammonia[3] or catalyze reactions such as olefin isomerization and the low-temperature polymerization of acetylene.[4] Despite this reactivity, several titanium(II) compounds such as bis(cyclopentadienyl)titanium(II) dicarbonyl and bis(cyclopentadienyl)titanium(II) 2,2′-bipyridyl have been synthesized and found to be relatively stable.[5-7,10] These two complexes are much less reactive than the parent compound, titanocene ((η^5-C_5H_5)$_2$Ti), which readily abstracts cyclopentadienyl ring hydrogen atoms to form bridged hydride species even at reduced temperatures.[8] Bis(cyclopentadienyl)titanium(II) dicarbonyl is a diamagnetic monomer with a pseudotetrahedral structure.[10] Hoffmann has carried out extended Hückel molecular orbital calculations for the dicarbonyl complex and has concluded that back-donation of electron density from the filled metal orbitals to the π^* orbitals of the carbonyl ligands is an important mechanism for stabilizing the electron-rich Ti(II) center.[11] The bipyridyl complex (η^5-C_5H_5)$_2$Ti(bpy) (where bpy = 2,2′-bipyridyl) appears to have a different electronic structure. Unlike the dicarbonyl complex, (η^5-C_5H_5)$_2$Ti(bpy) is weakly paramagnetic and gives rise to a room temperature EPR signal.[5,6]

The preparation of (η^5-C_5H_5)$_2$Ti(bpy) was reported simultaneously by two groups using different synthetic procedures. Calderazzo et al. prepared the complex by reacting (η^5-C_5H_5)$_2$TiCl$_2$ with the dilithium salt of 2,2-bipyridyl dianion.[6] They observed a magnetic moment of 0.6 μ_B and a solid-state EPR resonance. Fischer and Aumann synthesized (η^5-C_5H_5)$_2$Ti(bpy) by reacting (η^5-C_5H_5)$_2$Ti(CO)$_2$ with free 2,2′-bipyridine.[5] Their product had a magnetic moment of 0.8 μ_B. They pointed out that the oxidation state of the titanium in the bipyridyl complex is ambiguous because the ligand as well as the metal exhibits a number of stable oxidation states. One could view (η^5-C_5H_5)$_2$Ti(bpy) as a titanium(II) species complexed to a neutral bipyridyl molecule, a titanium(III) species bound to a bipyridyl radical anion, or a titanium(IV) species bound to a bipyridyl dianion. None of these descriptions readily explains the weak paramagnetism exhibited by the complex.

This paper presents the results of a magnetic, spectroscopic, and theoretical investigation of (η^5-C_5H_5)$_2$Ti(bpy). A simple model which provides a rational basis for explaining the properties of this and related complexes is discussed.

Experimental Section

Starting Materials and Synthetic Procedures. Commercially purchased bis(η^5-cyclopentadienyl)titanium dichloride (Alfa Inorganics) and 2,2′-bipyridyl (Aldrich) were used without additional purification. The bis(η^5-methylcyclopentadienyl)titanium dichloride and bis(η^5-cyclopentadienyl)titanium dicarbonyl were prepared by methods

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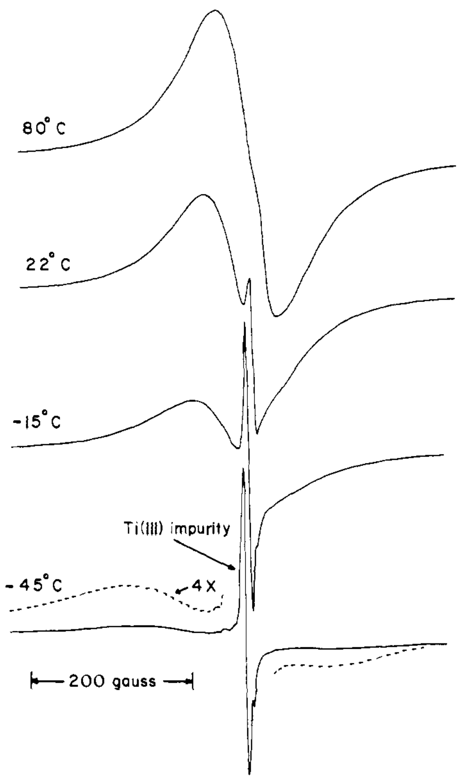


Figure 1. The X-band EPR spectrum of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ in toluene solution. The dotted portion of the −45 °C spectrum was recorded with the spectrometer gain increased by a factor of 4.

outlined in the literature.[5,7,12] Solvents were distilled from sodium and benzophenone under dry nitrogen. Syntheses were carried out under argon or helium in a Vacuum Atmospheres drybox. Elemental analyses were performed by the University of Illinois Chemical Sciences Microanalytical Laboratory. Mass spectra were recorded on a Varian CH5 mass spectrometer by the University of Illinois Mass Spectral Laboratory.

Bis(η^5-cyclopentadienyl)titanium 2,2′-Bipyridyl. The $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ complex was prepared by several different literature methods using either $(\eta^5\text{-}C_5H_5)_2TiCl_2$ or $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ as starting materials.[5,6] These methods produced equivalent products which were crystallized from heptane or hexane–toluene solutions. Anal. Calcd for $C_{20}H_{18}N_2Ti$: C, 71.86; H, 5.43; N, 8.38; Ti, 14.33. Found: C, 72.17; H, 5.71; N, 7.70; Ti, 14.16. A low-resolution mass spectrum of the complex showed a peak at *m/e* 334 corresponding to the parent ion and a peak at *m/e* 269 corresponding to the ion resulting from the loss of one cyclopentadienyl ring.

Bis(η^5-methylcyclopentadienyl)titanium 2,2′-Bipyridyl. $(\eta^5\text{-}C_5H_4CH_3)_2Ti(bpy)$ was synthesized by dissolving 1.5 g (9.6 mmol) of 2,2′-bipyridine in 25 mL of tetrahydrofuran and adding 0.50 g (22 mmol) of sodium sand. After 1 day of stirring, excess sodium was removed by filtration and 2.60 g (9.4 mol) of bis(η^5-methylcyclopentadienyl)titanium dichloride was added. The solution was then stirred for 1 day. The solvent was removed under reduced pressure and the residue was extracted with refluxing hexane. The hexane solution was filtered while hot through a medium glass frit and slowly cooled. Dark purple crystals were formed in a yield of 81%. Anal. Calcd for $C_{22}H_{22}N_2Ti$: C, 72.93; H, 6.12; N, 7.73; Ti, 13.22. Found: C, 72.65; H, 6.14; N, 8.28; Ti, 12.93. A low-resolution mass spectrum of the complex showed a peak at *m/e* 362 corresponding to the parent ion and a peak at *m/e* 283 corresponding to the ion resulting from the loss of one methylcyclopentadienyl ring.

Bis(η^5-cyclopentadienyl)titanium 2,2′-Bipyridyl Hexafluorophosphate. $[(\eta^5\text{-}C_5H_5)_2Ti(bpy)]PF_6$ was prepared by the method of Green and Lucas.[13] 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.

Magnetic Susceptibility Measurements. Magnetic susceptibility data were determined as a function of temperature using the Evans' method.[14] Spectra were recorded on a Varian A-60 NMR spectrometer with a calibrated variable-temperature attachment which maintains constant temperatures within ±2 °C. Concentric NMR tubes were purchased from Wilmad Glass Co. Toluene was used as the solvent for the $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ and $(\eta^5\text{-}C_5H_4CH_3)_2Ti(bpy)$ complexes. The concentrations of the solutions ranged from 0.1 to 0.4 M. The solutions were placed in the outer portion of the coaxial NMR tube while the inner portion was filled with pure toluene. The solutions were loaded in an inert atmosphere, and the tubes were sealed on a vacuum line in order to prevent exposure to the atmosphere. The chemical shift differences between toluene in the solution and pure solvent were found to be the same for both the methyl and phenyl protons. The NMR spectra were studied at several temperatures and the magnetic susceptibilities were calculated from the observed differences in chemical shift.[15] These values were corrected for diamagnetism according to the constants given by Mabbs and Machin.[16]

The magnetic susceptibility of $[\eta^5\text{-}C_5H_5)_2Ti(bpy)][PF_6]$ was determined in the same manner as the other two titanium complexes except that acetone rather than toluene was used as the solvent.

EPR Spectra. The EPR spectra were recorded on Varian E-3 and E-9 X-band spectrometers using field modulation. Variable-temperature studies were carried out using a Varian variable-temperature accessory which was calibrated with a thermocouple and gave temperature readings to ±2 °C. The g values were determined by using polycrystalline diphenyldipicrylhydrazyl (g = 2.0036) as a reference.

Molecular Orbital Calculations. Nonparametrized restricted Hartree–Fock–Roothann molecular orbital calculations for $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ and $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ were carried out using the method developed by Fenske and Hall.[17] In order to simplify interpretation of the orbital interactions, the molecular geometries used in these calculations correspond to idealized structures having C_{2v} symmetry. The cyclopentadienyl rings of both complexes were treated in the same fashion as in earlier calculations.[18] The distance from the metal to the centroid of the cyclopentadienyl ring was taken as 2.03 Å and the centroid–metal–centroid angle 138°. For the dicarbonyl complex the titanium–carbon and carbon–oxygen distances were set at 2.03 and 1.15 Å, respectively, and the OC–Ti–CO angle at 88°. For the bipyridyl complex, the carbon–carbon and carbon–nitrogen distances in the bipyridyl ligand were set at 1.39 Å with internal ring angles of 120°.[19] The two nitrogen atoms were positioned at a distance of 2.14 Å from the titanium atom. A second calculation was performed on the bipyridyl complex with the angle between the plane of the bipyridyl ligand and the N–Ti–N plane set at 25°, in agreement with the molecular structure determined by X-ray diffraction.[19]

Computer Calculations. Computer calculations were performed on the XDS Sigma V computer operated by the Materials Research Laboratory at the University of Illinois and on the Cyber 175 computer at the University of Arizona.

Results and Discussion

Magnetic and Spectroscopic Properties of Bis(η^5-cyclopentadienyl)titanium 2,2′-Bipyridyl. The $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ complex would be expected to have a singlet ground state since the molecule contains an even number of electrons. At room temperature, however, the complex exhibits an EPR signal. A single broad resonance is observed in solution as well as in the polycrystalline solid. This resonance loses intensity dramatically as the temperature is lowered (see Figure 1). A sharp signal appears and becomes more distinct as the broad resonance vanishes. It is likely that this sharp signal arises from a titanium(III) species which occurs as an impurity in the $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$. Such an impurity could easily result from the partial oxidation of a small amount of the parent complex. This conclusion is supported by the observation that short exposure of the EPR samples to air causes the intensity of the sharp resonance to increase dramatically at the expense of the broad resonance.

If the sharp signal is ignored, the temperature dependence of the EPR spectrum is suggestive of a system which is diamagnetic in the ground state but has a paramagnetic excited state which is thermally accessible. As the temperature is lowered the population of the paramagnetic state is depleted, causing a loss of EPR signal intensity. The lowest energy

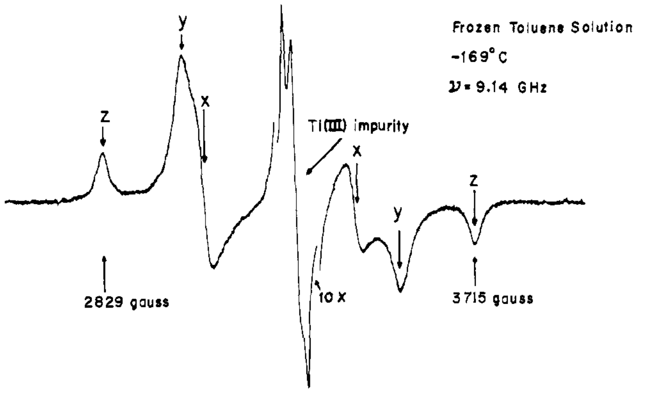


Figure 2. The X-band EPR spectrum of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ in frozen toluene. The center portion of the spectrum marked by 10X was recorded with the spectrometer gain reduced by a factor of 10.

Table I. Spin Hamiltonian Parameters for the Triplet State of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$

$g_x = 2.013$	$D = 0.0412\ \text{cm}^{-1}$
$g_y = 1.990$	$E = 0.0025\ \text{cm}^{-1}$
$g_z = 1.993$	
Toluene at Room Temperature	
$g_{av} = 1.99$	
Polycrystalline Solid at Room Temperature	
$g_{av} = 1.994$	

paramagnetic state of a molecule such as $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ will almost certainly be a triplet ($S = 1$). A triplet species may be readily identified by the fine structure which appears in the spectrum when the species is trapped in a rigid medium. This fine structure arises from a zero-field splitting produced by the spin–spin interactions of the two-electron system. Even in randomly oriented samples, such as frozen solutions, the fine structure is easily observed. It is clear that the spectrum of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ in frozen toluene (Figure 2) contains resonances from a triplet species. When the frozen solution is cooled to approximately −150 °C the fine structure components of an $S = 1$ system begin to be resolved. At −169 °C the features expected of a triplet with a rhombic zero-field splitting tensor can be clearly observed. The fine structure components are labeled by x, y, and z according to the convention of Wasserman, Snyder, and Yager, who have calculated the EPR line shapes expected from samples of various types of randomly oriented triplet molecules.[20] As the temperature is further reduced these features rapidly lose intensity. At liquid nitrogen temperature (−196 °C) the x, y, and z components are almost unobservable. This loss of intensity is due to the thermal depopulation of the triplet state. The frozen solution spectrum also provides insight into the nature of the impurity which gives rise to the sharp resonance appearing in the center of the spectrum (see Figure 2). This resonance contains the features characteristic of an $S = 1/2$ system with an anisotropic g tensor. The three principal g values are 2.001, 1.988, and 1.969 and are very similar to those observed by Kenworthy and coworkers for a series of bis(cyclopentadienyl)titanium(III) complexes.[21,22] If hyperfine interactions are neglected, the spectrum of a triplet-state species can be described by the following spin Hamiltonian.

$$\hat{H} = g_x\beta H_x\hat{S}_x + g_y\beta H_y\hat{S}_y + g_z\beta H_z\hat{S}_z + D\left[\hat{S}_z^2 - \frac{2}{3}\right] + E[\hat{S}_x^2 - \hat{S}_y^2]$$

The spin Hamiltonian parameters can be readily determined from the observed positions of the x, y, and z features according to the treatment presented by Wasserman and coworkers.[20] The parameters for the triplet state of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ in frozen toluene at −169 °C are given in Table I. There is a small but significant rhombic component in the zero-field splitting tensor, and the g values are noticeably anisotropic. This is consistent with the low symmetry of the complex (C_{2v} or lower).

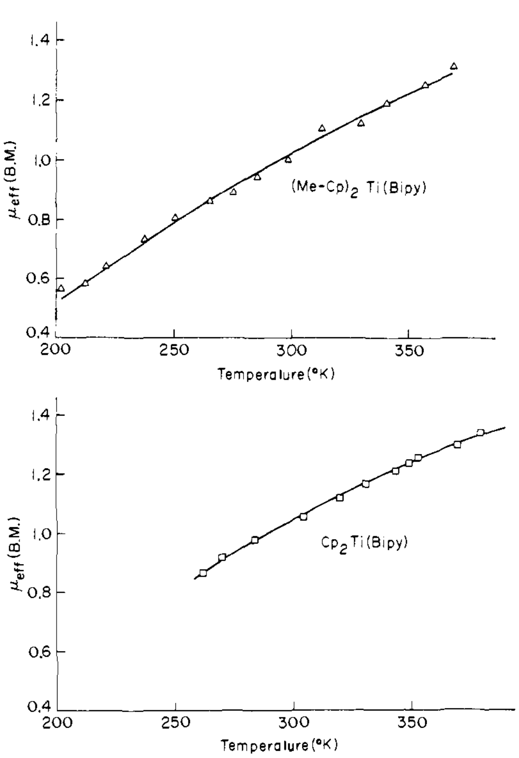


Figure 3. Variation in effective magnetic moment as a function of temperature for $(\eta^5\text{-}CH_3C_5H_4)Ti(bpy)$ (top trace) and $(\eta^5\text{-}C_5H_5)Ti(bpy)$ (bottom trace). The solid lines were calculated using singlet–triplet separations of 625 and 590 cm^{-1} for the $(\eta^5\text{-}CH_3C_5H_4)_2Ti(bpy)$ and $(\eta^5\text{-}C_5H_5)Ti(bpy)$, respectively.

The energy separation between the singlet ground state and the triplet excited state can be determined by following the temperature dependence of either the magnetic susceptibility or the intensity of the EPR signal. In solution, the magnetic susceptibility of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ can be conveniently determined by NMR techniques.[14,15] As would be expected, the susceptibility of the complex drops rapidly as the temperature is lowered. The methyl-substituted compound, $(\eta^5\text{-}CH_3C_5H_4)_2Ti(bpy)$, behaves in a similar fashion. In both cases the temperature dependence of the susceptibility is accurately described by the Bleany-Bowers equation (see Figure 3).[23] This equation, which was derived to explain the behavior of copper(II) acetate, assumes that the populations of the singlet and triplet state obey Boltzmann statistics. Figure 3 shows a comparison of the observed and calculated temperature dependences of the effective magnetic moments of the two complexes. The calculated values were obtained from the Bleaney-Bowers expression using a singlet-triplet separation of 590 cm^{-1} for $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ and 625 cm^{-1} for $(\eta^5\text{-}CH_3C_5H_4)_2Ti(bpy)$. Since the difference between these two energies is smaller than the experimental uncertainties (at least 10%), it appears that in toluene solution the magnetic properties of the two complexes are nearly identical. In the solid state the two complexes differ significantly. While the intensity of the EPR signal from $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ drops dramatically as the temperature is lowered, the intensity of the signal from $(\eta^5\text{-}CH_3C_5H_4)_2Ti(bpy)$ actually increases when the sample is cooled. If the behavior of the solid $(\eta^5\text{-}CH_3C_5H_4)_2Ti(bpy)$ is not an artifact of a paramagnetic impurity, these observations indicate that the singlet-triplet separation of the

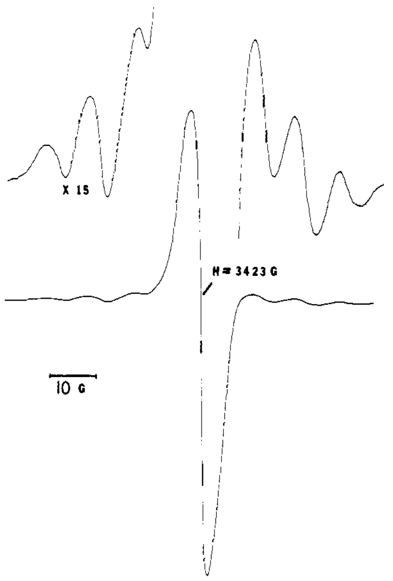


Figure 4. The X-band EPR spectrum of $[(\eta^5\text{-}C_5H_5)_2Ti(bpy)]PF_6$ in solution (toluene-benzene, 4:1) at room temperature. The raised portion of the spectrum was recorded with the spectrometer gain increased by a factor of 15.

methyl-substituted complex is much smaller (200 cm^{-1} or less) in the solid state than in toluene solution. In contrast, the singlet-triplet separation of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ in the solid is comparable to that in solution. A quantitative treatment of the temperature dependence of the EPR spectrum (see Appendix) gives a value of 750 cm^{-1} for the singlet-triplet separation of solid $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$.

The possibility that the observed magnetic and spectroscopic behavior results from extended Ti-Ti interaction is ruled out both by the similarity of behavior in the solid state and solution and by a preliminary X-ray crystallographic analysis of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$.[19] The structure of the title compound is monomeric with a distorted tetrahedral geometry. The cyclopentadienyl rings are bonded in a η^5 fashion while the bipyridyl functions as a bidentate ligand. The shortest Ti-Ti distances between monomeric units is 6.53 Å. There is no evidence that the molecules form any type of clusters or aggregates. This is consistent with the observation that $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ is monomeric in benzene solution.[6] It seems certain that the magnetic and spectroscopic properties of the material reflect the characteristics of an individual molecule.

Magnetic and Spectroscopic Properties of Bis(η^5-cyclopentadienyl)titanium 2,2′-Bipyridyl Hexafluorophosphate. It is possible to prepare the cationic complex, $[(\eta^5\text{-}C_5H_5)_2Ti(bpy)]^+$, which corresponds to the one-electron oxidation product of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$. This cation can be isolated as the hexafluorophosphate salt. In acetone the cationic complex exhibits a magnetic susceptibility characteristic of a species with a single unpaired electron ($\mu_{eff} = 1.74\ \mu_B$). As would be expected, the susceptibility follows Curie law behavior. The solution EPR spectrum consists of a single strong resonance with a series of weak satellite peaks (see Figure 4). The weak satellites result from hyperfine interactions with the ^{47}Ti ($I = 5/2$) and ^{49}Ti ($I = 7/2$) nuclei which have natural abundances of 7.9 and 5.3%, respectively. The hyperfine coupling constants for both isotopes are approximately 8 G while the g value for the spectrum is 1.98. The magnetic properties are typical of a bis(cyclopentadienyl)titanium(III) species.[21,22] It appears that the $[(\eta^5\text{-}C_5H_5)_2Ti(bpy)]^+$ cation behaves as a simple d^1 system.

Electronic Structure of Bis(η^5-cyclopentadienyl)titanium 2,2′-Bipyridyl. The spectroscopic and magnetic studies clearly show that the $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ molecule has a triplet state within 1000 cm^{-1} (2.9 kcal/mol) of the ground-state singlet. The appearance of a low-energy paramagnetic state in conjunction with a diamagnetic ground state is relatively rare in monomeric metal complexes; this type of behavior is generally associated with dinuclear or polynuclear metal complexes. Molecular orbital calculations for the $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ molecule were carried out in an effort to gain insight into the origin of the low-energy triplet. The calculations, based on the method developed by Fenske and Hall, were of the nonparametrized restricted Hartree-Fock-Roothaan type.[17] This procedure has been used successfully in interpreting the electronic structures of open- and closed-shell M(IV) $(\eta^5\text{-}C_5H_5)_2ML_2$ complexes.[18] Calculations were also carried out for the analogous dicarbonyl complex, $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$. The dicarbonyl complex, although isoelectronic with and structurally similar to $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$, behaves as a normal diagmagnetic molecule. It was hoped that a comparison of the two complexes would delineate the unique features of the $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ molecule which give rise to the low-energy triplet state.

The results of this analysis are illustrated in the molecular orbital diagram in Figure 5. These diagrams indicate the electronic interactions between the $(\eta^5\text{-}C_5H_5)_2Ti$ fragment and the appropriate symmetry orbitals of the bipyridyl or carbonyl ligands, assuming that both complexes have C_{2v} geometries. The electronic structure of the $(\eta^5\text{-}C_5H_5)_2Ti$ fragment bound to a variety of ligands has already received considerable attention.[11,18] Lauher and Hoffmann have carried out extended Hückel calculations for the dicarbonyl complex.[11] The orbitals of the $(\eta^5\text{-}C_5H_5)_2Ti$ fragment in the molecular orbital diagrams are labeled according to the notation of Lauher and Hoffmann. The relative energies and nodal characteristics obtained from our calculations are not much different than those from the extended Hückel treatment. The b_2 and $2a_1$ orbitals which are primarily composed of titanium d orbitals have the correct symmetry to interact with the 5σ orbitals of the two carbonyl molecules. The destabilization of these predominantly metal orbitals which results from the σ bonding to the carbonyl molecules is clearly evident in the molecular orbital diagram. The two carbonyl moieties lie very close to the nodal surface of the $1a_1$ orbital which is also mainly metal in character. This gives the $1a_1$ orbital essentially π symmetry with respect to the carbonyl groups. Overlap with the vacant π^* orbitals of the carbonyl groups significantly lowers the energy of the $1a_1$ orbital. In the $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ molecule the $1a_1$ orbital is the highest occupied molecular orbital. Occupation of this orbital tends to strengthen the titanium-carbonyl bonds by back-donation.

The σ bonding interaction of the bipyridyl ligand with the $(\eta^5\text{-}C_5H_5)_2Ti$ fragment is similar to that of the dicarbonyl complex. The two nitrogen lone pairs donate to the predominantly metal b_2 and $2a_1$ orbitals. The important difference between the dicarbonyl and bipyridyl complexes is that bipyridyl ligand possesses no π^* orbitals of the correct symmetry and spatial characteristics for interaction with the metal $1a_1$ level. The $1a_1$ orbital actually shows a slight destabilization through interaction with the bipyridyl molecule, but retains nearly 100% of its isolated character. Although there is no interaction, the bipyridyl does have several π^* orbitals in the same energy vicinity as the $1a_1$ orbital. The bipyridyl molecule b_1 (π^*) level in Figure 6 requires special attention. This orbital, which has two nodal surface perpendicular to each pyridine ring, is the lowest unoccupied orbital of bipyridyl. The b_1 (π^*) orbital is slightly stabilized through interaction with a b_1 level of the $(\eta^5\text{-}C_5H_5)_2Ti$ fragment, but retains nearly 90% of its isolated character. This orbital is so close in energy to the $1a_1$ orbital of the $(\eta^5\text{-}C_5H_5)_2Ti$ fragment that it is not possible to converge the calculations with an Aufbau filling of the mo-

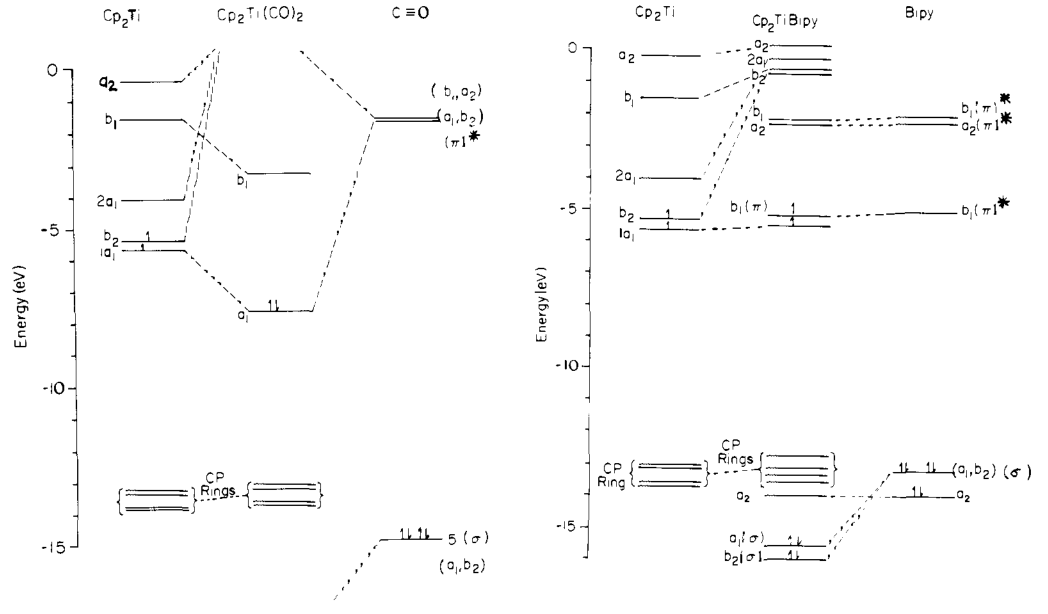
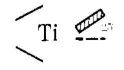


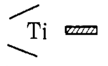
Figure 5. Molecular orbital energy level diagrams for $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ and $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ (C_{2v} symmetry). In both diagrams, the orbitals of the $(\eta^5\text{-}C_5H_5)_2Ti$ fragment are shown on the right while the orbitals of the carbonyl or bipyridyl ligands are represented on the left.

lecular orbitals and two electrons in either the $1a_1$ orbital or the b_1 (π^*) orbital. The molecular orbital diagram of Figure 5 results from one electron assigned to each orbital. The electronic structure of the triplet state of the complex is approximately described as a titanium(III) center bound to a bipyridyl radical anion. However, the σ donation of the nitrogen lone pairs to the metal center produces a greater charge neutrality in each portion of the molecule than this model implies.

In the solid state $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ does not really have a structure with C_{2v} symmetry since the bipyridyl binds in a "bent" fashion.[19] The plane of the bipyridyl ligand is tilted approximately 25° from the plane defined by the titanium atom and the two bipyridyl nitrogen atoms. With one important exception, the results of the molecular orbital calculation for the bent geometry are almost identical with those obtained for the C_{2v} structure. The significant difference between the two geometries is that the metal $1a_1$ and the bipyridyl b_1 (π^*) orbitals mix strongly in the bent structure. As a result, the energy of the $1a_1$ orbital is lowered by approximately 0.6 eV while the energy of the b_1 (π^*) orbital is increased by a similar amount. (Strictly speaking the a_1 and b_1 labels are no longer appropriate since the system does not have C_{2v} symmetry.) The calculations suggest that the bent structure is the preferred geometry for the singlet configuration while the C_{2v} structure would be favored by a triplet configuration. We suggest that the $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ complex undergoes a significant structural change, i.e., from C_s to C_{2v} symmetry, when a molecule is excited from the singlet to the triplet state. Since a large majority of the molecules at room temperature occupy the singlet state, the bent geometry observed in the solid state is the result of electronic factors rather than crystal-packing effects.



singlet geometry



triplet geometry

It is not possible with these approximate calculations to accurately predict the singlet–triplet energy interactions between these levels. Nonetheless, these calculations provide a strong indication that the predominantly metal $1a_1$ orbital and the predominantly bipyridyl b_1 (π^*) orbital have nearly the same energy. This result is significant since the calculations contain no parameters and are iterative on the charge distribution and potential within the molecule. On the whole the experimental observations in the previous section are quite compatible with the molecular orbital description. The spin Hamiltonian parameters seem reasonable for a triplet species derived from the combination of a bipyridyl radical anion with a bis(cyclopentadienyl)titanium(III) fragment. The average g value of 1.99 for the triplet is intermediate between that expected of a titanium(III) complex (g = 1.98) and that of an organic radical anion (g = 2.00). Assuming that the zero-field splitting arises primarily from dipolar interactions, an estimate of the effective separation between the two electrons of the triplet system can be computed from the simple point dipole expression $R = (g^2\beta^2/D)^{1/3}$ where g and D are taken from the EPR spectrum of the triplet species. Using the experimental values of g and D, a separation (R) of 3.5 Å is calculated for the triplet of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$. This separation is at least qualitatively consistent with the view that the triplet has one unit of spin on the $(\eta^5\text{-}C_5H_5)_2Ti$ fragment and the other delocalized on the bipyridyl ligand. The basic correctness of the molecular orbital description is also supported by the behavior of the one-electron oxidation product of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$. Although $1a_1$ and b_1 levels are energetically similar, the calculations indicate that the $1a_1$ metal orbital is slightly lower in energy than the b_1 orbital. After the loss of one electron from the complex, the remaining unpaired electron would be expected to occupy the $1a_1$ metal orbital rather than the bipyridyl orbital. The EPR spectrum of the $(\eta^5\text{-}C_5H_5)_2Ti(bpy)^+$ cation clearly exhibits the characteristics of a titanium(III) complex

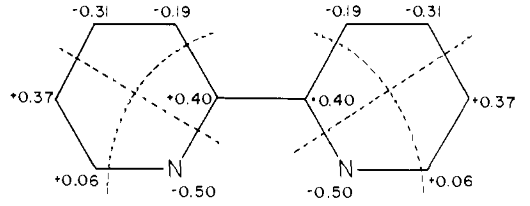


Figure 6. Approximate nodal characteristics of the lowest unoccupied molecular orbital (b_1 (π^*)) of 2,2'-bipyridine. The numbers are the coefficients of the p-orbital functions.

in which the unpaired electron is primarily localized on the titanium atom.

It seems unlikely that the $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ molecule is a totally unique system. One might expect to observe a low-energy triplet state in other similar molecules. From our analysis it is possible to make some general observations with respect to the occurrence of a low-energy triplet in the $(\eta^5\text{-}C_5H_5)_2ML_2$ and related organometallic complexes. The phenomenon almost certainly requires that the metal atom have a d^2 configuration, at least in a formal sense. The metal must have electrons that are easily lost through oxidation, which implies that the metal should have a low formal oxidation state. The ligand(s) bound to the $(\eta^5\text{-}C_5H_5)_2M$ fragment must have a vacant orbital with an energy similar to that of the highest occupied metal orbital. The symmetry and spatial properties of this ligand orbital must be such that there is little or no interaction in a molecular orbital sense with any of the orbitals of the metal center. It is likely that these conditions will occur in complexes of the group 4B metals in which the $(\eta^5\text{-}C_5H_5)_2M$ moiety is σ bonded to a planar aromatic ligand which has low-energy, vacant π^* orbitals. It is interesting to note that the zirconium complex $(\eta^5\text{-}C_5H_5)_2Zr(bpy)$[24] exhibits a very weak temperature-dependent paramagnetism which suggests that it has a singlet–triplet system similar to that of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$.

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Appendix

The following procedure was used to determine the singlet–triplet energy separation of solid $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ from the temperature dependence of the EPR spectrum. Under an inert atmosphere several crystals of the complex were ground to a fine powder and loaded into a quartz tube. A small piece of DPPH (~0.1 mm in diameter) which had been sealed in a short length of 0.3-mm glass capillary was also added to the quartz tube. This tube was then sealed off without exposure to the atmosphere. The DPPH serves as an intensity standard. The EPR spectrum of the sample was recorded at a number of temperatures between −90 and 60 °C. Above 60 °C $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ begins to decompose, while below −90 °C the EPR resonance from the complex is too weak to accurately measure. It was assumed that the integrated intensity of an EPR line (the usual derivative presentation) is proportional to the product of the peak to peak amplitude and the square of the peak to peak width ($I \alpha A w^2$). The ratio between the intensities of the DPPH resonance and the resonance from the titanium complex was calculated for each temperature ($R = I_{Ti}/I_{DPPH}$).[25] If the populations of the singlet and triplet states obey Boltzmann statistics, the temperature dependence of the intensity ratio is described by the expression

$$\frac{R(T_1)}{R(T_2)} = \frac{3 + \exp(E/kT_2)}{3 + \exp(E/kT_1)}$$

where E is the energy between the singlet and triplet states, T is the temperature, and k is Boltzmann's constant. The value of E was iterated to give the best least-squares fit to the data from all the different temperatures. This procedure was repeated several times with different samples of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$. The results indicate that the singlet–triplet separation is about 750 cm^{-1}. Since measurements of this sort are subject to errors from many sources, it is likely that this energy is only accurate to within ±200 cm^{-1}.

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(19) A. M. McPherson, Ph.D. Dissertation, University of Illinois, Urbana, 1974. A single-crystal X-ray diffraction study of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ was attempted and gave the following results: space group *Iba*2, a = 16.61 (1) Å, b = 27.66 (20) Å, c = 7.005 (4) Å, ρ_{obsd} = 1.23 (2) g/cm^3, ρ_{calcd} = 1.24 g/cm^3 for eight monomeric units in the unit cell. Over 40 crystals were examined in order to find one suitable for data collection; however, none was truly satisfactory in that all diffracted poorly and exhibited relatively large mosaicities. The best sample was chosen and two forms of data were measured on a FACSI Picker diffractometer. Using 1562 reflections, of which 620 had intensities greater than background, a structural solution was obtained. Full-matrix least-squares isotropic refinement of the carbon atoms in the cyclopentadienyl ring and anisotropic refinement of all other atoms gave R_1 (omitting unobserved data) = 0.116 and R_2 (including unobserved data) = 0.111 where $R_1 = (\Sigma(||F_o| - |F_c||))/\Sigma F_o$ and $R_2 = (\Sigma w|F_o - F_c|^2)/|\Sigma w|F_o|^2$. The results indicated a monomeric molecule with a Ti–N distance of 2.14 (2) Å and a closest intermolecular Ti–Ti approach of 6.53 Å. The angle between the plane of the bipyridyl ligand and the N–Ti–N plane was 25 (1)°.
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