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# Zero Field Splitting and Exchange Interactions in Bis(cyclopentadienyl)titanium(III) Dinuclear Compounds with Short Metal–Metal Distances: Synthesis, X-ray Structure, and EPR Spectroscopy of Methoxo- and Ethoxo-Bridged Dimers

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The synthesis, crystal structure, and magnetic properties of $[Cp_2Ti(\mu\text{-}OCH_3)]_2$ (**1**) ($Cp = \eta^5\text{-}C_5H_5$) and $[Cp_2Ti(\mu\text{-}OC_2H_5)]_2$ (**2**) are described. The two compounds are obtained from $[Cp_2Ti(CH_3)_2]$ and trimethoxy- and triethoxysilane, respectively, in hexane. Both crystallize in the tetragonal system, space group $P\bar{4}n2$. Data for **1**: $a = 8.003$ (1) Å, $b = 8.003$ (1) Å, $c = 16.078$ (4) Å, and $Z = 2$; Ti–O = 2.065 (2) Å, Ti–O–Ti = 108.8 (1)°; $R_w = 0.039$. Data for **2**: $a = 8.238$ (1) Å, $b = 8.238$ (1) Å, $c = 15.717$ (2) Å; Ti–O = 2.076 (3) Å, Ti–O–Ti = 108.0 (2)°; $R_w = 0.029$. The Ti–Ti distances of 3.35 Å for both compounds are remarkably short. **1** and **2** are paramagnetic dimers exhibiting antiferromagnetic behavior with $J = -268 \pm 4$ cm$^{-1}$ for **1**. Their frozen-solution EPR spectra are typical of triplet states with a rhombic zero field splitting (ZFS) tensor ($D = -0.0446$ and $-0.0463$ cm$^{-1}$ and $E = -0.0069$ and $-0.0066$ cm$^{-1}$ for **1** and **2**, respectively). Analysis of this ZFS tensor is presented in terms of dipolar and pseudodipolar magnetic interactions, the latter in connection with exchange interactions between the ground state of one metal center with excited states of the other center. EPR spectra of the $[Cp_2TiCl]_2$ (**3**) dimer are also presented, and the parameters are compared with those of **1** and **2**.

Organometallic chemistry literature abounds with examples of dinuclear compounds where the two metallic centers are held together by a variety of bridging ligands. Such compounds provide good models for the study of cooperative effects between adjacent metal atoms in catalysis. The recent surge of interest in the chemistry of fulvalenes is motivated by the aptitude of the fulvalene ligand to confine two metallic fragments within a semirigid backbone, thus yielding complexes with properties interesting to explore.[1] For various reasons, however, the majority of such compounds are diamagnetic. When the two metals individually bear unpaired electrons, the resulting complexes are liable to possess magnetic properties, and their study by EPR especially in frozen solution affords information about their ground states, the extent of metal–metal separation, and the importance of the exchange interaction between the two metal centers.

Transition metals of group 4 at their oxidation state III have one unpaired electron, and the complexes are of d$^1$ electronic configuration; their study by EPR spectroscopy in most cases is relatively simple and does not afford the complexity encountered in other paramagnetic transition metal ions, where sometimes considerable complications are introduced by the fine structure for example (or a degenerate ground state). However, in these electron-poor compounds, and at least in the case of Ti, coordination of donor ligands inevitably takes place in order to achieve a tetrahedral metal environment and the paramagnetic compounds are mononuclear.[2,3] Otherwise dimerization occurs through ligand bridges to compensate the lack of electron density at the metal, and this results in the formation of two Ti centers at close proximity, with the possibility of interaction between their unpaired spins.

The existence of such complexes has been demonstrated for a long time. Thus, the dimeric structure of $[Cp_2TiCl]_2$ ($Cp = \eta^5\text{-}C_5H_5$) was soon recognized and its antiferromagnetic behavior was deduced from magnetic susceptibility measurements,[4–7] which showed a thermally populated triplet state, but to our knowledge, no reliable EPR data on this compound seem to have been reported to date.

Some years later, in an elegant study published in a series of papers, Stucky and co-workers undertook the synthesis and magnetic investigations by EPR and susceptibility measurements on a series of titanocene dimers connected by bridging organic ligands of increasing sizes designed to produce metal–metal separations of variable magnitudes.[8] The purpose was to study the importance of the exchange interaction and its mechanism, whether it was dependent on the nature of the organic ligands or on the metal–metal distance. In most of the cases, triplet-state spectra ($S = 1$) were observed by EPR spectroscopy in frozen solution exhibiting zero field splitting (ZFS) characteristic of interacting paramagnetic metal centers.

In such a situation one of the important parameters to be obtained from these spectra is an estimate of the metal–metal distance $R$ without having recourse to crystal structural determination. This was what the authors did. By taking into account the axial component $D$ and ignoring the nonaxial component $E$ of the ZFS tensor, and also assuming only a point dipole–dipole

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interaction, calculations were simplified but yielded only a rough agreement with the crystal structure data in the few cases when these could be determined.[9] Moreover, the interpretation of the ZFS tensor was done by neglecting the pseudodipolar interaction. This interaction, which originates from a synergic effect of the spin–orbit and exchange interactions, is effectively negligible when the $g$ shifts are small such as in organic triplet states or when the exchange interactions are weak such as in titanium dimers with long distances $R$.[8] When $R$ is small, it normally implies relatively large values of the exchange interactions in addition to a large $g$ shift inherent to metallic complexes. In that case, one may anticipate that the pseudodipolar interaction will contribute significantly to the ZFS tensor, introducing further complications in its treatment for the measurement of $R$.

In the course of our study on the reactivity of $[Cp_2TiMe_2]$ with alkoxysilanes,[10] we discovered a convenient method for the preparation of the two alkoxy-bridged Ti(III) dimers $[Cp_2Ti(\mu\text{-}OCH_3)]_2$ (**1**) and $[Cp_2Ti(\mu\text{-}OC_2H_5)]_2$ (**2**), the X-ray structure of which will be described in this work. Compound **2** obtained by a different route has been briefly mentioned earlier.[11] Both compounds give in frozen solution well-resolved triplet-state EPR spectra. Their analysis shows that despite the short Ti–Ti distance $R$, the axial component $D$ of the ZFS is of purely magnetic dipolar character, so that $R$ can be deduced accurately from this parameter. Moreover, the nonaxial component $E$ of the ZFS is of purely pseudodipolar character, which gives information about exchange interactions between the ground state of one Ti(III) center with excited states of the other Ti(III). For the sake of comparison, we present also a brief study by EPR spectroscopy in frozen solution of $[Cp_2TiCl]_2$ (**3**). The crystal structure of this dimer has already been determined and the $J$ value measured,[12] but surprisingly the only EPR parameter recorded was the trivial isotropic $g$-value of a single-line signal, which is always observed in liquid solution and which may belong to an $S = {}^1/_2$ impurity and not to the dimer itself. In contrast with **1** and **2**, it is found that the ZFS of **3** is almost axial and the component $D$ significantly deviates from a pure dipole–dipole interaction so that $R$ cannot be reliably deduced.

## Experimental Section

All manipulations were conducted under argon. Solvents were dried by the usual methods. EPR measurements were performed in toluene with a Bruker ER 220D or ER 10 X-band spectrometer. Because of low solubility, saturated solutions of both compounds were used for these measurements.

In a typical preparation, 50 mg of $[Cp_2Ti(CH_3)_2]$ was dissolved in 2 mL of toluene, and 0.03 mL of trimethoxysilane or triethoxysilane (Petrarch Systems) was added. The reaction mixture was exposed to daylight for a few hours and then left to stand for 24 h. Well-formed crystals of **1** or **2** settled at the bottom of the Schlenk tube; the solution was removed, and the crystals were washed twice with hexane and dried. Yield: 50%. Anal. Calcd for $C_{11}H_{13}OTi$: C, 63.16; H, 6.22; Ti, 22.91. Found: C, 60.25; H, 5.99; Ti, 23.06. Calcd for $C_{12}H_{15}OTi$: C, 64.6; H, 6.2; Ti, 21.4. Found: C, 61.96; H, 6.61; Ti, 20.21. Compound **1** is moderately soluble in toluene, whereas **2** is very sparingly soluble. Both can be sublimed under vacuum without decomposition. Although air-sensitive, they can be handled for a few minutes in air without change. The crystals obtained from these preparations were quite suitable for X-ray measurements and therefore were used as such.

**Crystal Structure.** Dark green crystals of the compounds were introduced in sealed glass capillaries and mounted on the diffractometer. Accurate unit cell dimensions and crystal orientation matrices together with their estimated standard deviations were obtained from least-squares refinements of 25 automatically centered reflections in the range $14° < \theta < 20°$. Data collection was performed at room temperature in the $\theta$–$2\theta$ scan mode. A variable scan range and a variable scan speed were used with a 25% extension at each end of the scan range for background determination. As a subtle twinning generating a pseudo-4-fold axis has been noticed by Stucky et al.[12] for similar Ti(III) compounds, we recorded one full octant. Thus, equivalent $hkl$ and $khl$ can be checked. Two standard reflections were monitored periodically and remained constant during data collection. Lorentz and polarization factors were applied, while absorption corrections were not considered as necessary ($\mu < 8.2$ cm$^{-1}$, flat $\psi$-scan curves). All calculations were performed by using the crystallographic computing program CRYSTALS adapted on a MicroVax II computer. All pertinent crystallographic data are given in Table I.

**Table I.** Relevant Crystallographic Data for Compounds **1** and **2**

| | | |
|---|---|---|
| formula | $Ti_2O_2C_{22}H_{26}$ | $Ti_2O_2C_{24}H_{30}$ |
| fw | 418.2 | 446.3 |
| space group | $P\bar{4}n2$ (No. 118) | $P\bar{4}n2$ (No. 118) |
| $a$, Å | 8.003 (1) | 8.238 (1) |
| $b$, Å | 8.003 (1) | 8.238 (1) |
| $c$, Å | 16.078 (4) | 15.717 (2) |
| $V$, Å | 1029.6 (3) | 1066.7 (3) |
| $Z$ | 2 | 2 |
| temp, °C | 20 | 20 |
| $\lambda$(Mo K$\alpha$), Å | 0.710 69 | 0.710 69 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 8.2 | 7.9 |
| $d_{calc}$, g cm$^{-3}$ | 1.35 | 1.39 |
| transm coeff | 1.00–0.93 | 1.00–0.88 |
| $R^a$ | 0.035 | 0.029 |
| $R_w{}^a$ | 0.039 | 0.029 |

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_c)^2]^{1/2}$.

**Structure Solution and Refinement.** Among the three possible space groups $P4_2nm$ (No. 102), $P\bar{4}n2$ (No. 118), and $P4_2/mnm$ (No. 136) corresponding to systematic absences, we discarded the centrosymmetric one ($P4_2/mnm$) on the basis of the statistics of the normalized structure to be noncentrosymmetric. As we found two molecules of the title compounds in the cell while the space groups have eight equivalent positions, the molecules must lie on symmetry elements. The Patterson maps showed the Ti atom. Fourier syntheses calculated in the two possible noncentrosymmetric space groups showed all the non-hydrogen atoms. The refinement was carried out in the two space groups, but the only solution which gave a satisfactory convergence of the least-squares fit and a satisfactory nondistorted geometry for the cyclopentadienyl groups was in space group $P\bar{4}n2$. Further calculations were carried out using isotropic and then anisotropic thermal parameters for all non-hydrogen atoms; all hydrogen atoms were found on a difference Fourier synthesis; they were included in theoretical calculated positions, and their coordinates were not refined.

For compound **1**, as the C(1) atom lies on a binary axis, the hydrogen atoms of the methyl group were introduced with one of them trans to the Ti atom and occupancy factors 0.5. For compound **2**, the ethyl group is disordered; it can be described by a statistical distribution on two sites related by a binary axis. The real and imaginary parts of the scattering factors were taken from ref 13. Some selected bond distances and angles are given in Table II.

The final atomic coordinates and the anisotropic thermal parameters are listed in the supplementary material.

**Synthesis of 1 and 2.** Dimethyltitanocene, $Cp_2Ti(CH_3)_2$, reacts with trimethoxy- or triethoxysilane at room temperature in toluene/diethyl ether mixture (1:1) or in hexane to yield after several hours dark-green well-shaped crystals of **1** and **2**, which separate from the reaction medium. These compounds were identified as the alkoxy-bridged dimers from elemental analyses, mass spectroscopy, and the X-ray crystal structures:

$$2Cp_2Ti(CH_3)_2 + Si(OR)_3H \rightarrow [Cp_2Ti(OR)]_2 + 2CH_4 + 2Si(OR)_2(CH_3)_2 + Si(OR)_2H_2 + ROH$$

$$R = CH_3, C_2H_5$$

The mass spectra show principal peaks for **1** at $m/e$ 209 (M/2) and 178 (M/2 – $OCH_3$) and for **2** at $m/e$ 223 (M/2), 193 (M/2 – $CH_2$), and 178 (M/2 – $OC_2H_5$). Two features common to both compounds seem therefore to be (i) the absence of the dimer molecular ion peak because of bridge splitting under electron impact to give the monomer and (ii)

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**Table II.** Selected Interatomic Distances (Å) and Angles (deg) for Compounds **1** and **2**

| | | | |
|---|---|---|---|
| | **Compound 1** | | |
| | Distances | | |
| Ti–O | 2.065 (2) | O–C(1) | 1.401 (7) |
| Ti–Ti | 3.358 (2) | C(2)–C(3) | 1.33 (1) |
| Ti–C(2) | 2.446 (7) | C(2)–C(6) | 1.37 (1) |
| Ti–C(3) | 2.408 (7) | C(3)–C(4) | 1.31 (1) |
| Ti–C(4) | 2.416 (6) | C(4)–C(5) | 1.41 (1) |
| Ti–C(5) | 2.369 (9) | C(5)–C(6) | 1.38 (1) |
| Ti–C(6) | 2.384 (9) | | |
| | Angles | | |
| Ti–O–Ti | 108.8 (1) | C(6)–C(2)–C(3) | 109.1 (13) |
| O–Ti–O | 71.24 (3) | C(4)–C(3)–C(2) | 109.6 (11) |
| C–O–Ti | 125.62 (7) | C(5)–C(4)–C(3) | 108.2 (9) |
| | | C(6)–C(5)–C(4) | 105.9 (10) |
| | | C(5)–C(6)–C(2) | 107.0 (11) |
| | **Compound 2** | | |
| | Distances | | |
| Ti–O | 2.076 (3) | O–C(1) | 1.481 (8) |
| | | C(1)–C(11) | 1.472 (9) |
| Ti–C(2) | 2.440 (13) | C(2)–C(3) | 1.359 (8) |
| Ti–C(3) | 2.398 (13) | C(2)–C(6) | 1.376 (8) |
| Ti–C(4) | 2.402 (12) | C(3)–C(4) | 1.362 (9) |
| Ti–C(5) | 2.424 (13) | C(4)–C(5) | 1.381 (8) |
| Ti–C(6) | 2.407 (14) | C(5)–C(6) | 1.384 (8) |
| | Angles | | |
| Ti–O–Ti | 108.0 (2) | C(6)–C(2)–C(3) | 108.9 (6) |
| O–Ti–O | 72.0 (2) | C(2)–C(3)–C(4) | 107.2 (6) |
| | | C(4)–C(5)–C(6) | 106.1 (6) |
| Ti–O–C(1) | 132.1 (9) | C(3)–C(4)–C(5) | 109.7 (6) |
| O–C(1)–C(11) | 110.4 (7) | C(5)–C(6)–C(2) | 107.9 (6) |

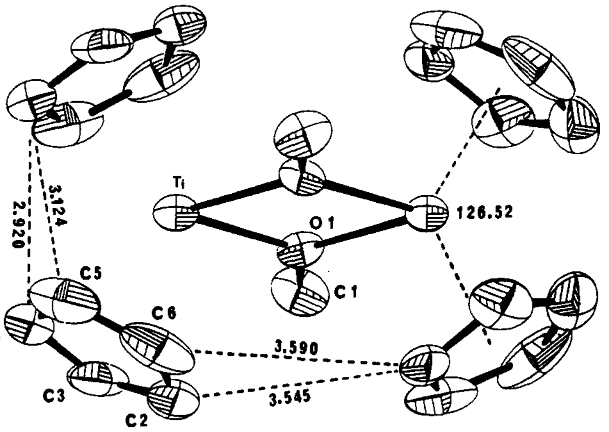

**Figure 1.** ORTEP view of compound **1**.

the loss of alkoxy groups by fragmentation to give the bis(cyclopentadienyl)titanium molecular ion peak at *m/e* 178.

Compound **2** has been briefly described in the literature[11] as a dark brown microcrystalline compound prepared from chlorobis(cyclopentadienyl)titanium(III) and lithium ethoxide or from the reaction of ethanol with bis(cyclopentadienyl)(dimethylamido)titanium(III). Although a dimeric structure was postulated, no evidence was provided in support. Compound **1** does not seem to have been described earlier.

**Crystal and Molecular Structure.** Figures 1 and 2 show ORTEP views of the two molecules **1** and **2**, respectively. Since the Ti and oxygen atoms lie on orthogonal binary axes, the atoms Ti, O(1), and C(1) and the symmetry-related ones in **1** are coplanar, as are Ti, O, and the symmetry-related ones through the 2-fold axes in **2**. Comparison with similar systems such as $[(CH_3C_5H_4)_2TiCl]_2$, $[(CH_3C_5H_4)_2TiBr]_2$, and $[(C_5H_5)_2TiCl]_2$ shows the influence of the size of the bridging group.[12] In the title compounds the Ti–Ti distance is 3.358 Å, while for Cl and Br bridging atoms it increases respectively to 3.926 and 4.126 Å. In the same way the Ti–O–Ti angles are about 9° higher, while the O–Ti–O angles are about 8° lower than the corresponding halogen-bridged analogs. The distances of Ti to the carbon atoms of the cyclopentadienyl groups range from 2.369 (9) to 2.446 (7) Å, and there is no significant difference with the above-mentioned halide dimers. The distances between the two adjacent cyclopentadienyl rings linked to the same Ti atom are not different from those found for bulky bridging compounds, while those between cyclopentadienyl rings belonging to two different Ti atoms are shortened by about 0.4 Å (from 4.25 Å in **3** to 3.73 Å).

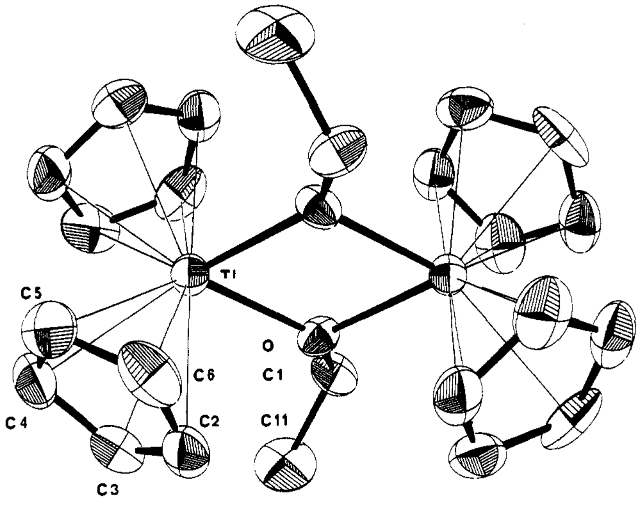

**Figure 2.** ORTEP view of compound **2**.

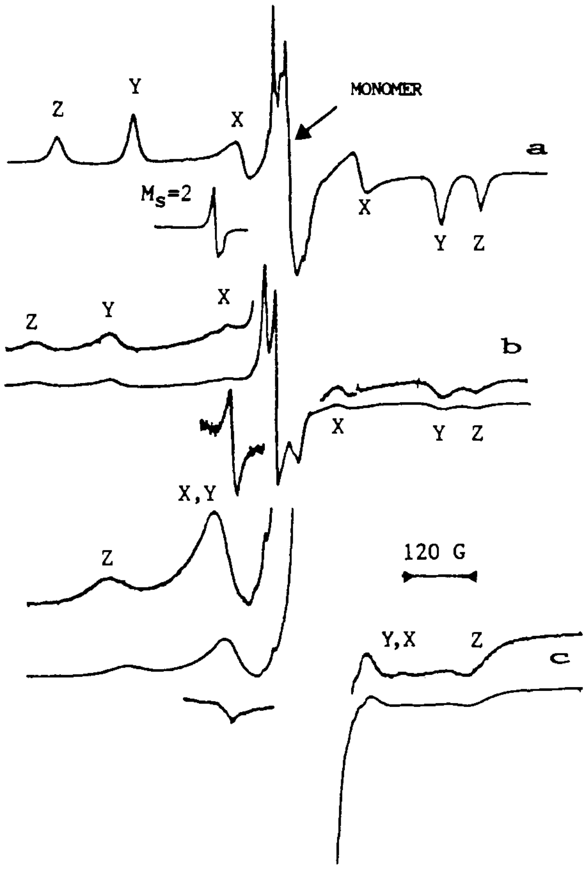

**Figure 3.** EPR spectra of (a) compound **1**, (b) compound **2**, and (c) compound **3** in frozen-toluene solution (140 K). Frequency: 9427 GHz. Modulation: 2 $G_{pp}$ (1 G = 0.1 mT). Gain: 5 × $10^4$.

**EPR Measurements.** In frozen solution, both compounds **1** and **2** exhibit EPR spectra of rhombic triplet states ($S = 1$) (Figure 3), typical of magnetic exchange between interacting binuclear Ti(III) complexes. The spectral features are well resolved for compound **1**. They consist of a six-line pattern labeled *X*, *Y*, and *Z*, representing the allowed $\Delta M_s = 1$ transitions of the triplet state with rhombic *g* and zero field splitting (ZFS) tensors. Between the two *X* lines, a broad and partially resolved

**Table III.** EPR Parameters of Compounds **1–3** at 130 K in Toluene Solution

| compd | $g_z$ | $g_y$ | $g_x$ | $D$, cm$^{-1}$ | $E$, cm$^{-1}$ |
|---|---|---|---|---|---|
| **1** | 2.001 (7) | 1.980 (3) | 1.964 (7) | −0.0446 | −0.0069 |
| **2** | 1.997 (5) | 1.976 (0) | 1.958 (4) | −0.0463 | −0.0066 |
| **3** | 2.00 (0) | 1.98 (6) | 1.97 (9) | −0.037 (5) | ≈(+)0.000 (5) |

EPR line indicates the presence of a doublet state ($S = {}^1/_2$) due to a mononuclear Ti(III) impurity. The high intensity of this line compared to the other components does not essentially indicate a higher concentration of this monomer but rather an angular variation of the spectrum within a narrower magnetic field range than that of the dimer. This monomer signal was found to be present in many EPR spectra of binuclear titanium(III) compounds exhibiting a triplet state,[8] and it is of much higher intensity in **2** compared to **1**. Compound **2** exhibits identical features but with a poor signal to noise ratio due to low solubility. In addition, the central line of the impurity doublet state is more intense than in **1**.

In addition to the six $\Delta M_s = 1$ transitions, a formally forbidden $\Delta M_s = 2$ transition is seen at midfield. Figure 3 also shows the EPR spectrum at 140 K of the monochloride dimer **3**. It exhibits some similarity to that of compound **1** but with a somewhat poorer resolution. Four $\Delta M_s = 1$ lines are observed with the forbidden $\Delta M_s = 2$ transition at midfield, but the resolution of the signals is of much lower quality than for that of **1** and **2**, which leads to some uncertainties in the determination of the EPR parameters. These are given in Table III. Because of the good quality of the EPR spectrum of **1**, we have essentially focused our attention on this compound.

In the analysis of the EPR spectrum, we must first consider the relative orientations of the g tensors of the two metal centers and the ZFS tensor. If we represent the Cp ligands as isolated atomic ligands, the symmetry of complex **1** is close to $D_{2h}$ and is thus centrosymmetric. In that case, we are dealing with the simple situation where the two Ti(III) $g$ tensors and the ZFS tensor are colinear. The spin Hamiltonian for the $S = 1$ state of this binuclear complex is

$$H = \beta S_g B + D(S_z^{\,2} - {}^1/_3 S^2) + E(S_x^{\,2} - S_y^{\,2}) \qquad (1)$$

where $D$ and $E$ are respectively the axial and the rhombic components of the ZFS tensor. The expressions for the resonance fields of the six $\Delta M_s = 1$ transitions for a randomly oriented dinuclear complex whose $g$ and $D$ tensors are colinear are given by[14]

$$B_{z1} = (2.0023/g_z)[(B_0 - D)^2 - E^2]^{1/2} \qquad (2a)$$

$$B_{z2} = (2.0023/g_z)[(B_0 + D)^2 - E^2]^{1/2} \qquad (2b)$$

$$B_{x1} = (2.0023/g_x)[(B_0 - D + E)(B_0 + 2E)]^{1/2} \qquad (2c)$$

$$B_{x2} = (2.0023/g_x)[(B_0 + D - E)(B_0 - 2E)]^{1/2} \qquad (2d)$$

$$B_{y1} = (2.0023/g_y)[(B_0 - D - E)(B_0 - 2E)]^{1/2} \qquad (2e)$$

$$B_{y2} = (2.0023/g_y)[(B_0 + D + E)(B_0 + 2E)]^{1/2} \qquad (2f)$$

where $B_0$ is the resonance field of a free electron spin.

The isotropic exchange interaction $J$ can be conveniently determined from the temperature dependence of the EPR intensity of the $\Delta M_s = 1$ transition according to the expression

$$I_{\rm EPR} = (A/T - \Theta)[1 + {}^1/_3 \exp(-2J/kT)]^{-1} \qquad (3)$$

where $\Theta$ is the Weiss constant. In the case of an antiferromagnetic dimer in frozen solution, however, expression (3) can be used only if the curve has a maximum slightly above or below the freezing point of the solution (about 150 K for toluene), i.e., in the case where the $J$ value is small as for example in $[(\mathrm{Cp_2TiCl})_2\mathrm{ZnCl_2}]$.[15] For a large $J$ value, the variation of the EPR intensity below freezing is too small to allow an accurate determination of $J$. Another way to measure a large $J$ is from the intensity of the broad and structureless EPR line of a polycrystalline sample. Since the EPR line of the dimer is superimposed on that of the $S = {}^1/_2$ impurity, one must add a paramagnetic contribution $I'_{\rm EPR} = B/T$ to expression (3) which becomes important at low temperature. We observed that for the powder samples of **1**, this contribution is negligible above about 140 K. On the contrary, the $\Delta M_s = 1$ lines of dilute frozen solution of **1** are well resolved only below 140 K, because they rapidly broaden above this temperature. Figure 4 shows the temperature variation of the EPR intensity measured from both the frozen-solution and the powder samples. These data were least-squares fit to expression (3), with the parameters $J = -268 \pm 4$ cm$^{-1}$ and $A = 98\,300 \pm 3000$. Since the frozen solution spectrum of **2** exhibited a very intense central $S = {}^1/_2$ EPR signal, no attempt was made to measure $J$ in an analogous fashion, the Curie portion of the curve being largely predominant, and the uncertainty on the $J$ value becomes too high to be reliable. However, judging from the EPR parameters and the Ti–Ti distance, this value is expected to be close to that of **1**.

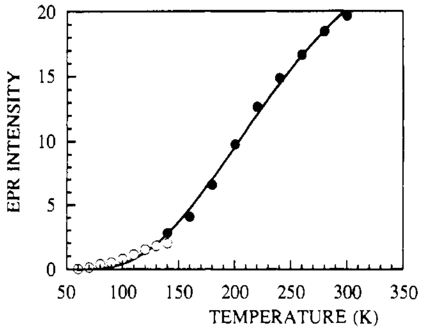

**Figure 4.** Temperature dependence of the EPR intensity (in arbitrary units) for compound **1**. The solid line corresponds to a least-squares fit of the data to expression (3) with $J = -268 \pm 4$ cm$^{-1}$ and the coefficient $A = 98\,300 \pm 4000$. Key: Full circles, powder sample; empty circles, low-field $y$ transition of dilute frozen solution.

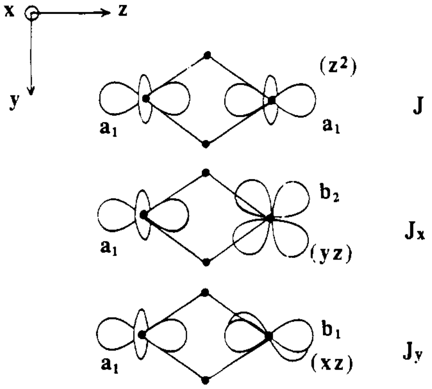

**Figure 5.** Titanium d orbitals involved in the isotropic exchange interactions $J$, $J_x$, and $J_y$.

For compound **3**, the EPR parameters are more difficult to extract from the spectrum because of poor resolution. Nevertheless, by comparison with **1**, one may assign the outer lines to the $z$ components of the $\Delta M_s = 1$ transitions. The high intensity of the EPR line at the lower field of the central impurity line indicates that the former results from the overlap of the $x$ and $y$ low-field $\Delta M_s = 1$ transitions. These parameters, shown in Table III, are quite similar to those of **1** and **2**, save for the ZFS which is close to axial in **3** as shown by its very low $E$ value, with a slightly rhombic character of the $g$ factor.

## Discussion

**(a) Magnetic Orbitals.** From the $g$ tensor we shall first determine the magnetic orbitals, i.e. the metal orbitals containing the unpaired electrons. Their identification is of interest if we want to discuss the characteristics of the ZFS tensor and the isotropic exchange interaction. A possible qualitative approach for the theoretical determination of the magnetic orbitals is to consider the energy level diagram of an isolated $[\mathrm{Cp_2TiL_2}]$ monomer (L = ligand) and to identify the modifications brought about by the formation of the dimer with a short Ti–Ti distance. If we choose the Ti–Ti direction as the $z$ axis and the $x$ axis perpendicular to the $\mathrm{ML_2}$ plane (Figure 5), the metal orbitals involved in the bent $\mathrm{Cp_2Ti}$ fragment with $C_{2v}$ symmetry are in

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[14] Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

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the following sequence:[16] $1a_1(x^2-y^2) < b_2(yz) < 2a_1(z^2) < b_1(xz) < a_2(xy)$. The orbitals are unoccupied in [$Cp_2TiL_2$] complexes, while one electron occupies the $1a_1$ orbital in [$Cp_2VL_2$] complexes. In $C_{2v}$ symmetry, $x^2 - y^2$ and $z^2$ belong to the same representation $a_1$ and these orbitals are thus mixed so that $1a_1$ and $2a_1$ have the form

$$|\Psi_0\rangle = a|z^2\rangle + b|x^2-y^2\rangle \tag{4}$$

with theoretically $a < b$ and $a > b$ for the $1a_1$ and $2a_1$ orbitals, respectively.[16] Casey and Raynor[17] studied by EPR a variety of [$Cp_2VL_2$] compounds and found that the SOMO is the $1a_1$ orbital with the $a$ parameter ranging from 0.31 to 0.51 and $b$ from 0.69 to 0.49, i.e. an almost equal amount of $z^2$ and $x^2 - y^2$ orbitals but with $x^2 - y^2$ being predominant. The ground-state orbital can thus be described as similar to a $y^2$ orbital. Following these considerations, one can anticipate that the magnetic orbitals have the form (4) in compounds **1**–**3**, in principle with $a < b$. Experimentally, the ground state can be determined from the $g$ tensor, and the three $g$-shift components are related to $a$ and $b$ by the following expressions:[18]

$$\Delta g_x = \frac{-2\lambda(\sqrt{3}a + b)^2}{\Delta_x} \tag{5a}$$

$$\Delta g_y = \frac{-2\lambda(\sqrt{3}a - b)^2}{\Delta_y} \tag{5b}$$

$$\Delta g_z = \frac{-8\lambda b^2}{\Delta_z} \tag{5c}$$

The energy separations $\Delta_x$, $\Delta_y$, and $\Delta_z$ are given by

$$\Delta_z = E_{a1} - E_{xy} \tag{6a}$$

$$\Delta_x = E_{a1} - E_{yz} \tag{6b}$$

$$\Delta_y = E_{a1} - E_{xz} \tag{6c}$$

$\lambda$ is the effective spin–orbit coupling constant of Ti(III), which approaches the free ion value if we neglect the ligand terms in the ground-state orbital $a_1$. It should be noted that the experimental value $\Delta g_z = -0.0006$ is negligible compared to the other components $\Delta g_x = -0.0376$ and $\Delta g_y = -0.022$ in compound **1**. This implies that in eqs 5a–c, we have either $\Delta_z \gg \Delta_x, \Delta_y$ or $b \ll a$.

If the ground state is the same as in $Cp_2VL_2$ complexes with $b > a$, we expect[17] $|\Delta g_y| \approx 0 < |\Delta g_x| < |\Delta g_z|$, which is different from the experimental results for **1**–**3**. There is no objective reason for the $xy$ orbital to be much higher in energy than $yz$ or $xz$ orbitals in dimers compared to monomers, so that the inequality $\Delta_z \gg \Delta_x, \Delta_y$ becomes unrealistic. More probably, the inequality $b \ll a$ holds better to account for the origin of the lack of $g$ shift along the $z$ direction, which implies magnetic orbitals mostly of $z^2$ character. This predominantly $z^2$ ground state is found in the three dimers **1**–**3** under study, and seems to be different from the case of titanium dimers with extended bridging ligands with long Ti–Ti distances, for which the magnetic orbitals are of the same type as those in $Cp_2VL_2$ series,[8] i.e. of $y^2$ character. The three dimers under study are characterized by very short Ti–Ti distances, equal to 3.35, 3.35, and 3.96 Å for **1**–**3**, respectively. This situation should stabilize the empty $z^2$ orbitals of the two metal centers because of a significant overlap of the two orbitals. This stabilization should reduce the splitting between the $x^2 - y^2$ and $z^2$ orbitals and thus should increase the amount of mixing of $z^2$ into the $x^2 - y^2$ orbital. If the stabilization of $z^2$ is such that it becomes lower in energy than $x^2 - y^2$, the magnetic orbital should be in that case characterized by $b \ll a$. This would explain the experimental results which indicate that the magnetic orbitals of the three dimers are mainly of the $z^2$ type (Figure 5).

**Table IV.** Recapitulation of the Exchange Parameters and the Different Components of the Zero Field Splitting Tensor (cm$^{-1}$)

| | 1 | 2 | 3 | |
|---|---|---|---|---|
| $D$ | –0.0446 | –0.0463 | –0.037 (5) | *a* |
| $E$ | –0.0069 | –0.0066 | ≈(+)0.000 (5) | *a* |
| $D_d$ | –0.0458 | –0.0455 | –0.0278 | *b* |
| $E_d$ | –0.0004 | –0.0016 | –0.0001 | *b* |
| $D_e$ | +0.0012 | –0.0008 | –0.009 (7) | *c* |
| $E_e$ | –0.0065 | –0.0050 | ≈(+)0.000 (6) | *c* |
| $J$ | –268 ± 4 | nm | –111 | *f* |
| $J_x$ | –131 | –52 | (+455) | *d* |
| $J_y$ | +265 | +201 | (+820) | *d* |
| $R_{cal}$, Å | 3.38 | 3.33 | 3.58 | *e* |
| $R$, Å | 3.35 | 3.35 | 3.96 | *f* |

[a] Measured. [b] Calculated from expressions (8). [c] Calculated from expressions (7). [d] Calculated from expressions (16). [e] $R_{cal}$ is the Ti–Ti distance calculated from a purely dipole–dipole interaction with $D \approx D_d$. [f] From ref 12.

**(b) ZFS Tensor.** The fairly good resolution of the EPR spectrum of **1** gave us accurate values for the axial $D$ and rhombic $E$ components of the ZFS tensor. Since **1** and **2** are titanium dimers which possess to our knowledge the shortest Ti–Ti distances, the analysis of their ZFS is of particular importance. In a symmetrical dimer such as **1**, $D$ and $E$ comprise dipolar contributions $D_d$ and $E_d$ and pseudodipolar contributions $D_e$ and $E_e$ according to the following expressions:

$$D = D_d + D_e \tag{7a}$$

$$E = E_d + E_e \tag{7b}$$

In most cases in the literature, the data are interpreted in terms of $D_d$ because simple through-space dipolar interactions are easy to handle when the distance between the unpaired spins is larger than about 2 Å. The pseudodipolar contributions $D_e$ and $E_e$ to the ZFS are however more difficult to treat because they arise from a spin–orbit interaction of ground state of the Ti(III) center with an excited state, where the excited state is involved in an exchange interaction with the other Ti(III) center. Because of the complicated nature of this interaction, it is generally neglected or only roughly estimated as $D_e \approx \Delta g^2 J^*$, where $J^*$ represents the exchange interaction with the excited state. In the present discussion we derive simple expressions for the two pseudodipolar components $D_e$ and $E_e$ in the case of $z^2$ ground states, which allows us to appreciate their respective contributions to the ZFS.

For an anisotropic $g$ tensor, the dipole–dipole ZFS parameters $D_d$ and $E_d$ are given by[19]

$$D_d = \frac{-\beta^2}{3R^3}\left[2g_z^{\,2} + \frac{g_x^{\,2} + g_y^{\,2}}{2}\right] \tag{8a}$$

$$E_d = \frac{\beta^2}{2R^2}(g_x^{\,2} - g_y^{\,2}) \tag{8b}$$

From the Ti–Ti distance $R$ obtained from crystallographic data and the experimental $g$ tensors, one can calculate the parameters $D_d$ and $E_d$. These are given in Table IV.

It appears that the purely dipole–dipole interaction $D_d$ is very close to the experimental axial component of the ZFS for **1** and

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**2**. Using expression (8a) with the experimental value $D$ instead of $D_d$ leads to calculated Ti–Ti distances equal to 3.38 and 3.33 Å, respectively, compared to the distance 3.35 Å obtained from X-ray structures for **1** and **2**. One may thus conclude that the pseudodipolar parameter $D_e$ is close to zero in these types of dimers (Table IV), i.e. $D \approx D_d$, and also that, despite the short Ti–Ti distances, the dipole–dipole approximation remains valid for the calculation of $R$ from the axial component of the ZFS.

On the contrary, the rhombic component $E$ of the ZFS in **1** and **2** is much larger than the calculated dipole–dipole contribution $E_d$ (Table II). According to expression (7b), this important difference between $E$ and $E_d$ points to an important contribution of the pseudodipolar parameter $E_e$, i.e. $E \approx E_e$. The pseudodipolar interaction originates from a synergic effect of the isotropic exchange and the spin–orbit interaction $\lambda LS$. It can be accounted for by a third-order perturbation term in the Hamiltonian, of the form[19,20]

$$H' = \sum_{i=1,2} \frac{\langle \Psi_{0i}\Psi_{0j}|\lambda L_i S_i|\Psi^*{}_i\Psi_{0j}\rangle \langle \Psi^*{}_i\Psi_{0j}|H_{ex}|\Psi^*{}_i\Psi_{0j}\rangle \langle \Psi^*{}_i\Psi_{0j}|\lambda L_i S_i|\Psi^*{}_i\Psi_{0j}\rangle}{(E^* - E_0)^2} \tag{9}$$

where $H_{ex}$ is the exchange Hamiltonian. The sum runs over the two unpaired electrons $i = 1, 2$ with ground states $|\Psi_{0i}\rangle$, which are $1a_1$ for the two electrons. The ket $|\Psi^*{}_i\rangle$ represents the excited states coupled to the ground state by the spin–orbit interaction. $E_0$ and $E^*$ are respectively the electron ground-state and excited-state energies. If we calculate the matrix elements of the Hamiltonian (9) for the three components of $\lambda LS$ and for the two electrons, one obtains the following expression:

$$H' = D'_{xx}S_x^2 + D'_{yy}S_y^2 + D'_{zz}S_z^2 \tag{10}$$

Here $D'_{xx}$, $D'_{yy}$, and $D'_{zz}$ are the three components of the pseudodipolar tensor, given by

$$D'_{xx} = {}^1/_4(a_xJ_x - a_yJ_y - a_zJ_z) \tag{11a}$$

$$D'_{yy} = {}^1/_4(-a_xJ_x + a_yJ_y - a_zJ_z) \tag{11b}$$

$$D'_{zz} = {}^1/_4(-a_xJ_x - a_yJ_y + a_zJ_z) \tag{11c}$$

The parameters $J_x$, $J_y$, and $J_z$ represent the isotropic exchange interaction between one electron in the ground-state orbital of one center and the other electron in the excited state of the other metal center. The coefficients $a_x$, $a_y$, and $a_z$ are given by the following expressions:

$$a_x = \lambda^2 \frac{|\langle \Psi^*{}_x|L_x|\Psi_0\rangle|^2}{\Delta_x^2} \tag{12a}$$

$$a_y = \lambda^2 \frac{|\langle \Psi^*{}_y|L_y|\Psi_0\rangle|^2}{\Delta_y^2} \tag{12b}$$

$$a_z = \lambda^2 \frac{|\langle \Psi^*{}_z|L_z|\Psi_0\rangle|^2}{\Delta_z^2} \tag{12c}$$

Here $\Delta_x$, $\Delta_y$, and $\Delta_z$ are defined in expression (6) for the $a_1$ ground state. The Hamiltonian (10) can be written in a more suitable form

$$H' = D_e(S_z^2 - {}^1/_3S^2) + E_e(S_x^2 - S_y^2) + {}^1/_3(D'_{xx} + D'_{yy} + D'_{zz})S^2 \tag{13}$$

with the axial and rhombic terms $D_e$ and $E_e$ of the pseudodipolar component of the ZFS given by

$$D_e = {}^1/_4(2a_zJ_z - a_xJ_x - a_yJ_y) \tag{14a}$$

$$E_e = {}^1/_4(a_xJ_x - a_yJ_y) \tag{14b}$$

The third term in (13) is a constant which shifts all the spin states equally, and its coefficient is proportional to the trace of the pseudodipolar tensor $D'$. At this stage one can calculate $D_e$ and $E_e$ from expressions (12) and (13) with the appropriate ground state in expression (4). In the analysis of the $g$ tensor, we found that the nearly zero value of the $g$ shift is explained by a ground state of almost purely $z^2$ character, i.e. $|\Psi_0\rangle \approx |z^2\rangle$. With this reasonable approximation, the coefficients $a_x$, $a_y$, and $a_z$ in expression (12) become equal to

$$a_z \approx 0 \tag{15a}$$

$$a_x = \frac{3\lambda^2}{(E_{yz} - E_0)^2} \approx \frac{\Delta g_x^{\,2}}{12} \tag{15b}$$

$$a_y = \frac{3\lambda^2}{(E_{xz} - E_0)^2} \approx \frac{\Delta g_y^{\,2}}{12} \tag{15c}$$

and the pseudodipolar parameters are thus given by the simple expressions

$$D_e = -{}^1/_{48}(\Delta g_x^{\,2}J_x + \Delta g_y^{\,2}J_y) \tag{16a}$$

$$E_e = +{}^1/_{48}(\Delta g_x^{\,2}J_x - \Delta g_y^{\,2}J_y) \tag{16b}$$

For a $z^2$ ground state, $J_x$ ($J_y$) represents the isotropic exchange interaction between one unpaired electron in the $z^2$ orbital of a Ti(III) center and the other electron in the $yz$ ($xz$) orbital of the other Ti(III) center (Figure 5). Expressions (16) indicate that one can have $D_e < E_e$ if $J_x$ and $J_y$ are of opposite signs, i.e. one interaction is ferromagnetic while the other is antiferromagnetic. Expressions (16) form a system of equations with two unknowns $J_x$ and $J_y$, which can be determined from $\Delta g_x^2$ and $\Delta g_y^2$, and the values $D_e$ and $E_e$ can be deduced from $D$, $E$, $D_d$, and $E_d$ according to expressions (7). The parameters $J_x$ and $J_y$ are gathered in Table IV for compounds **1** and **2**.

From these results, one can conclude that the exchange interactions $J_x$ ($J_y$) between the d$z^2$ and $yz$ ($xz$) orbitals is antiferromagnetic (ferromagnetic). The consequence is that these two interactions compensate each other to give a nearly zero contribution to the axial ZFS parameter $D$, while they are essentially responsible for the nonaxial component $E$. The observation of isotropic antiferromagnetic exchange and ferromagnetic exchange interactions with the excited state has also been recorded in the case of bridged Cu(II) dimers.[21]

The situation in **3** appears to be significantly different from that in **1** and **2**, despite the uncertainties of its EPR parameters resulting from low spectral resolution. It turns out that the axial component $D_e$ of the pseudodipolar tensor is much larger than the rhombic component $E_e$, i.e. $D_e > E_e$, which is the reverse situation of **1** and **2**, where $D_e < E_e$. The inequality $D_e > E_e$ found for **3** implies that the exchange interactions $J_x$ and $J_y$ in expressions (16) are of the same signs. However, because of the large uncertainties on the experimental parameters $D$, $E$, and the $g$ shifts $\Delta g_x$ and $\Delta g_y$, the values of $J_x$ and $J_y$ in Table II are most probably of no great significance. The most important consequence of the inequality $D_e > E_e$ is that the Ti–Ti distance obtained

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from $D$ by using the dipole–dipole expression (8) and neglecting $D_e$ leads to a poor agreement between the calculated distance $R_{cal}$ = 3.58 Å and the distance 3.96 Å measured from X-ray diffraction.

**(c) Isotropic Exchange Interaction.** Despite the fact that considerable progress has been achieved during the last two decades in the understanding of the nature and magnitude of the exchange interaction which occurs in polynuclear complexes with paramagnetic centers;[22] its interpretation in the case of $[Cp_2TiL]_2$ dimers is not a simple task and does not seem to have been undertaken up to today. Instead of discussing the variation of $J$ across the known series of titanium dimers, which strongly depends on the nature of the bridging ligands, we shall qualitatively discuss the nature and the signs of the exchange interactions $J$, $J_x$, and $J_y$ in a dimer such as **1** or **2**. Whatever the resulting nature of the exchange, ferromagnetic or antiferromagnetic, the singlet–triplet separation may always be interpreted as resulting from a competition between a positive (ferromagnetic) contribution $J^F$ and a negative (antiferromagnetic) contribution $J^{AF}$ [23]

$$J = J^F + J^{AF} \tag{17}$$

with equivalent expressions for $J_x$ and $J_y$. For a nonsymmetrical dimer,[24] $J^{AF}$ is given by the following expression:

$$J^{AF} = -2(\delta^2 - \Delta^2)^{1/2}S \tag{18}$$

Here $S$ is the overlap integral between the two magnetic orbitals, $\Delta$ is the energy gap between the two magnetic orbitals, and $\delta$ is the energy gap between the two molecular orbitals in the binuclear complex built from the two magnetic orbitals. If we consider the antiferromagnetic interaction $J^{AF}$ between the $z^2$ orbitals of the two Ti(III) centers, the energy gap $\Delta$ is equal to zero. In the case of $J^{AF}x$ and $J^{AF}y$, the energy gaps $\Delta_x$ and $\Delta_y$ have been defined in expression (6b) and (6c). The general expression for $J$, $J_x$, and $J_y$ may thus be written:

$$J = J^F - 2\delta S \tag{19a}$$

$$J_x - J^F{}_x - 2(\delta_x{}^2 - \Delta_x{}^2)^{1/2}S_x \tag{19b}$$

$$J_y = J^F{}_y - 2(\delta_y{}^2 - \Delta_y{}^2)^{1/2}S_y \tag{19c}$$

Here $S_x$ ($S_y$) is the overlap integral between the $z^2$ orbital of one center and the $yz$ ($xz$) orbital of the other center. The term $(\delta^2 - \Delta^2)^{1/2}$ in expression (18) is proportional to $S$, so that the antiferromagnetic interactions $J^{AF}$, $J^{AF}{}_x$, and $J^{AF}{}_y$ are proportional to $S^2$, $S_x{}^2$, and $S_y{}^2$.[24] It is expected that the main factor governing the magnitude of the exchange interactions will be the overlap of the magnetic orbitals, which favors the antiferromagnetic interactions.[22] For symmetry considerations and owing to the fact that the Ti–O–Ti angle is about 108°, the overlap integral $S$ of the two $a_1(z^2)$ orbitals is nonzero so that the resultant interaction $J$ is negative as expected for these kinds of dimers. The situation is different for $J_x$ and $J_y$. The orbital $a_1(z^2)$ is symmetric with respect to the two mirror planes containing the Ti–Ti bond, while the $b_2(yz)$ orbital is antisymmetric with respect to one of these planes and the $b_1(xz)$ orbital is antisymmetric with respect to the other. Thus strictly speaking, the overlap integrals $S_x$ and $S_y$ should be equal to zero and $J_x$ and $J_y$ should be positive, contrary to what is observed for $J_x$. However, the opposite signs of $J_x$ and $J_y$ may be qualitatively understood by considering the nature of the metal–ligand bonds in these two types of dimers and the overlap density between the magnetic orbitals around the bridging atoms.[22] The $b_1(xz)$ and $a_2(xy)$ orbitals, on one hand, and the $a_1(z^2, x^2 - y^2)$ and $b_2(yz)$ orbitals, on the other, do not have the same role in the metal–ligand bonding. The $b_1$ and $a_2$ orbitals interact only with the Cp molecular orbitals of the appropriate symmetry and do not interact with the oxygen orbitals, so that the overlap density between $a_1$ and $b_1$ orbitals around the bridging oxygen ligands is zero, making $S_y$ equal to zero. This can also be formulated in another way. Because of the zero interaction between the $a_1$ and $b_1$ orbitals, the energy gap $\delta_y$ in (19c) should be equal to $\Delta_y$. Consequently, the term $J^{AF}{}_y$ should be very close to zero, which should also explain why $J_y = J^F{}_y$ is positive. Alternatively, metal–oxygen bonds are formed by interactions of the p orbitals of the oxygen ligands with the $b_2(yz)$ orbital and some combination of the two $a_1(z^2, x^2 - y^2)$ metal orbitals,[16] which should result in nonzero overlap density around the bridging oxygen atoms, making $S_x$ different from zero. The consequence is a nonzero antiferromagnetic term $J^{AF}{}_x$ responsible for the negative sign of $J_x$. It is evident that such simple qualitative considerations can explain neither the relative magnitude of the exchange interactions nor the reason that the ferromagnetic term $J^F{}_y$ is so high.

In the interpretation of the exchange interactions in dinuclear complexes, it is generally assumed that the metal–metal distance is too large to allow direct metal–metal interactions, and such interactions are thus neglected. However, dimers **1** and **2** have very short Ti–Ti distances of 3.35 Å so that direct interactions are not necessarily negligible. Indeed, we determined from the $g$ tensor that the predominantly $z^2$ character of the magnetic orbitals contrasts with the expected $y^2$ character for the corresponding monomers. This stabilization of the $z^2$ orbitals with respect to $x^2 - y^2$ points to the existence of nonnegligible direct Ti–Ti interactions. However, these interactions are probably too small to modify the exchange mechanism between the two metal centers discussed above, so that the essential overlap density between the two centers should remain localized around the bridging atoms. The situation could be different if the magnetic orbitals are $4d_{z^2}$ orbitals instead of $3d_{z^2}$ orbitals. The radial extension of the former is more important so that there could be a significant direct overlap density along the metal–metal axis. This would explain why zirconium dimers such as $[CpZr(\mu\text{-}X)]_2$ or $[(MeCp)_2ZrX]_2$ (X = halogen), isoelectronic with the case under study, are diamagnetic.[25,26]

A survey of the literature shows that a number of bis(cyclopentadienyl)titanium(III) dimers with N, S, and P bridging ligand atoms (other than those described in refs 6–9) such as $[Cp_2TiN(CH_3)_2]_2$,[27] $[Cp_2TiSPh]_2$ (Ph = $C_6H_5$),[28] and $[Cp_2TiPR_2]_2$ (R = $CH_3$, $C_2H_5$)[29] have been synthesized and their crystal structures determined, but the magnetic data are rather uncertain, and in any case none of them was reported to exhibit well-defined antiferromagnetic behavior. The closest analog of **1** or **2** would be the $[(MeCp)Ti(OCH_3)Cl]_4$ tetramer,[30] which contains both chloro- and methoxo-bridging units with Ti–Ti distances of 3.772 and 3.236 Å, respectively, but again no magnetic measurements were reported other than the magnetic moment value of $\mu = 1.40$ $\mu_B$/Ti. It is therefore not possible with the present available data to define clearly to what measure the nature of the bridging atom or the metal–metal separation distance contribute to the antiferromagnetic behavior in this family of dinuclear compounds.

## Conclusion

The purpose of this work was to study the magnetic properties of the methoxo- and ethoxo-bridged Ti dimers, compounds **1** and

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**2**, with short Ti–Ti distances. In addition to the anticipated antiferromagnetic character of the isotropic exchange interaction, $J = -268 \pm 4$ cm$^{-1}$ for **1**, good resolution of the EPR spectra allowed us to reveal some relevant features of the ZFS tensor:

(i) The axial component $D$ of the ZFS of **1** and **2** is almost of purely magnetic dipolar character, and even for this short Ti–Ti distance, the usual point dipole–dipole expression for $D$ can still be used to determine the intermetallic distance with a good precision.

(ii) The nonaxial component $E$ of the ZFS is of almost purely pseudodipolar character, which results from a synergic effect of the spin–orbit interaction and the exchange interaction. From the experimental values of $E$, we could estimate the isotropic exchange interactions $J_x$ and $J_y$ between the ground-state orbital $z^2$ of one Ti(III) center and the virtually excited $yz$ and $xz$ orbitals of the other Ti(III) center. These interactions are of opposite signs and consequently are responsible for the nonaxial character of the ZFS tensor.

(iii) In contrast, the EPR spectrum of **3** has an almost axial ZFS tensor. In this case $J_x$ and $J_y$ are of the same sign, which also explains why $D$ is not purely dipolar and why the intermetallic distance cannot be accurately measured from $D$.

It is expected that the above study which associates X-ray crystallographic data with parameters derived from EPR spectra of homodinuclear Ti(III) compounds exhibiting excited triplet states will serve as a model for rational investigations of magnetic behavior in similar already existing systems or others to be synthesized to which increasing attention is being devoted.

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**Supplementary Material Available:** Listings of fractional atomic coordinates with standard deviations, least-squares planes, bond distances and angles, and experimental parameters of the X-ray structure analysis and crystal data (8 pages). Ordering information is given on any current masthead page.