Dinuclear Titanium(III) Complexes. Exchange Coupling in $(Cp_2Ti)_2(\mu\text{-}O)$

Wayne W. Lukens, Jr., and Richard A. Andersen*

Chemistry Department and Chemical Sciences Division of Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Received July 29, 1994[⊗]

Addition of 0.5 equiv of water in tetrahydrofuran to Cp_3Ti in tetrahydrofuran yields the known bridging oxo derivative of Ti(III), $(Cp_2Ti)_2(\mu\text{-}O)$, in high yield. Use of labeled water gives $(Cp_2Ti)_2(\mu\text{-}^{18}O)$. The EPR spectrum of a toluene glass at 2 K gives a spectrum due to a triplet ground state with $g_{\parallel} = 1.979$, $g_{\perp} = 1.981$, and $|D| = 0.0249$ cm^{-1}. The variable-temperature magnetic susceptibility above 20 K shows intramolecular ferromagnetic coupling and weak intermolecular ferromagnetic coupling; the intramolecular coupling constant is 8.3 cm^{-1}. Below 20 K, the susceptibility is field dependent. An orbital diagram is presented which accounts for the magnetic behavior in this d^1d^1 dinuclear metallocene.

Introduction

Wieghardt recently published a paper on dititanium(III)–μ-oxo compounds with nearly linear oxo bridges, $(Me_3tacn)_2Ti_2(X)_4(\mu\text{-}O)$ where X is Cl, NCS, or NCO and Me_3tacn is *N,N,N*-trimethyl-1,4,7-triazacyclononane.[1,2] These d^1d^1 dinuclear complexes are weakly antiferromagnetically coupled with a coupling constant of *ca.* −7 cm^{-1}. A model has been advanced to explain the small coupling in these compounds; *viz.*, the single d electron on each octahedral titanium(III) center occupies a d_{xy} orbital (taking the Ti–Ti direction as *z*) and these orbitals are orthogonal to the 2p orbitals of the bridging oxygen atom so that no antiferromagnetic coupling can occur through superexchange *via* the oxygen atom. In order to account for the observed magnetic behavior, they postulate that the antiferromagnetic coupling results from overlap of the two d_{xy} orbitals through space and that this interaction is greater than the ferromagnetic potential exchange between the electrons. Wieghardt notes that $(Cp_2Ti)_2(\mu\text{-}O)$ also contains two d^1-metal centers connected by a nearly linear oxo bridge but that no magnetic studies have been described.

As part of a recent study of cyclopentadienylmetal oxo compounds,[3] we have developed a new, high-yield synthesis of $(Cp_2Ti)_2O$. The new synthesis gives $(Cp_2Ti)_2O$ in high purity, which is an essential prerequisite for examining magnetic behavior. The original synthesis of $(Cp_2Ti)_2O$ was the reaction between titanocene and nitrous oxide.[4,5] The khaki-green material was said to be explosively pyrophoric. The identity of the compound was inferred from the molecular ion in the mass spectrum and a *g* value of 1.975 in the EPR spectrum of a toluene solution at room temperature. The crystal structure of $(Cp_2Ti)_2O$ was recently determined on a crystal that was obtained by air oxidation of Cp_2Ti(tmed).[6] The idealized geometry of $(Cp_2Ti)_2O$ shows that the cyclopentadienyl rings on the bent sandwich fragment are rotated 90° relative to the other bent sandwich fragment, giving the molecule idealized D_{2d} symmetry. The Ti–O distance is 1.838(1) Å and the Ti–O–Ti angle is 170.9(4)°, values similar to those in Wieghardt's compounds. In this paper, we show that the magnetic behavior of $(Cp_2Ti)_2O$ is similar to that shown by Wieghardt's compounds.

Results

$(Cp_2Ti)_2O$ was prepared by the reaction of Cp_3Ti with 0.5 equiv of water in tetrahydrofuran at −78 °C. Crystallization from toluene gives green plates which are brown when powdered. The powdered compound is very air sensitive but not pyrophoric. To show that the bridging oxygen was derived from the added water, the ^{18}O-labeled compound was prepared from ^{18}O-enriched water. Mass spectroscopy confirms the incorporation of the labeled oxygen. The isotopically labeled compound also has a new absorption in the infrared spectrum at 725 cm^{-1} assignable to the Ti–^{18}O stretching frequency. For the unlabeled compound, the Ti–O absorption is found at 780 cm^{-1}, but it is partially obscured by the C–H out-of-plane wagging absorptions of the C_5H_5 ligands.[7] In order to verify that this compound was the same as that which Honold *et al.* characterized by crystallography, the unit cell of a single crystal was determined and found to be identical to the published unit cell, the details of which are given in the Experimental Section.[6]

EPR spectroscopy shows that $(Cp_2Ti)_2O$ has a triplet ground state. For the powder, the room-temperature EPR spectrum of $(Cp_2Ti)_2O$ is isotropic with a *g* value of 1.977; at 2 K, the spectrum is also isotropic with a *g* value of 1.979, and a half-field signal is observed at $g = 3.974$. As a toluene glass at 2 K, $(Cp_2Ti)_2O$ gives the triplet spectrum shown in Figure 1, which yields the parameters $g_{\parallel} = 1.979$, $g_{\perp} = 1.981$, and $|D| = 0.0249$ cm^{-1}. The additional signal seen at $g = 1.975$ in Figure 1 is thought to be due to oxidized $(Cp_2Ti)_2O$ since its intensity varies between EPR samples prepared from the same batch of $(Cp_2Ti)_2O$.

The variable-temperature magnetic susceptibility was measured from 5 to 300 K at 0.5 and 4 T and is shown in Figure 2. Below 20 K, the susceptibility is field dependent. We believed the field dependence results from saturation magnetization due to intermolecular ferromagnetic coupling, so we examined the

---

* Address correspondence to this author at Chemistry Department, University of California, Berkeley, CA 94720.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

(1) Bodner, A.; Jeske, P.; Weyhermuller, T.; Wieghardt, K.; Dubler, E.; Schmalle, H.; Nuber, B. *Inorg. Chem.* **1992**, *31*, 3737–3748.

(2) Jeske, P.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1994**, *33*, 47–53.

(3) Smith, M. R., III; Matsunaga, P. T.; Andersen, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7049–7050.

(4) Bottomley, F.; Brintzinger, H. H. *J. Chem. Soc., Chem. Commun.* **1978**, 234–235.

(5) Bottomley, F.; Lin, I. J. B.; Mukaida, M. *J. Am. Chem. Soc.* **1980**, *102*, 5238–5242.

(6) Honold, B.; Thewalt, U.; Herberhold, M.; Alt, H. G.; Kool, L. B.; Rausch, M. D. *J. Organomet. Chem.* **1986**, *314*, 105–111.

(7) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 7281–7285.

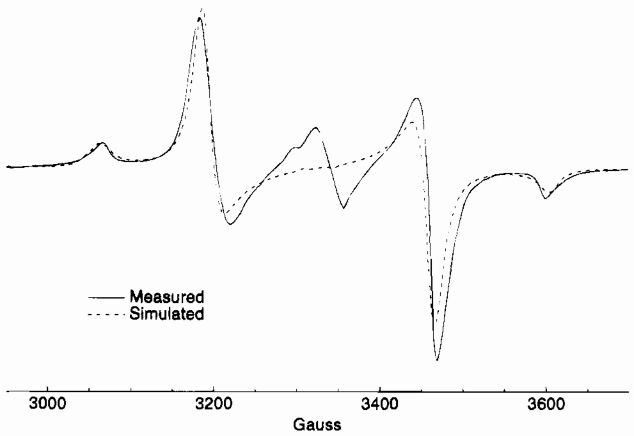

Figure 1. Observed and calculated EPR spectra of $(Cp_2Ti)_2(\mu\text{-}O)$. The calculation parameters are $g_{\parallel} = 1.979$, $g_{\perp} = 1.981$, and $|D| = 0.0249$ cm^{-1}.

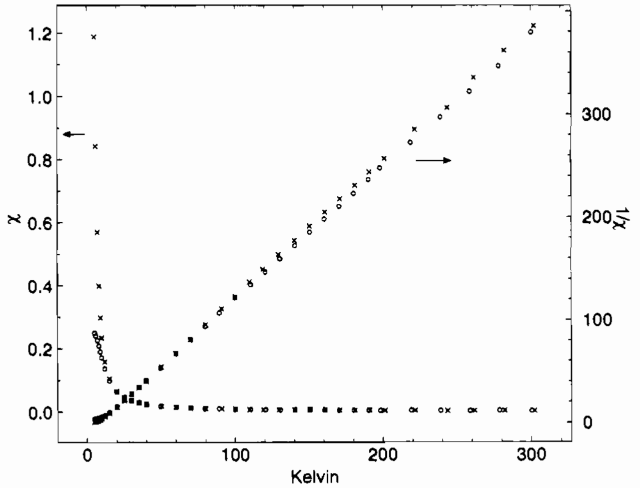

Figure 2. Variable-temperature magnetic susceptibility of $(Cp_2Ti)_2(\mu\text{-}O)$. The circles correspond to the 4 T data; the crosses, to the 0.5 T data.

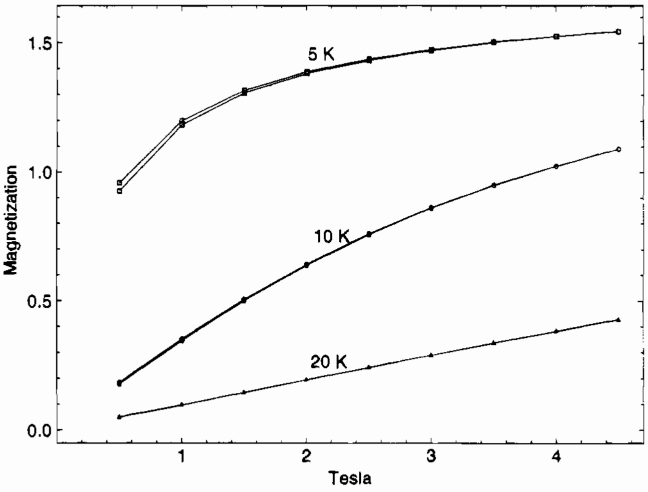

Figure 3. Variable-field magnetism of $(Cp_2Ti)_2(\mu\text{-}O)$. The squares, circles, and triangles correspond to 5, 10, and 20 K, respectively.

magnetization at 5, 10, and 20 K as a function of applied field as shown in Figure 3. At 20 K, the magnetization increases almost linearly with applied field, as expected for a paramagnetic system in which intermolecular interactions are weak. However, at lower temperatures, the magnetization no longer increases linearly with applied field, indicating that intermolecular ferromagnetic interactions are lowering the internal field of the sample and, therefore, the observed magnetization.[8]

Above 20 K, the susceptibility is independent of the applied field, and a least-squares fit of the data using the Curie–Weiss equation gives $\mu_{\text{eff}} = 2.47\ \mu_B$ and $\Theta = 8.3$ K per dinuclear molecule; the positive sign of Θ is consistent with an intermolecular ferromagnetic interaction.[8,9] Because of the field dependence of the susceptibility below 20 K, only the 0.5 T data from 10 to 300 K were used for fitting. The Bleaney–Bowers equation (1), where χ is per dinuclear molecule,[8] gives

$$\chi = \frac{2Ng^2\mu_B{}^2}{kT(3 + \exp(-2J/kT))} + N\alpha \qquad (1)$$

only a mediocre least-squares fit (χ^2(of fit) $= 6.6 \times 10^6$) where $g = 1.979$ (fixed, from the EPR spectrum), $J = 22$ cm^{-1}, $N\alpha = 357 \times 10^{-6}$ cm^3/mol, and the other symbols have their usual meaning.[8,10] The intramolecular ferromagnetic interaction was treated using the Weiss molecular field approximation (2),[9,11]

$$\chi = \frac{\chi'}{1 - (2zJ'/Ng^2\mu_B{}^2)\chi'} \qquad (2)$$

where z is the number of neighbors, J' is the intermolecular coupling constant for the z nearest neighbors, and χ' is the χ in the Bleaney–Bowers equation, (1). A much better fit is obtained (χ^2(of fit) $= 1.3 \times 10^4$) with the parameters $g = 1.979$ (fixed, from the EPR spectrum), $J = 11$ cm^{-1}, $zJ' = 3.2$ cm^{-1}, and $N\alpha = -28 \times 10^{-6}$ cm^3/mol.[12] From the value of zJ', the Weiss constant can be calculated to be 6 K from eq 3 where S

$$\Theta = \frac{2J'zS(S+1)}{3k} \qquad (3)$$

$= 1$ for each dinuclear molecule. Since the Weiss molecular field approximation is only valid above this temperature, we did not try to fit the data below 10 K to this model. The variable-temperature susceptibility and the least-squares fits are shown in Figure 4, and μ_{eff} and the least-squares fits versus temperature are shown in Figure 5.

As far as we know, this is the only bimetallic titanocene compound in which the titanium centers are coupled ferromagnetically. Stucky et al. have studied a large number of titanocene dimers and have found antiferromagnetic coupling in all cases which they explain mainly through superexchange *via* the bridging ligand.[13-18] In the case of $(Cp_2Ti)_2O$, as in Wieghardt's oxo-bridged dimer, no superexchange pathway

---

(8) Carlin, R. L.; Duyneveldt, A. J. v. *Magnetic Properties of Transition Metal Compounds*; Springer-Verlag: New York, 1977.

(9) Smart, J. S. *Effective Field Theories of Magnetism*; W. B. Saunders and Co.: Philadelphia, PA, 1966.

(10) The effect of the zero-field splitting was not included since a zero-field splitting of 0.025 cm^{-1} will not affect the susceptibility until the temperature is in the range of $D/k = 0.036$ K.

(11) O'Connor, C. J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley and Sons: New York, 1982; Vol. 29; pp 203–285.

(12) As noted by a reviewer, the error in J obtained from the susceptibility is somewhat large since the data are not fit below 10 K and because intermolecular exchange is present. However, the ground state is clearly $S = 1$ even in the absence of intermolecular effects as evidenced by the strong triplet EPR spectrum observed at 2 K.

(13) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 1841–1848.

(14) Sekutowski, D.; Jungst, R.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 1848–1855.

(15) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2078–2084.

(16) Kramer, L. S.; Clauss, A. W.; Francesconi, L. C.; Corbin, D. R.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2070–2077.

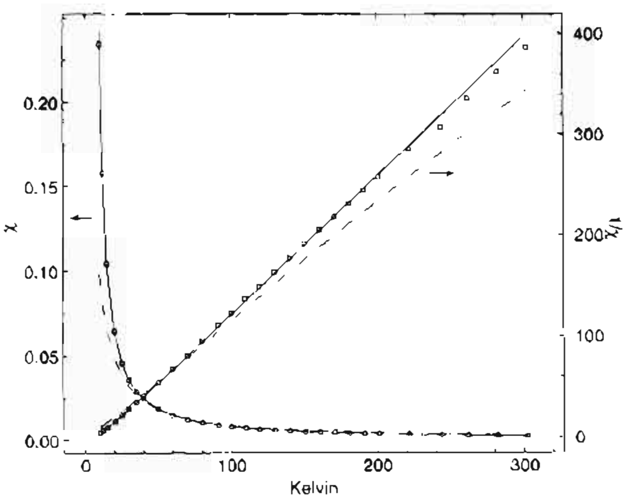

Figure 4. Variable-temperature magnetic susceptibility of $(Cp_2Ti)_2(\mu\text{-}O)$. The broken line shows the least-squares fit using the Bleaney–Bowers equation. The solid line shows the least-squares fit using the Weiss molecular field approximation with the Bleaney–Bowers equation.

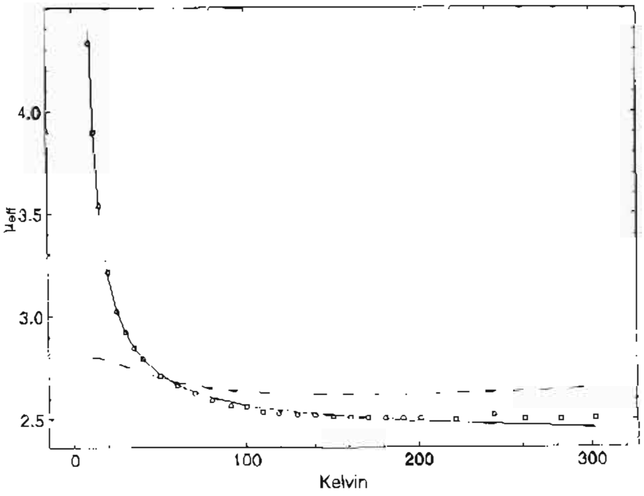

Figure 5. μ_{eff} versus temperature for $(Cp_2Ti)_2(\mu\text{-}O)$. The broken line shows the least-squares fit using the Bleaney-Bowers equation. The solid line shows the least-squares fit using the Weiss molecular field approximation with the Bleaney–Bowers equation.

exists. As shown in Figure 6, the $2p_x$ and $2p_y$ orbitals on the oxo bridge are orthogonal to the $1a_1$ orbital of the titanocene fragment. Since $1a_1$ has little or no electron density along the z axis,[19,20] it cannot interact effectively with either the 2s or $2p_z$ orbitals of the oxo bridge. Additionally, the two $1a_1$ orbitals cannot interact through space; in $(Cp_2Ti)_2O$ the $1a_1$ orbitals are rotated 90° relative to each other and should have little overlap. Since no mechanism exists for coupling the electrons of the titanium centers in $(Cp_2Ti)_2O$, the coupling is ferromagnetic due to potential exchange.[21-23] In Wieghardt's bridging oxo dimer, the lack of a superexchange pathway did not result in antiferromagnetic coupling presumably due to overlap of the two d_{xy} orbitals through space; nonetheless, the magnitude of the coupling was small.[1,2]

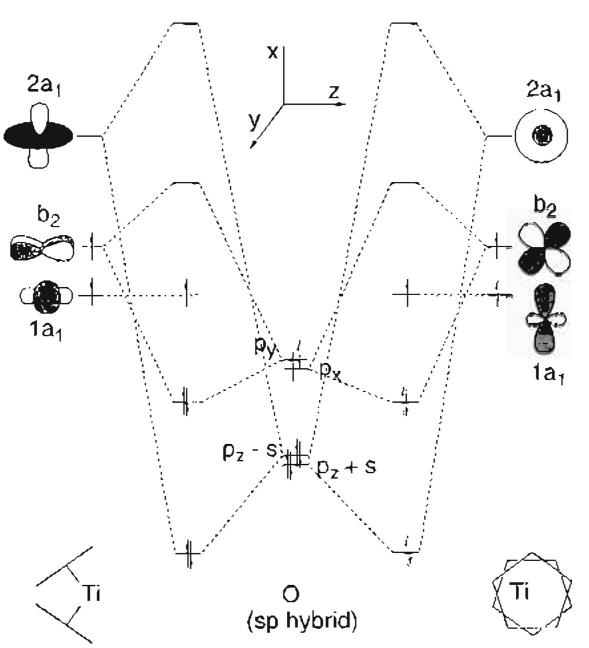

Figure 6. A qualitative molecular orbital diagram for $(Cp_2Ti)_2(\mu\text{-}O)$.

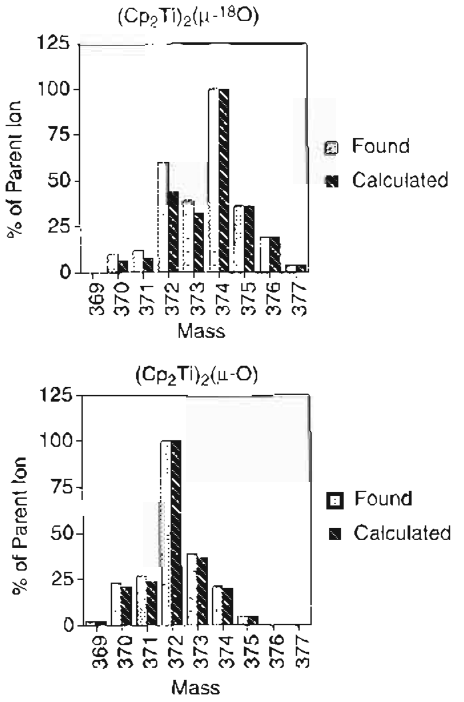

Figure 7. Observed and calculated mass spectra for $(Cp_2Ti)_2(\mu\text{-}^{18}O)$ and $(Cp_2Ti)_2(\mu\text{-}O)$.

Experimental Section

All reactions and manipulations were carried out in an inert atmosphere using standard Schlenk and drybox techniques. Hexane, diethyl ether, and tetrahydrofuran were dried over sodium benzophenone ketyl and distilled and degassed immediately prior to use. Toluene, methylcyclohexane, and deuterated NMR solvents were dried over and distilled from potassium or sodium. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer as Nujol mulls between CsI plates. Melting points were measured on a Buchi melting point apparatus in sealed capillaries and are uncorrected. EPR spectra were obtained on a Varian E-12 spectrometer. The microwave frequency was measured

---

(17) Francesconi, L. C.; Corbin, D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2059–2069.

(18) Francesconi, L. C.; Corbin, D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2078–2083.

(19) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6416–6422.

(20) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

(21) Anderson, P. W. In *Magnetism*; Rado, G. T., Suhl, H., Eds.; Academic Press Inc.: New York, 1963; Vol. I, pp 25–81.

(22) Bencini, A.; Gatteschi, D. *EPR of Exchange Coupled Systems*; Springer-Verlag: New York, 1990.

(23) Hotzelmann, R.; Wieghardt, K.; Florke, U.; Haupt, H.; Weatherburn, D. C.; Bonovoisin, J.; Blondin, G.; Girerd, J. *J. Am. Chem. Soc.* **1992**, *114*, 1681–1696.

using an EIP-548 microwave frequency counter, and the magnetic field was measured using a Varian E-500 NMR gaussmeter. Spectra were digitized using UNPLOTIT. Susceptibility measurements carried out on an SHE Model 800 SQUID susceptometer. Least-squares fits of the magnetic susceptibility were performed using the program Horizon II, and EPR simulations were done using the program ABVG.[24] Electron impact mass spectra were determined by the mass spectroscopy laboratory and microanalyses were performed by the microanalytical laboratories, both at the University of California, Berkeley.

$(Cp_2Ti)_2(\mu\text{-}O)$. Cp_3Ti[25-27] (0.50 g, 2.1 mmol) was dissolved in 50 mL of THF, and the solution was cooled to −78 °C. A solution of water (0.018 g, 1.0 mmol) dissolved in 40 mL of tetrahydrofuran was added slowly using a cannula. The deep green solution became red. The mixture was allowed to warm to room temperature and stirred for 10 h. The tetrahydrofuran was removed under reduced pressure, and the solid residue was dissolved in 60 mL of toluene. The mixture was filtered, and the volume of the filtrate was reduced to *ca.* 15 mL. Cooling to −20 °C produced shiny green plates (0.25 g, 75%). Mp: 230−234 °C. IR: 1125 (m), 1010 (s), 890 (m), 845 (m), 780 (s), 610 (m), 410 (s), 240 cm^{-1} (m). MS (calcd, found): *m/z* 369 (2, 2), 370 (21, 23), 371 (24, 27), 372 (100, 100), 373 (37, 39), 374 (20, 21), 375 (5, 5). Anal. Calcd for $C_{20}H_{20}OTi_2$: C, 64.5; H, 5.42. Found: C, 64.9; H, 5.81.

$Cp_4Ti_2{}^{18}O$. The isotopomer was prepared as described above except that 80% $^{18}OH_2$ was used. IR: 1125 (m), 1010 (s), 890 (m), 790 (s), 775 (s), 760 (s), 725 (s), 610 (m), 405 (s), 240 cm^{-1} (w). MS (calcd, found): *m/z* 370 (6, 10), 371 (8, 12), 372 (44, 60), 373 (32, 39), 374 (100, 100), 375 (36, 36), 376 (19, 19), 377 (4, 4). The mass spectra for the labeled and unlabeled compounds are represented as histograms in Figure 7.

Unit Cell Determination of Cp_4Ti_2O. A crystal measuring 0.1 × 0.2 × 0.4 mm was sealed in a 0.2 mm quartz capillary tube in an argon-filled drybox, and mounted on an automated Picker FACS-1 diffractometer. An automated search followed by indexing yielded the following unit cell: $a = 7.95(4)$ Å, $b = 10.96(4)$ Å, $c = 19.8(1)$ Å, $\alpha = 89.3(4)^\circ$, $\beta = 89.5(5)^\circ$, $\gamma = 88.3(3)^\circ$. These values are in agreement with the reported values in the orthorhombic space group *Pbcn*: $a = 7.946(1)$ Å, $b = 11.102(2)$ Å, $c = 19.780(3)$ Å.

Acknowledgment. This work was partially supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098. W.W.L. thanks the National Science Foundation for a graduate fellowship.

IC940902Z

---

(24) Daul, C.; Schlapfer, C. W.; Mohos, B.; Ammeter, J.; Gamp, E. *Comput. Phys. Commun.* **1981**, *21*, 385−395.

(25) Canty, A. J.; Coutts, R. S. P.; Wailes, P. C. *Aust. J. Chem.* **1968**, *21*, 807−810.

(26) Siegert, F. W.; Meijer, H. J. D. L. *J. Organomet. Chem.* **1969**, *20*, 141−145.

(27) Fischer, E. O.; Lochner, A. *Z. Naturforsch.* **1960**, *15B*, 266−267.