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W.W. Lukens, Jr. and R.A. Andersen

August 1994

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# Dinuclear Titanium(III) Complexes; Exchange Coupling in $(Cp_2Ti_2)(\mu\text{-}O)$

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

Department of Chemistry
University of California, Berkeley

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

August 1994

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

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**Abstract.** Addition of one-half of an equivalent 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 $d^1\ d^1$ dinuclear metallocene.

**Introduction.** Wieghardt has 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 $d^1$ $d^1$ 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 $d_{xy}$ orbital through space, and that this interaction is greater than the ferromagnetic potential exchange between the electrons. Wieghardt notes that $(Cp_2Ti)_2\text{-}(\mu\text{-}O)$ 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 cyclopentadienylmetaloxo 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 by 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 by 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 one-half of an equivalent 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. In the unlabelled compound, the Ti-O absorption is found at 780 $cm^{-1}$, but it is partially obscured by the C-H out of plane wagging absorption's 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 in the experimental section.[6]

Insert Figure 1 here

EPR spectroscopy shows that $(Cp_2Ti)_2O$ has a triplet ground state. As a powder, the room temperature EPR spectrum of $(Cp_2Ti)_2O$ is isotropic with a g value of 1.977; at 2K, 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 a triplet spectrum shown in Figure 1 which yields the parameters $g_{||}$ = 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 $(Cp_2Ti)_2O$.

Insert Figure 2 and 3 here

The variable temperature magnetic susceptibility was measured from 5 to 300 K at 0.5 and 4 T. Below 20 K, the susceptibility is field dependent possibly due to an intermolecular ferromagnetic interaction. 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 $\mu_{eff}$ = 2.47, and $\theta$ = 8.3 K per dinuclear molecule.[8] The least-squares fit of the susceptibility per dinuclear molecule to the Bleaney-Bowers equation (1)[8]

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

gives only a mediocre least squares fit ($\chi^2$(of fit)=3.9 x $10^6$) with g = 1.979 (fixed, from the EPR spectrum), J = 32 $cm^{-1}$, $N\alpha$ = 6.2 x $10^{-6}$ $cm^3$/mol, and the other

symbols have their usual meaning. Correcting for the observed zero field splitting of 0.0249 $cm^{-1}$ makes almost no difference in the fit regardless of the sign chosen for D.[8] This is not too suprising since the zero field splitting is very small. The intramolecular ferromagnetic interaction may be treated using the Weiss Molecular Field approximation (2):[9,10]

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

where z is number of neighbors, J' is the intermolecular coupling constant between the z nearest neighbors, and $\chi'$ is from the Bleaney-Bowers equation. A much better fit is obtained ($\chi^2$(of fit) = 1.4 x $10^4$) with the parameters g = 1.979(fixed, from the EPR spectrum), J = 8.3 $cm^{-1}$, zJ' = 0.61 $cm^{-1}$, and $N\alpha$ = 72 x $10^{-6}$ $cm^3$/mol. The variable temperature susceptibility and the least squares fits are shown in Figure 2, and $\mu_{eff}$ and the least squares fits versus temperature are shown in Figure 3.

Insert Figure 4 here

As far as we know, this is the only bimetallic titanocene compound in which the titanium centers are coupled ferromagnetically. Stucky has studied a large number of titanocene dimers and has found antiferromagnetic coupling in all cases which they explain mainly through superexchange *via* the bridging ligand.[11-16] In the case of $(Cp_2Ti)_2O$, as in Wieghardt's oxo bridged dimer, no superexchage pathway exists. As shown in Figure 4, 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[17,18], 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 by 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.[19-21] 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]

**Experimental.**

All reactions and manipulations were carried out in an inert atmosphere using standard Schlenk and dry box 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 measure 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.[22] 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.

**$(Cp_2Ti)_2(\mu\text{-}O)$.** $Cp_3Ti$[23-25](0.50 g, 2.1 mmol) was dissolved in 50 mL of THF and 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 hr. The tetrahydrofuran was removed under reduced pressure and the solid residue was dissolved in 60 mL of toluene, 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(m). MS(calc,found): 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(w). MS(calc, found): 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 unlabelled compounds are represented as histograms in Figure 5.

Inset Figure 5 here

**Unit Cell Determination of $Cp_4Ti_2O$.** A crystal measuring 0.1 x 0.2 x 0.4 mm was sealed in a 0.2 mm quartz capillary tube in an argon filled dry box 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 $\alpha$ = 89.3(4) °
b = 10.96(4) Å $\beta$ = 89.5(5) °
c = 19.8(1) Å $\gamma$ = 88.3(3) °

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.

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Captions for Figures in "Dinuclear Titanium(III) Complexes; Exchange Coupling in $(Cp_2Ti)_2(\mu\text{-}O)$":

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 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 3: $\mu_{eff}$ 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.

Figure 4: A qualitative molecular orbital diagram for $(Cp_2Ti)_2(\mu\text{-}O)$.

Figure 5: Observed and calculated mass spectra for $(Cp_2Ti)_2(\mu\text{-}^{18}O)$ and $(Cp_2Ti)_2(\mu\text{-}O)$.

Figure 1

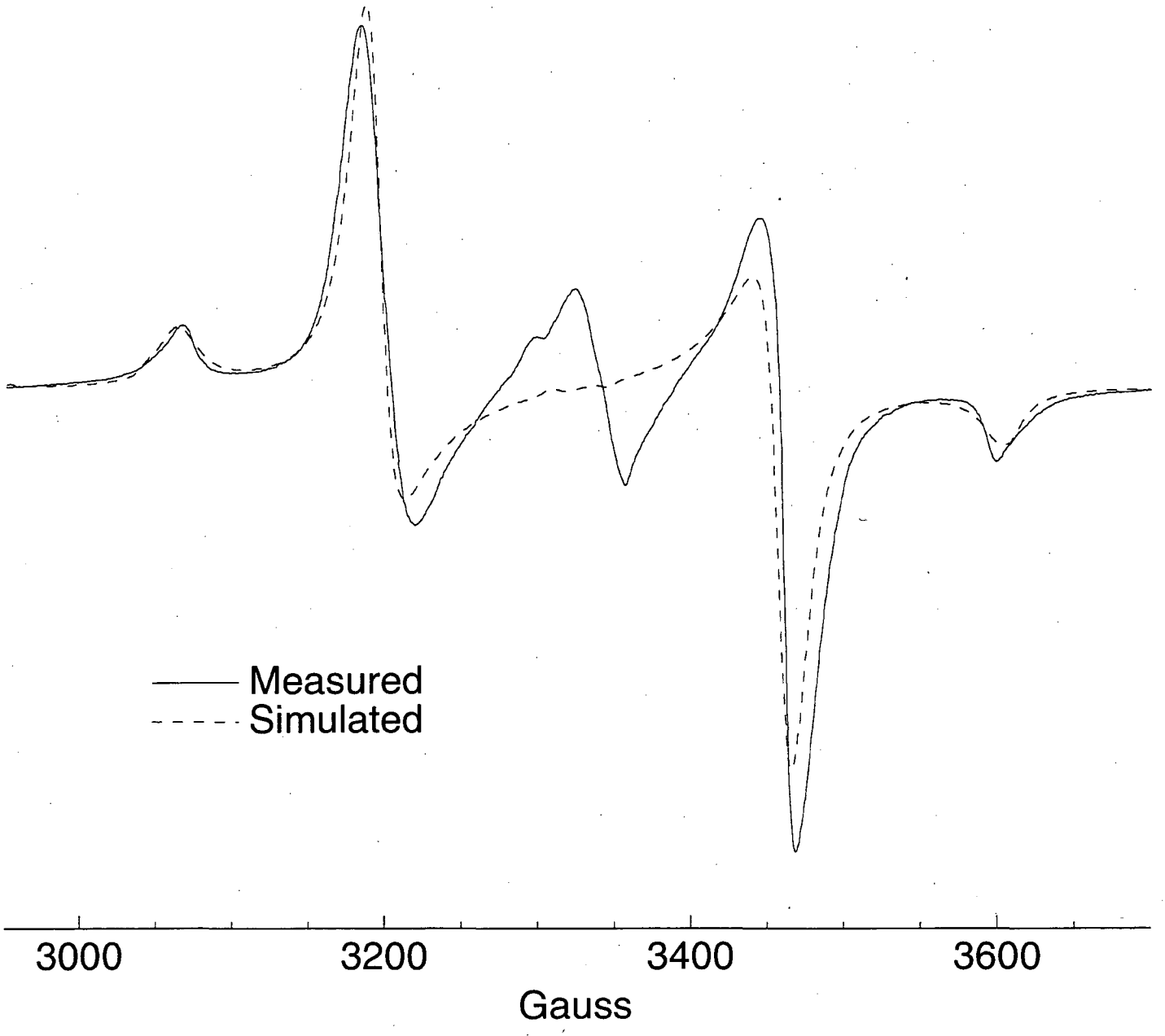


Figure 2

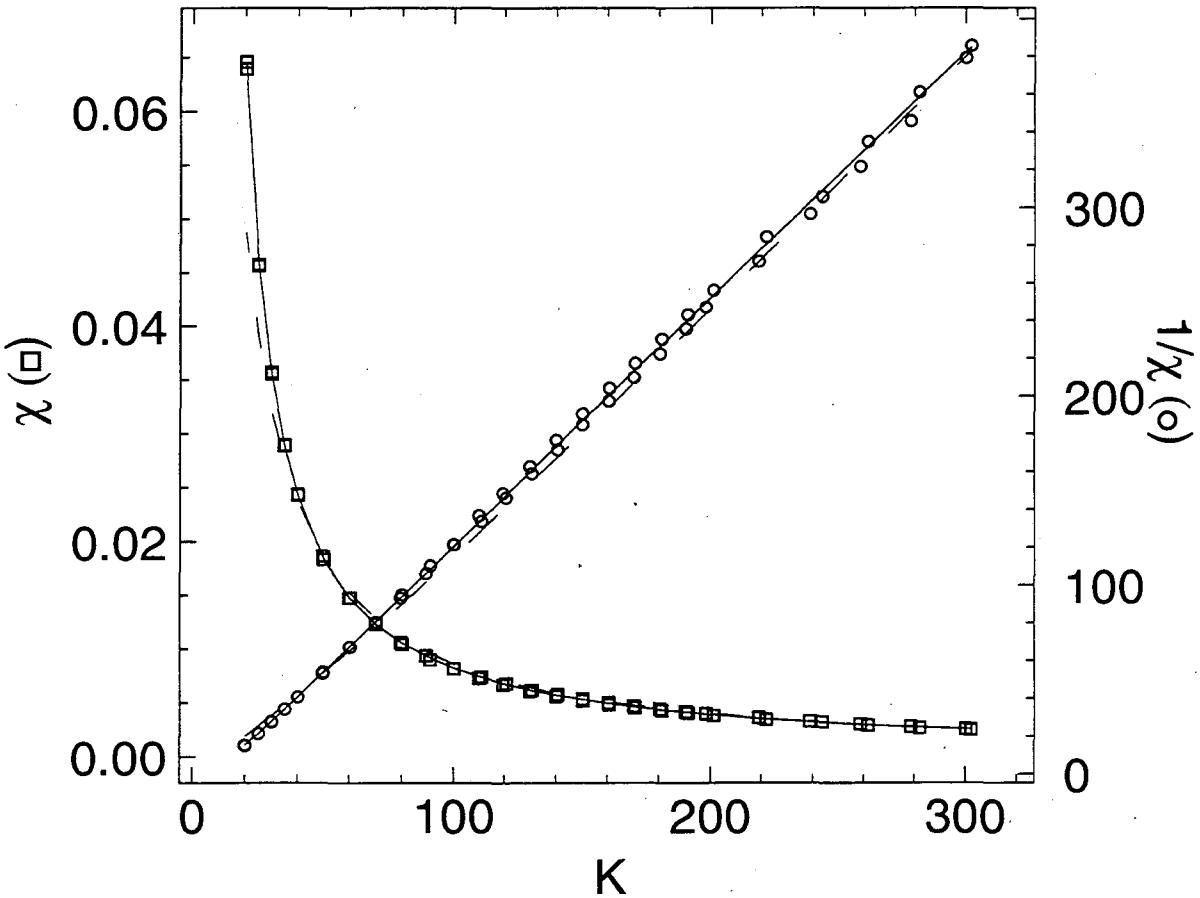


Figure 3

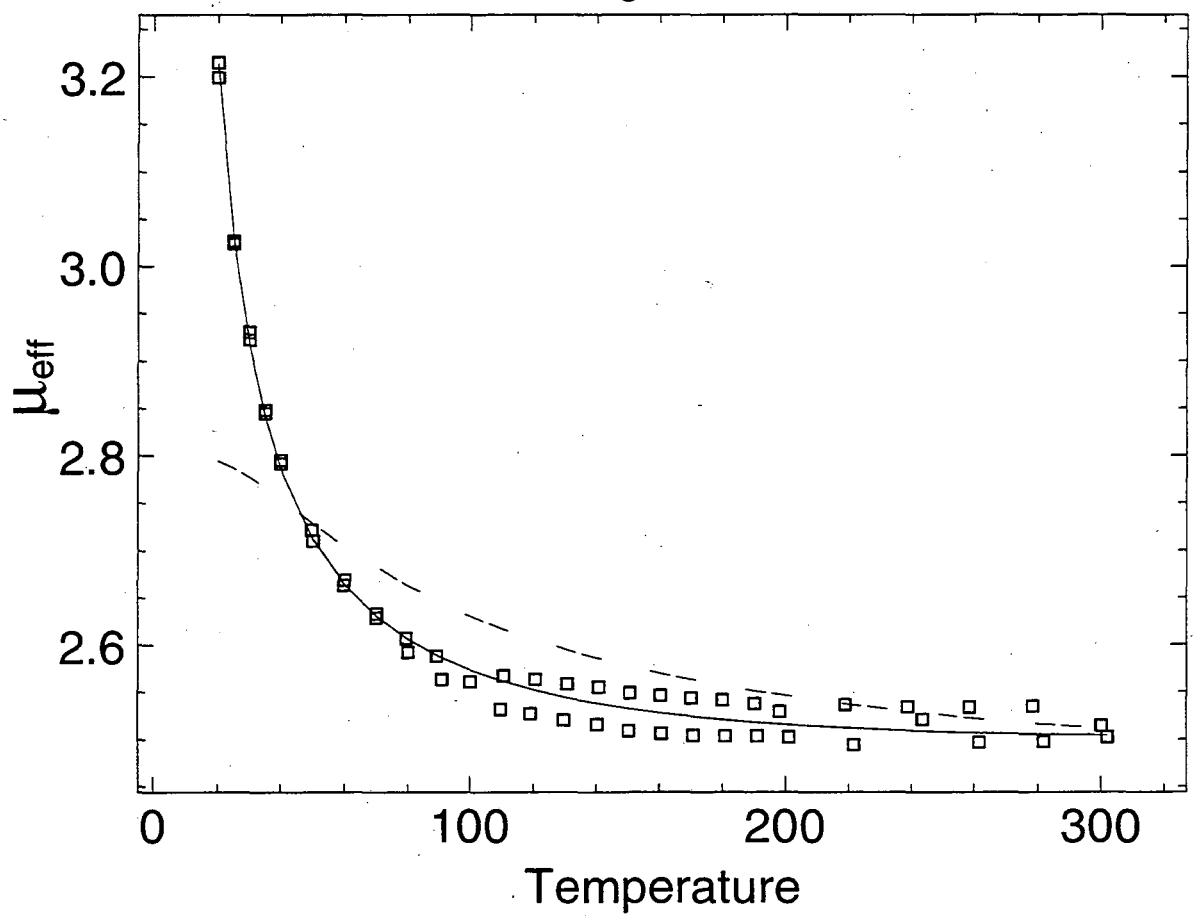
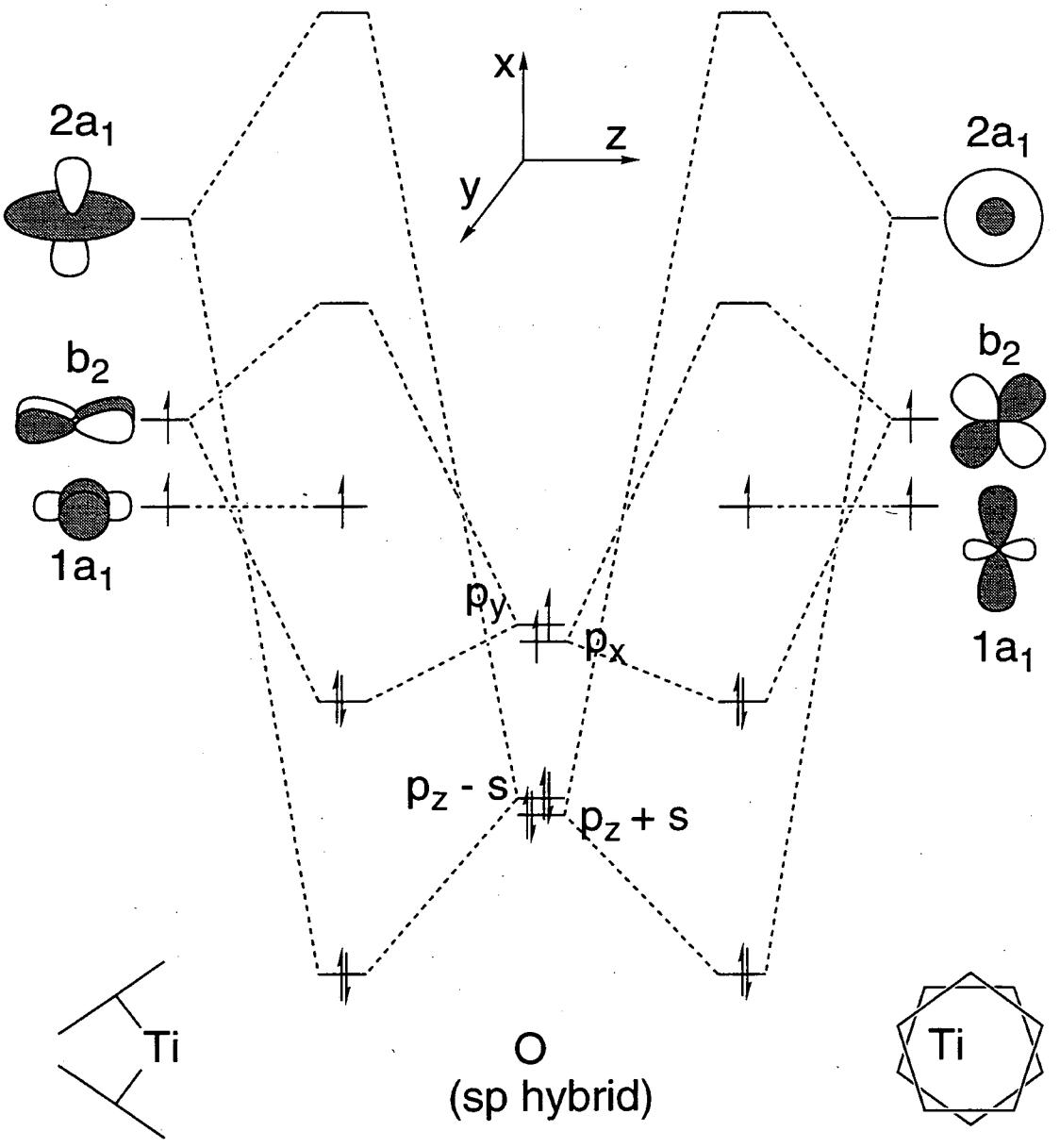
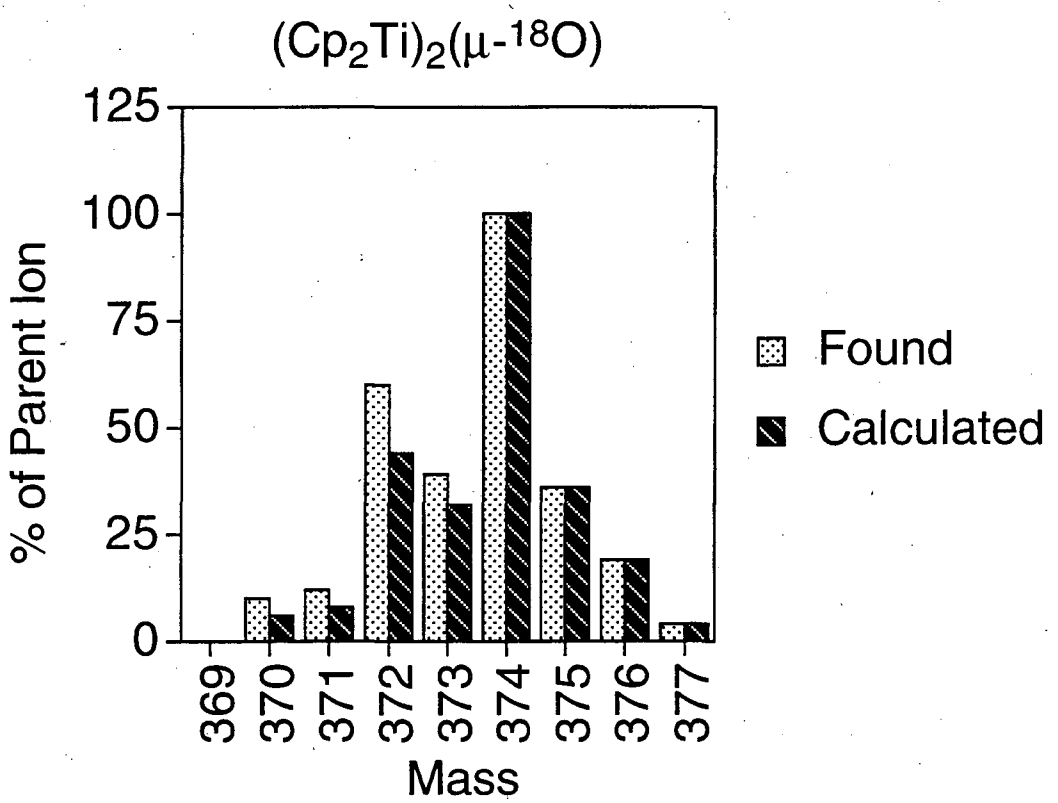


Figure 4

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% of Parent Ion
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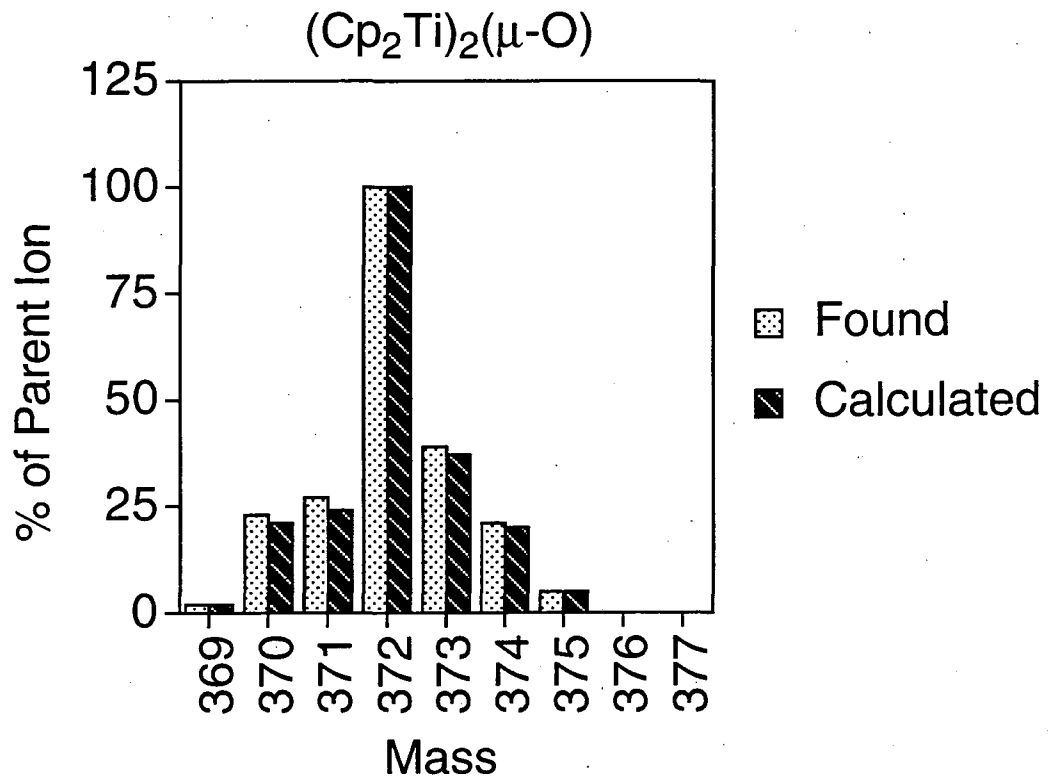
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Figure 5

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