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Preparation and Characterization of a Diamagnetic and Dinuclear Titanium(III) Formamidinate Complex. Evidence for the Existence of a Ti−Ti Bond?

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The new diamagnetic Ti(III) complex $(CyNC(H)NCy)_4Ti_2Cl_2 \cdot 2THF$ (**1**) containing a short Ti−Ti distance was prepared and crystallographically characterized. *Ab initio* unrestricted Hartree−Fock calculations suggested the presence of a Ti−Ti bonding interaction. Crystal data for **1** are as follows: $C_{60}H_{108}N_8Ti_2Cl_2O_2$, FW 1140.27, monoclinic *Pn*, $a = 10.4688(9)$ Å, $b = 14.4579(9)$ Å, $c = 21.421(1)$ Å, $\beta = 100.227(9)°$, $V = 3190.6(7)$ Å^3, $Z = 2$, $D_{calc} = 1.187$ g/cm^3, $F_{000} = 1236$, $\mu = 3.75$ cm^{-1}, $T = -158$ °C, $R = 0.074$, $R_w = 0.075$, GOF = 3.64 for 540 parameters and 4630 reflections out of 5771 unique reflections observed.

Introduction

In this article we describe the preparation and characterization of a rare example of a dinuclear and diamagnetic Ti(III) nonorganometallic species.[1] The rationale for this work was provided by the observation that dinuclear complexes of Ti(III) are usually paramagnetic[2] and antiferromagnetically coupled,[3] with intermetallic distances well above 3 Å. However, there are some exceptions. For example, the bridging fulvalene $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)(TiCp)_2(\mu\text{-}Cl)_2]$ complex[4] is diamagnetic, in sharp contrast to its considerably long intermetallic distance (3.638 Å). Conversely, the almost isostructural complex $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)(TiCp)_2(\mu\text{-}OH)_2]$,[5] which has a significantly shorter intermetallic distance (3.195 Å), displays a residual paramagnetism. Similar behavior can also be observed in the chemistry of mono- and bis(cyclopentadienyl)titanium(III) systems. While the dimeric derivatives of bridging thiolates,[6] amides,[7] phosphides,[8] and carboxylates[9] are usually diamagnetic, with intermetallic distances up to 3.72 Å, the bridging alkoxides[6,10] and hydride analogues[11] are paramagnetic in spite of much shorter Ti−Ti distances. Obviously, this contradictory behavior is difficult to rationalize with the existence of significant Ti−Ti bonds. As a result, superexchange was invariably invoked to account for the diamagnetism of some of these species, such as in the case of the $[(C_5H_4)TiHAlEt_2]_2(C_{10}H_8)$ complex, which displays the shortest Ti−Ti distance (2.910 Å)[12] between trivalent titanium atoms.

The aim of this work was to prepare a dinuclear and diamagnetic Ti(III) complex, possibly with a very short intermetallic contact, and which might work as a model compound to study the nature of the Ti−Ti interaction. For this purpose, we selected the dicyclohexylformamidinate anions $[CyNC(H)NCy]^-$ as ligand system. Amidinate ligands are extremely sensitive to steric factors and form either monomers or dimers with extremely short intermetallic contacts, depending on the ligand's skeletal deformations produced by the steric interactions between the substituents.[13] Furthermore, these anions are notoriously able to form dimers with several metals and metalloids across the periodic table[14] and often promote formation of short M−M bonds or multiple bonds.[15] In addition to using Ti(III) salts as a starting materials, we have also used for this work a Ti(II) compound in an attempt to extend this investigation to a Ti(II) d^2 system. Herein we report our findings.

Experimental Part

All operations were performed under the inert atmosphere of a nitrogen-filled drybox (Vacuum Atmospheres) or by using standard Schlenk techniques. All solvents were freshly distilled from the appropriate drying agent. CyNHC(H)NCy was prepared according to the published procedure.[16] The lithiation was carried out according to

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[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

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published procedures with either MeLi in ether or *n*-BuLi.[13a] $TiCl_2(TMEDA)_2$,[17] $TiCl_3(THF)_3$,[18] and $Ti_2Cl_6(THF)_4$[19] were prepared according to published procedures. Infrared spectra were recorded on a Michelson BOMEM FTIR instrument from Nujol mulls prepared in a drybox. Elemental analyses were carried out with a Perkin Elmer 2000 CHN analyzer. The ratio between Ti and Cl atoms was determined by X-ray fluorescence on a Philips XRF 2400 instrument. Data for X-ray crystal structures were obtained with a Rigaku AFC6S diffractometer. Variable-temperature NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer. Cyclic voltammetry experiments were performed in a specially designed air-tightened cell equipped with the cross section of a 0.1 mm diameter Pt wire as both working and counter electrode. The cell was loaded inside a drybox and connected to a PAR-273 potentiostat−galvanostat driven by a computer and Headstart software. The reference electrode was a silver wire in contact with a 0.29 M solution of $(TBA)BF_4$ in THF and a 0.01 M solution of $AgNO_3$. The measured potentials were referred to the ferrocene/ferrocenium potential obtained under identical conditions. A standard scan rate of 200 mV s^{-1} was used for all the experiments.

Preparation of $(CyNC(H)NCy)_4Ti_2Cl_2{\cdot}2THF$. Method A. A solution of [CyNCHNCy]Li·hexane (3.5 g, 11.6 mmol) in THF (100 mL) was stirred at room temperature in the presence of $TiCl_3(THF)_3$ (2.1 g, 5.7 mmol). Upon mixing, the color of the solution suddenly changed to dark greenish-brown. After further stirring for 2 h at room temperature, the solution was filtered and concentrated *in vacuo* to small volume. The solution was diluted with toluene and allowed to stand at −30 °C for 2 days, upon which dark red crystals of $(CyNC(H)NCy)_4Ti_2Cl_2{\cdot}2THF$ separated (1.5 g, 1.3 mmol, 46%). IR (Nujol, KBr, cm^{-1}) ν: 1666(w), 1576(s), 1541(s), 1457(s), 1420(w), 1376(s), 1366(s), 1351(s), 1335(s), 1317(s), 1257(s), 1232(s), 1192(m), 1164(s), 1145(w), 1129(m), 1082(s), 1054(w), 1023(w), 989(w), 958(w), 917(w), 886(m), 842(m), 808(w), 786(w), 723(m), 677(m), 555(w), 539(w), 511(s), 452(w), 430(s). ^{1}H-NMR (C_6D_6, 500 MHz, 25 °C): δ 8.74 (s, 1H, C-$H_{formamidine}$), 6.45 (s, 1H, C-$H_{formamidine}$), 3.82 (tt, 2H, *ipso* $H_{cyclohexyl}$), 3.67 (tt, 2H, *ipso* $H_{cyclohexyl}$), 3.58 (m, 4H, THF), 2.6−0.7 (series of multiplets, 40H, cyclohexyl), 1.73 (m, 4H, THF). Anal. Calcd (Found) for $C_{60}H_{108}N_8Ti_2Cl_2O_2$: C, 63.20 (63.09); H, 9.55 (9.43); N, 9.83 (9.77).

Method B. A solution of [CyNCHNCy]Li·hexane (2.8 g, 9.3 mmol) in toluene (30 mL) was treated with $Ti_2Cl_6(THF)_4$ (1.4 g, 2.3 mmol) at room temperature. The mixture was stirred at room temperature, and a rapid color change to dark greenish-brown was observed. After further stirring for 2 h at room temperature, the suspension was filtered to eliminate some light-colored solid, and the residue was allowed to stand at −30 °C for 2 days. Red microcrystals of $(CyNC(H)NCy)_4Ti_2Cl_2$ were obtained in moderate yield (1.1 g, 1.1 mmol, 48%). ^{1}H-NMR (C_6D_6, 500 MHz, 25 °C): δ 8.74 (s, 1H, C-$H_{formamidine}$), 6.45 (s, 1H, C-$H_{formamidine}$), 3.81 (tt, 2H, *ipso* $H_{cyclohexyl}$), 3.63 (tt, 2H, *ipso* $H_{cyclohexyl}$), 2.6−0.7 (series of multiplets, 40H, cyclohexyl). Anal. Calcd (Found) for $C_{52}H_{92}N_8Ti_2Cl_2$: C, 62.70 (62.55); H, 9.31 (9.17); N, 11.25 (11.17).

Method C. A solution of [CyNCHNCy]Li·hexane (3.3 g, 11 mmol) in THF (100 mL) was cooled to −78 °C and subsequently treated with solid $TiCl_2(TMEDA)_2$ (1.9 g, 5.4 mmol). As the temperature was allowed to rise slowly to room temperature, the initially violet color of the solution changed to dark green. After further stirring for 2 h at room temperature, a small amount of white solid was removed by filtration from the resulting dark green suspension, and the filtrate was concentrated to small volume (∼15 mL) *in vacuo*. The solution was layered with hexane (20 mL) and allowed to stand undisturbed at room temperature for several days, upon which red crystals of $(CyNC(H)NCy)_4Ti_2Cl_2{\cdot}2THF$ separated in low yield (0.3 g, 0.3 mmol, 11%).

Molecular Orbital Calculations. All molecular orbital calculations were performed on a Silicon Graphics computer by using the software package SPARTAN 4.0 (Wavefunction, Inc., 18401 Von Karman Ave., #370, Irvine, CA 92715; 1995**)**. The program's default parameters were used in the unrestricted Hartree−Fock *ab initio* calculations on the model compound $[(MeNC(H)NMe)_2Ti(\mu\text{-}Cl)]_2$ by using the STO-3G basis. The fractional atomic coordinates of the crystal structure were converted to the corresponding Cartesian coordinates by using a special device of the NRCVAX program. The cyclohexyl ring carbon atoms were deleted from the list with the exception of the *ipso* carbons of each ring, which were transformed into the corresponding methyl groups by introducing three hydrogen atoms at their idealized positions. The resulting symmetry of the molecule was C_1, thus reflecting the triclinic crystallographic symmetry of complex **1**. Calculations were also performed by imposing higher symmetries, without significantly modifying the final results.

Table 1. Crystal Data and Structure Analysis Results

formula	$C_{60}H_{108}Ti_2N_8Cl_2O_2$
formula weight	1140.27
space group	*Pn*
a (Å)	10.4688(9)
b (Å)	14.4579(9)
c (Å)	121.421(1)
β (deg)	100.227(9)
V (Å^3)	3190.6(7)
Z	2
radiation (Å)	Mo Kα
T (°C)	−158
D_{calcd} (g cm^{-3})	1.187
μ_{calcd} (cm^{-1})	3.75
R, R_w[a]	0.074, 0.075

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

X-ray Crystallography. The preparation of the crystals was hampered by difficulties arising mainly from spontaneous loss of solvent, and, in addition, the crystals scattered poorly. Nevertheless, it was possible to obtain a data set of sufficient quality to solve the crystal structure. Data were collected at −158 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.0° for a suitable air-sensitive crystal mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were averaged. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods. The positions of the major part of the non-hydrogen atoms were refined anisotropically. Complete anisotropic refinement was not possible for the two interstitial molecules of THF and for some of the cyclohexyl carbon atoms, due to the unsufficient number of observations. Hydrogen atom positions were introduced at their idealized positions. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with $[I > 2.5\sigma(I)]$. Neutral atomic scattering factors were taken from Cromer and Waber.[20] Anomalous dispersion effects were included in F_{calcd}. All calculations were performed using a TEXSAN package on a Digital VAX station. Details on crystal data and structure solution are given in Table 1. Selected bond distances and bond angles are given in Table 2. Listings of atomic coordinates and thermal parameters are given as Supporting Information.

Results and Discussion

According to Scheme 1, the reaction of [CyNC(H)NCy]Li·hexane with either $TiCl_3(THF)_3$ in THF or the dinuclear $Ti_2Cl_6(THF)_4$ in toluene afforded the red dinuclear and diamagnetic $(CyNC(H)NCy)_4Ti_2Cl_2{\cdot}2THF$ (**1**) in moderate yield. Although the products obtained from both reactions were the same, in the second case we found no evidence of retention of THF in the lattice. While qualitative tests for the presence of chloride were positive, the correct ratio Ti/Cl was determined by X-ray fluorescence. Combustion analysis data were in good agreement with the proposed formulation.

The diamagnetism of the compound was indicated by solid state measurements and confirmed by solution NMR experi-

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Table 2. Selected Bond Distances (Å) and Angles (deg)

Ti1−Cl1 = 2.433(3)
Ti1−Cl2 = 2.457(3)
Ti1−N2 = 2.086(9)
Ti1−N3 = 2.141(8)
Ti1−N7 = 2.125(8)
Ti1−N8 = 2.122(8)
Ti2−Cl1 = 2.422(3)
Ti2−Cl2 = 2.444(3)
Ti2−N1 = 2.142(9)
Ti2−N4 = 2.118(8)
Ti2−N5 = 2.142(8)
Ti2−N6 = 2.126(9)
Ti1−Ti2 = 2.942(2)

Cl1−Ti1−Cl2 = 105.5(1)
Cl1−Ti1−N2 = 85.2(2)
Cl1−Ti1−N3 = 85.0(2)
Cl1−Ti1−N7 = 95.7(2)
Cl1−Ti1−N8 = 158.9(2)
Cl2−Ti1−N2 = 85.8(2)
Cl2−Ti1−N3 = 85.7(2)
Cl2−Ti1−N7 = 158.8(2)
Cl2−Ti1−N8 = 95.7(2)
N2−Ti1−N3 = 164.9(3)
N2−Ti1−N7 = 97.8(3)
N2−Ti1−N8 = 96.8(3)
N3−Ti1−N7 = 94.6(3)
N3−Ti1−N8 = 96.5(3)
N7−Ti1−N8 = 63.2(3)
N7−C21−N8 =115.9(9)
N1−C1−N2 = 125.7(9)
C1−N2−C8 = 114.5(8)
C1−N1−C2 = 115.3(8)
C21−N7−C22 = 119.6(9)
C21−N8−C28 = 119.0(8)

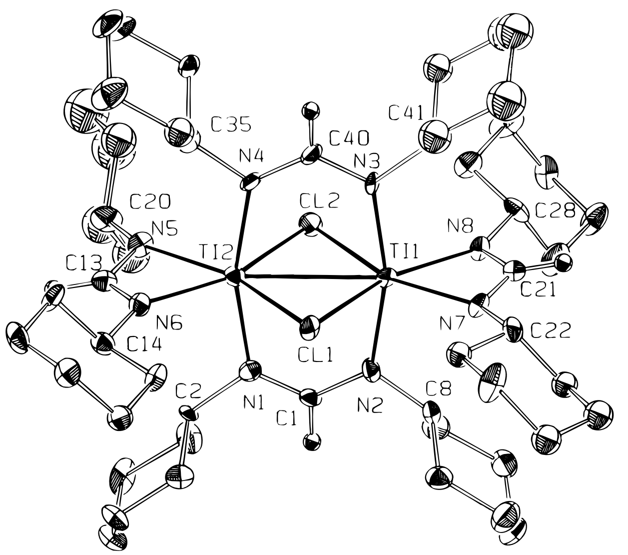
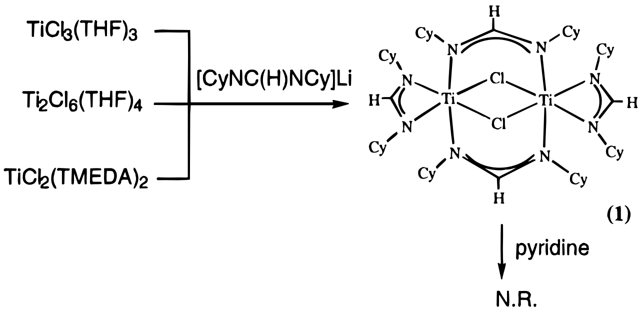


Figure 1. Thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 1



ments. The NMR spectra were sharp and well resolved and did not show any significant shift as a function of temperature, thus excluding the presence of a small underlying paramagnetism. The NMR spectrum showed two different sets of ligands in the ratio 1:1, arising from two different bonding modes of the formamidinate anion (bridging three-center chelating *versus* regular chelating). However, no fluxional behavior was observed in the range from +90 to −90 °C, thus suggesting a fairly rigid structure in solution. The presence of two molecules of THF, indicated by combustion analysis, was also confirmed by the NMR spectrum.

The dinuclear frame of **1** is remarkably robust and, unlike the multiply bonded systems of Cr and V with the same ligand,[13] was not cleaved by treatment with pyridine. In addition, the crystals of **1** were chemically inert and, apart from loss of THF, showed no sign of decomposition upon relatively long exposure to air. In reasonable agreement with these observations, the cyclic voltammogram of a solution of **1** in THF by using (TBA)-BF$_4$ as an electrolyte (see Supporting Information) and under inert atmosphere showed two reduction waves at −1.92 ($E_{pa} - E_{pc}$ = 84 mV) and −2.52 V. The peak separation indicated that the first reduction wave, arising from the formation of a Ti(III)/Ti(II) mixed-valence species, may be considered as quasi-reversible. The second reduction wave was irreversible as a probable result of the formation of a Ti(II) species that is unstable under these particular conditions. Similarly, two oxidation waves were observed at −0.65 ($E_{pa} - E_{pc}$ = 74 mV) and +0.80 V, respectively arising from the quasi-reversible formation of a mixed-valence Ti(III)/Ti(IV) species and the irreversible formation of a tetravalent complex.

The dinuclear structure, suggested by the diamagnetism in both solid state and solution, was confirmed by an X-ray crystal structure. The dinuclear frame is composed by two edge-sharing octahedral titanium atoms (Figure 1). Two bridging chlorides and two bridging formamidinates (adopting the well-known three-center chelating geometry) link together the two titanium atoms. Two other formamidinate anions, which adopt a regular chelating geometry, complete the octahedral coordination sphere around each Ti atom. Therefore, the coordination geometry of each titanium atom is defined by two bridging chloride [Cl1−Ti1−Cl2 = 105.5(1)°, Cl1−Ti2−Cl2 = 106.2(1)°] and two nitrogen atoms of one chelating formamidinate [N5−Ti2−N6 = 64.1(3)°, N7−Ti1−N8 = 63.2(3)°] which delimit the equatorial plane. Two nitrogen atoms of the two bridging formamidinates occupy the two axial positions. The central Ti$_2$-Cl$_2$ core is almost planar [torsion angle Ti1−Cl1−Ti2−Cl2 = 0.1(1)°] and is coplanar with the four nitrogen atoms of the terminal chelating formamidinate ligands. The distortion of the octahedral coordination geometry of each Ti atom is rather considerable and is probably due to the strong steric compression [N2−Ti1−N3 = 164.9(3)°, N1−Ti2−N4 = 163.4(3)×e7, Cl1−Ti1−N2 = 85.2(2)°, Cl1−Ti1−N3 = 85.0(2)°, N7−Ti1−N2 = 97.8(3)°, N7−Ti1−N3 = 94.6(3)°]. It is interesting to observe that the cyclohexyl rings of the two bridging formamidinate rings point the *ipso* hydrogens away with respect to the bridgehead H atom and inward with respect to the two titanium atoms. This is quite the opposite of the multiply bonded systems of the same ligand with both Cr[13b] and V,[13a] where the *ipso* hydrogen atoms of the cyclohexyl ring form short, nonbonding contacts with the bridgehead H atom. The Ti−Cl [Ti1−Cl1 = 2.433(3) Å, Ti1−Cl2 = 2.457(3) Å, T2−Cl1 = 2.422(3) Å, Ti2−Cl2 = 2.444(3) Å] and Ti−N [Ti1−N2 = 2.086(9) Å, Ti1−N3 = 2.141(8) Å, Ti1−N7 = 2.125(8) Å, Ti1−N8 = 2.122(8) Å] bond distances are as expected in spite of the distortion of the bonding angles.

Reaction of the Ti(II) derivative TiCl$_2$(TMEDA)$_2$ with [CyNC(H)NCy]Li·hexane also yielded the trivalent (CyNC(H)-NCy)$_4$Ti$_2$Cl$_2$·2THF, albeit in much lower yield. Given the ability of the Ti(II) starting salt to disproportionate toward higher oxidation states,[21,22] this result was not completely unexpected.

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The fact that the yield of **1** was considerably lower indicates that other products might be present in the reaction mixture, even though attempts to isolate other species were so far unsuccessful. This behavior is closely reminiscent of that of the amidinate Ti(III) complex $[(Me_3Si)NC(Ph)N(SiMe_3)]_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$,[22] which was also obtained *via* reaction of the amidinate anion with $TiCl_2(TMEDA)_2$. However, in sharp contrast with the dinuclear structure of **1**, the amidinate complex is monomeric. The large steric hindrance of the amidinate anion prevents this ligand from accommodating dinuclear structures, thus resulting in the formation of a mononuclear species. This striking difference of behavior between these two ligands follows the trend observed in the chemistry of Cr and V and is purely the result of the ligand skeletal deformation caused by the steric interaction between the ligand organic substituents.[13]

The short Ti−Ti distance [Ti1−Ti2 = 2.942(2) Å] and the diamagnetism of **1** might indicate the presence of a Ti−Ti single bond. Since M−M bonds between Ti(III) atoms are unprecedented, in an attempt to clarify the magnetic properties and the nature of the Ti−Ti interaction, we have performed *ab initio* HF/STO-3G calculations using $[(MeNC(H)NMe)_2Ti(\mu\text{-}Cl)]_2$ as a model, with the atomic coordinates of the non-hydrogen atoms obtained from the X-ray crystal structure. Given the diamagnetism, the singlet state was considered to be the most reasonable basis for the calculation. The program correctly predicted that the singlet state is more stable than the triplet by yielding a lower value of the total energy. The result showed a HOMO−LUMO gap (0.282 eV) which, although rather small, still accounts for the observed diamagnetism. The next MO was 0.21 eV lower in energy. To our surprise, the results of the calculation showed that the HOMO originates from the direct overlap of two lobes of the two $d_{x^2-y^2}$ orbitals, thus providing a significant accumulation of electronic density on the intermetallic vector (Supporting Information). In addition, the formation of this molecular orbital also involved the participation of two p_y orbitals of the two bridging chlorides which connect the other two lobes of the two $d_{x^2-y^2}$ orbitals, thus forming two small yet significant lobes on the two sides of the Ti−Ti vector. The contour density map (see Supporting Information) clearly indicates that the major contribution to the bonding is realized *via* the direct overlap of the two $d_{x^2-y^2}$ orbitals (Figure 2). Accordingly, a remarkably high bond order was obtained for the Ti−Ti single bond (Ti−Ti bond order = 0.96).

A word of caution should probably be issued while considering the implications of these theoretical calculations. In the case of **1**, the unique shape of the HOMO clearly suggests that the overall bonding interaction responsible for the diamagnetism is, in fact, a combination of direct Ti−Ti bond and ligand-mediated superexchange. However, M−M bonds between first row early transition metals are well known for their elusiveness and for being dominated by ligand features. The paradoxical weakness of the supershort Cr−Cr quadruple bond is a particularly striking example in this respect.[23] Therefore, given that the calculation is a single-configuration interaction, we are hesitant to draw definite conclusions from our calculations about the existence of Ti−Ti bonds. In addition, it should not be forgotten that the formamidinate ligand employed for this work always forms dimeric complexes with short intermetallic distances[13−15] and promotes efficient magnetic couplings between metal atoms. It is, therefore, well possible that both the short intermetallic distance and the diamagnetism result from the particular nature of the bridging ligand. On the other hand, we observe that the dinuclear frame of **1** is, indeed, unusually robust and that the complex is chemically inert, thus giving some credibility to the result of our calculations.

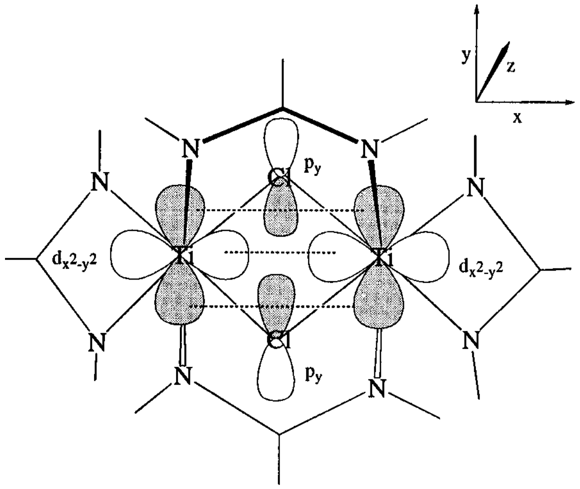

Figure 2. Pictorial view of the HOMO.

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Supporting Information Available: Listing of atomic coordinates, thermal parameters, and bond distances and angles for **1**, an isocontour map, and a cyclic voltammogram (28 pages). Ordering information is given on any current masthead page.

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