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A Diamagnetic Dititanium(III) Paddlewheel Complex with No Direct Metal–Metal Bond

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Reaction of Ti[N(Bu^t)Ar]$_3$ (Ar = 3,5-$C_6H_3Me_2$ or Ar′ = C_6H_5) with CO_2 at –40 °C produces diamagmetic Ti^{III} paddlewheel complexes with long Ti–Ti separations (>3.4 Å), thus excluding direct Ti–Ti bonding. ^{1}H NMR spectroscopy shows that the compounds are diamagnetic in solution in the temperature range of –65 to +70 °C. In the solid state, the diamagnetism was found to persist between 2 and 300 K. Calculations at the density functional theory level suggest that the diamagnetism results from antiferromagnetic coupling by superexchange through the ligand π system.

While the insertion of CO_2 into metal−amide bonds is a well-known reaction leading to metal carbamate systems,[1−4] complexes containing three of the sterically demanding −N(Bu^t)Ar ancillary ligands, where Ar = 3,5-$C_6H_3Me_2$, have not been shown previously to absorb CO_2. Accordingly, we have proposed that the odd-electron CO_2 adduct (CO_2)Ti[N(Bu^t)Ar]$_3$ is generated upon exposure of the titanium(III) trisamide Ti[N(Bu^t)Ar]$_3$ to 1 equiv of CO_2 at low temperature in an ether solution.[5,6] Carrying out a similar experiment in the presence of the benzonitrile adduct (PhCN)Mo[N(Bu^t)Ar]$_3$,[7,8] employed as a radical trap, led to heterobimetallic reductive cross-coupling of CO_2 with PhCN.[5] Now we report that extended treatment (2.5 h) of Ti[N(Bu^t)Ar]$_3$[9,10] with excess CO_2 (4 equiv) in Et_2O at −40 °C produces a lime-green precipitate, which has been identified as a diamagnetic dititanium(III) paddlewheel complex Ti$_2$[μ-O_2CN(Bu^t)-3,5-$C_6H_3Me_2$]$_4$(N(Bu^t)-3,5-$C_6H_3Me_2$)$_2$ (**1a**).

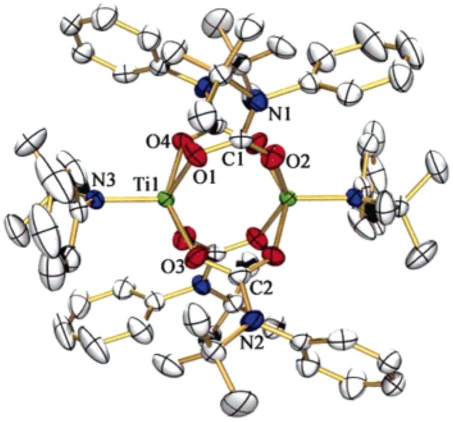

Figure 1. Structure of one of two crystallographically independent Ti$_2$[μ_2-O_2CN(Bu^t)Ph]$_4$(N(Bu^t)Ph)$_2$ molecules in **1b**·Et_2O. Each molecule has an inversion center. Displacement ellipsoids are shown at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Ti1−Ti1′, 3.515(1); Ti1−O1, 2.041(2); Ti1−N3, 1.920(3); N3−Ti1−O1, 105.7(1).

In the context of metal−metal bonding,[11] dinuclear d^1−d^1 systems of the paddlewheel variety have been elusive. Compound **1a** was not readily obtained as single crystals; therefore, the analogue Ti$_2$[μ-O_2CN(Bu^t)Ph]$_4$(N(Bu^t)Ph)$_2$ (**1b**) was prepared similarly from Ti[N(Bu^t)Ph]$_3$[10] and crystallized and its structure determined crystallographically (Figure 1). There are two crystallographically independent molecules, each possessing an inversion center. The cores are shown

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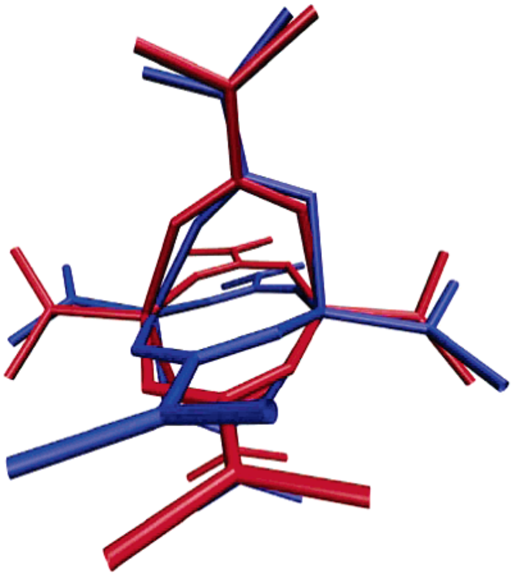

Figure 2. Overlay of the core structures of the two crystallographically independent molecules in **1b**·Et$_2$O. In red is the molecule containing Ti1 [Ti1−Ti1′ = 3.515(1) Å], and in blue is the molecule containing Ti2 [Ti2−Ti2′ = 3.426(1) Å].

as an overlay in Figure 2. The conformer drawn in blue and containing Ti2 shows an unsymmetrical bridging mode for its carbamate ligands, reminiscent of a carboxylate shift,[12] and its Ti2−Ti2′ interatomic distance is shorter by ca. 0.1 Å than is the Ti1−Ti1′ distance in the conformer drawn in red, which displays greater symmetry in its carbamate bridges. This paddlewheel system is both surprising and interesting because it combines diamagnetism with an intertitanium distance that surely precludes direct metal−metal bonding [3.515(1) and 3.426(1) Å for two crystallographically independent molecules]. We provide here a detailed account of the synthesis, solution behavior, and bonding in this unusual dititanium(III) paddlewheel system.

The syntheses of the new lime-green titanium(III) paddlewheel compounds are straightforward, involving simple exposure of the trisamide precursor molecules Ti[N(Bu^t)Ar]$_3$ or Ti[N(Bu^t)Ph]$_3$ to ca. 4 equiv of CO$_2$ at −40 °C in Et$_2$O. After removal of the solvent, the solid was easily purified by washing with pentane and then ether. The ^{1}H NMR spectrum at ambient temperature reveals broad resonances for **1a** and **1b**, and it is complex, especially in the aromatic region. To determine if the broadness of the signals is due to **1** being paramagnetic, a variable-temperature study with a 300-MHz spectrometer was undertaken. Selected spectra in the high-field region where signals from the methyl groups appear are shown in Figure 3. At a temperature of 70 °C (Figure 3a), there is a pair of singlets at 2.32 and 2.37 ppm in a 2:1 ratio. There is also a singlet at 1.32 ppm and a broad signal at 1.55 ppm, again in a 2:1 intensity ratio. Because the number of bridging groups is twice the number of terminal ligands in Ti$_2$[μ-O$_2$CN(Bu^t)-3,5-C$_6$H$_3$Me$_2$]$_4$(N(Bu^t)-3,5-C$_6$H$_3$Me$_2$)$_2$, the integration ratios are consistent with the solid-state structure, and we presume that this structure is retained in solution. At room temperature (Figure 3b), the signals have broad bases and relatively sharp tops. The two pairs of singlets observed at 70 °C have collapsed into signals centered at 2.42 and 1.42 ppm. Because of the 3:2 ratio for the peak at 1.42 ppm to the peak at 2.42 ppm, these signals can be assigned to the methyl groups located on the *tert*-butyl goups [−C(C*H*$_3$)$_3$] and those in the aromatic group (−C$_6$H$_3$Me$_2$). As the temperature was then lowered in 10 °C steps to −65 °C, the spectra became more and more complex. As shown in Figure 3c, in the spectrum at the lowest temperature to which we can safely cool the probe (−65 °C), most of the signals are sharp. However, there are still a few broad signals, indicating that a fluxional process is still occurring. We propose that the molecule is fluxional and that slower rotation around the Ti−N, N−C$_6$H$_3$Me$_2$, and N−Bu^t σ bonds at low temperatures accounts for the observations, but we have not attempted to perform a detailed analysis. However, it is evident that the compound is diamagnetic,[13] over the temperature range of −65 to +70 °C.

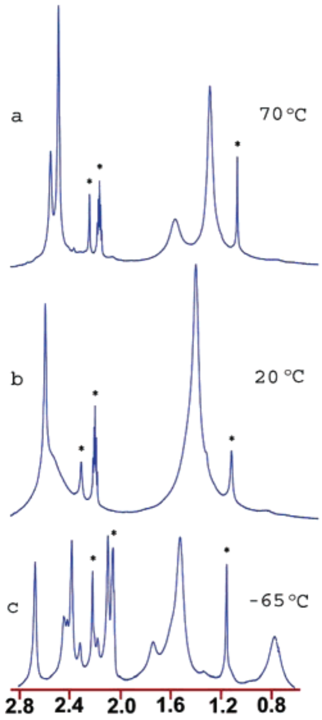

Figure 3. ^{1}H NMR spectra for **1a**. The signals marked with asterisks are due to protons in the methyl groups of the solvent toluene-d_8 (2.089 ppm) and in the free amine [HN(Bu^t)-3,5-C$_6$H$_3$Me$_2$] arising from a small amount of hydrolysis (singlets at 1.187 and 2.192 ppm).

To explain why the compound is diamagnetic despite the long Ti−Ti distance, density functional theory (DFT) calculations were performed on a simplified model.[14] Three different spin states were investigated. The first was a singlet ($S = 0$) model that assumes the presence of a metal−metal bond; the second was a triplet state ($S = 1$) that describes a

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[13] Magnetic susceptibility measurements of **1a**, using a SQUID instrument, in the temperature range of 2−300 K confirmed that the compound is diamagnetic.

[14] The DFT model was simplified to expedite the calculations by replacing all of the aryl groups with a hydrogen atom; similar simplifications in other systems have proved to be reasonable.

ferromagnetic interaction between the Ti d^1 electrons; the third model described an antiferromagnetically coupled unrestricted singlet state (broken symmetry). The latter gave the lowest energy among the three models and yielded an exchange coupling constant[15] of $-1266\ \mathrm{cm}^{-1}$ by Yamaguchi's method.[16,17] This low value is consistent with the magnetic studies.[13] The electronic structure of the antiferromagnetically coupled model shows that the α and β electrons in the HOMO are each localized on different Ti atoms,[18] as shown in Figure 4. Also, a significant amount of ligand character is found in both the α and β HOMOs.[19] This strong antiferromagnetic coupling takes place by superexchange through the ligand π system, in a manner similar to that in $Cu_2(CH_3COO)_4[H_2O]_2$,[20] and as in that case, no direct metal−metal bond between the metal atoms is present.[21]

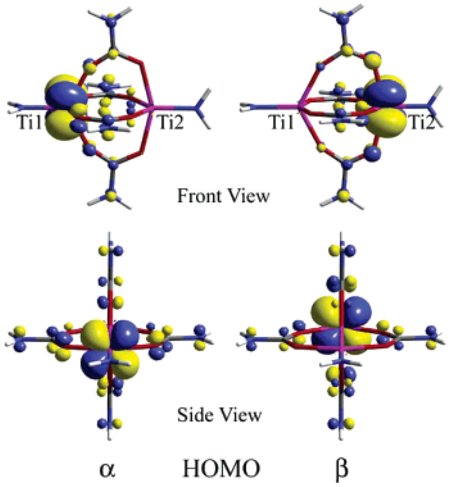

Figure 4. Illustrations of the 0.04 surface contour diagrams for the α and β HOMOs for the model of **1**.

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Supporting Information Available: Experimental details of syntheses and ^{1}H NMR analyses, a plot of χT vs T for **1a** in the solid state, and X-ray crystallographic files in CIF format for **1b**·Et_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The magnetic exchange coupling constant, $2J$, is based on the Heisenberg−Dirac−van Vleck spin Hamiltonian $H = -2JS_1S_2$.

(16) Yamaguchi's relationship is provided by the following equation: $J = E^{BS} - E^{HS}/\langle S^2\rangle^{HS} - \langle S^2\rangle^{BS}$, where E^{BS} and E^{HS} represent the total energy values of the broken-symmetry and high-spin DFT calculations, respectively. See: Soda, T.; Kitagawa, Y.; Onishi, T.; Takano, Y.; Shigeta, Y.; Nagao, H.; Yoshioka, Y.; Yamaguchi, K. *Chem. Phys. Lett.* **2000**, *319*, 223−230.

(17) The calculated antiferromagnetic exchange coupling constant, $2J$, is significantly more negative than the conventional $2J$ value ($-800\ \mathrm{cm}^{-1}$) used for diamagnetic compounds. See: Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273−325.

(18) In α HOMO: Ti1, 80.0%; Ti2, 0.6%. In β HOMO: Ti1, 0.6%; Ti2, 80.0%.

(19) Ligand character in α and β HOMOs: 19.4%.

(20) *Molecular Magnetism*; Kahn, O., Ed.; VCH: New York, 1993.

(21) It should be noted that there are a few nonpaddlewheel compounds containing Ti_2^{4+} units that are diamagnetic and for which Ti−Ti bonds have been suggested. For example, see: (a) Cotton, F. A.; Wojtczak, W. A. *Gazz. Chim. Ital*. **1993**, *123*, 499−507. (b) Hao, S.; Fegali, K.; Gambarotta, S. *Inorg. Chem*. **1997**, *36*, 1745−1748. (c) Utko, J.; Pryzbylak, S.; Jersykiewicz, L. B.; Mierzwicki, K.; Latajka, Z.; Sobota, P. *Inorg. Chem*. **2003**, *42*, 267−269.