Electronic Structure and Magnetic Properties of Y₂Ti₂(µ-X)₂Y₂(X, Y=H, F, Cl, Br)

Isomers

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Background

The magnetic properties of paramagnetic transition metal ions have been an interest of study for many years. Several physical and structural parameters are important in the understanding of these magnetic properties. The main parameters are the distance between the paramagnetic centers, the M-X-M angle, where X is the bridging ligand atom, and the nature of the bridging ligand, such as the electron density on the bridging ligand group and the intrinsic properties of the anions. Most studies deal with compounds containing two bridging monatomic groups between the metal ions. Particular interest has been focused on dinuclear copper (II) complexes for which correlations between the singlet-triplet splitting have been made.¹ Dinuclear copper (II) complexes bridged by hydroxo groups show antiferromagnetic or ferromagnetic interactions depending on the bridging structures. It has been suggested that both the extent of overlap and energy difference of the metal dₓ² orbitals with the σ orbitals of bridging atoms determine the magnitude (the J value) of the magnetic interaction. Based on experimentation with dinuclear copper (II) complexes it can be suggested that a direct or through-ligand charge transfer interaction is important in the propagation of the antiferromagnetic interaction.²

In compounds that are antiferromagnetic, the spins of magnetic electrons align in a regular pattern with neighboring spins pointing in opposite directions. Antiferromagnetic molecules exhibit antiferromagnetism at a low temperature, and
become disordered above a certain temperature; the transition temperature is called the Neel temperature, the temperature at which an antiferromagnetic material becomes paramagnetic. The magnetic susceptibility of an antiferromagnetic material will appear to go through a maximum as the temperature is lowered.\textsuperscript{3}

Ferromagnetism is a phenomenon by which a material can exhibit a spontaneous magnetization, and is one of the strongest forms of magnetism. It is responsible for most of the magnetic behavior encountered in everyday life, and is the basis for all permanent magnets.\textsuperscript{3}

Since bonding and magnetic properties of materials involve complex interactions between metal centers and ligands it is important to understand how changes in ligands affect the magnetic properties of a system. Copper (II) compounds have been studied exclusively in the past.\textsuperscript{4} Research has been done on dinuclear copper(II) compounds with 1,2,4-triazole ligands. In these compounds the unpaired electron on the copper (II) ion occupies a magnetic orbital, which is pointing toward the coordinating triazole nitrogen atoms. As a result, a considerable electron delocalization may take place through these nitrogens and magnetic superexchange interaction becomes possible via mainly the $\sigma$ orbitals of the triazole ligand. Changes in the bridging geometry of the ligand are therefore likely to directly influence the efficiency of the exchange pathway.\textsuperscript{1}

**Introduction**

Like the copper (II) compounds titanium (III) compounds have one unpaired electron on each metal center, but differ from copper in orbital occupation and size. Many of titanium (III) compounds have a planar ring structure so the model $Y_2Ti_2(\mu-X)_2Y_2$ is used.\textsuperscript{4}
Compounds containing titanium have long been studied for their magnetic properties. Based on studies performed it is clear that the bonding and magnetic properties of these titanium molecules arise from complex interactions between the two metal centers and between the metal centers and bridging (and possibly terminal) ligands.

Recently, linear oxobridged heterodinuclear and homodinuclear compounds of titanium (III) have been examined using electron paramagnetic resonance (EPR), magnetic susceptibility, and ab initio calculations and some compounds have been found to be ferromagnetic.

When the two metals individually bear unpaired electrons, the resulting complexes are liable to possess magnetic properties, and their study by EPR in frozen solution presents information about their ground states, the extent of metal-metal separation, and the importance of the exchange interaction between the two metal centers.
In most of the cases, triplet-state spectra (S=1) were observed by EPR spectroscopy in frozen solution exhibiting zero field splitting characteristic of interacting paramagnetic metal centers. EPR is used to study this because it is the process of resonant absorption of microwave radiation by paramagnetic ions or molecules, with at least one unpaired electron spin, and in the presence of a static magnetic field. Multifrequency EPR provides an experimental route to study the magnetic interactions in paramagnetic materials. In EPR spectroscopy one studies the energy differences due to the interaction of unpaired electrons in the sample with an external magnetic field produced by the EPR spectrometer. This effect is called Zeeman Effect.

Magnetic susceptibility is the degree of magnetization of a material in response to a magnetic field. The dimensionless volume magnetic susceptibility is represented by the symbol \( \chi \). Magnetic susceptibility is equal to the magnetization of the material (M) which is the magnetic dipole moment per unit volume divided by the magnetic field strength (H). Ab initio calculations compute solutions to the Schrodinger equation using a series of rigorous mathematical approximations. The Ab initio molecular orbital theory predicts the properties of atomic and molecular systems.

The possible explanations for the origin of the Ti-Ti exchange interaction that is responsible for the observed magnetic properties is either the direct overlap of the occupied Ti d orbital or an intramolecular superexchange pathway by means of the bridging ligands, a ligand attached to a central metallic atom. For an exchange pathway involving the direct overlap of d orbital, a decrease in the metal-metal distance generally leads to an increase in the magnitude of the antiferromagnetic interaction. In a system
with sizable bridging ligands, a larger distance between the two Ti’s is created and this prevents the direct overlap of d orbital which facilitates a superexchange pathway. A superexchange pathway is created by conjugated bridging ligands allow the metal atoms to interact through the adjoining π segment, influencing the metal-metal communication. Such pathways normally result in a smaller antiferromagnetic effect than the direct overlap pathway.

Most of the dinuclear titanium (III) complexes studied are antiferromagnetic, although a few have been reported to be weakly ferromagnetic. Ti2H6 has previously been studied, which is the simplest form of the dititanium bridged compounds which a planar ring structure. Based on the criteria that paramagnetic homodinuclear titanium (III) compounds for with the singlet is lower in energy than the triplet are antiferromagnetic H2Ti2 (µ-H)2H2 was found to be antiferromagnetic. It was concluded that this was due to a small bonding interaction between Ti’s in the singlet. This article’s focus is to understand the changes in magnetic properties and electronic structure in the Y2Ti2 (µ-X)2Y2 system by varying the bridging and terminal ligands with the halogens H, F, Cl, and Br.

In highly symmetric titanium (III) molecules isotropic interaction and Zeeman perturbation contribute to the magnetic properties of these dinuclear compounds. The dominant effect is the isotropic interaction which is an electrostatic phenomenon that is a coupling between local spin operators S_a and S_b. The Hamiltonian for the coupling is:

\[ H = -2J S_a S_b \]

The isotropic exchange interaction parameter is:

\[ 2J = E(S=0) - E(S=1) \]
In molecules that interact through bridging ligands, the two local spin states $S_a$ and $S_b$ have singlet and triplet coupling.\textsuperscript{6} When the $J<0$, the singlet state is the ground state and the interaction is antiferromagnetic. But when the $J>0$, the triplet state is the ground state and the interaction is ferromagnetic. For an antiferromagnetic compound ($J<0$), the magnetic susceptibility $\chi$ goes through a maximum at the Neel temperature such that:

$$\frac{2J}{kT_{max}} = 1.599$$

where $k$ is the Boltzmann constant.\textsuperscript{4}

When the isotropic interaction is small or the triplet state is ground state other magnetic properties can be important such as Zero-field splitting. Zero-field splitting in an EPR spectrum is caused by the interaction of two local doublets according to:

$$H = \beta S \cdot gH + S \cdot D \cdot S$$

The $H$ is the magnetic field, the $\beta$ is the Bohr magneton, $S$ is the spin operator ($S=S_a=S_b$), $g$ is the $g$ tensor, and $D$ is the zero-field splitting tensor.\textsuperscript{4}

**Computation Details**

The $(14s11p6d/10s8p3d)$ basis set was used for titanium. For hydrogen, $(5s1p/3s1p)$ basis set was used. For fluorine, $(10s6p/5s3p)$ basis set was used; for chlorine the $(12s9p/6s5p)$ basis set was used; and for bromine, the $(14s11p5d/9s6p2d$ basis set was used. Collectively, this basis set is referred to as TZV(p).\textsuperscript{6}

To predict reasonable energy-related quantities, polarization functions were added to the TZV(p) basis set. The basis set TZVP(f) adds f functions to the titanium, two sets of d polarization functions to the halides, and diffuse s and p functions to the halides as well. The 2d polarization and diffuse sp function exponents are default values in GAMESS. For singlets TCSCF geometry optimizations were performed and ROHF
geometry optimizations were performed for the triplets. Multireference second-order perturbation theory (MRMP2) single-point energy calculations were carried out at the TCSCF singlet geometries and ROHF triplet geometries. Hessians were used to characterize stationary points.6

Excited-state calculations required fully optimized reaction space (FORS) multiconfigurational SCF (MCSCF) calculations. Spin – orbit coupling effects (SOC) were determined in three ways: a one-electron spin-orbit coupling operator method (HSO1), a partial two-electron and full one-electron method (P2E), and the full Pauli-Breit operator method (HSO2).

All calculations were made using GAMESS (General Atomic and Molecular Electronic Structure System).11

Results and Discussion

Electronic Structure

The lowest energy singlet and triplet states are \(^1\text{A}_g\) and \(^3\text{B}_{\text{uu}}\), respectively. The natural orbital analysis shows that the lowest-energy singlets all have at least 0.87 electrons in the lowest virtual orbitals. Mulliken populations show charges on Ti range from +0.73 to +1.78, indicating highly polarized Ti-ligand bonds. The Ti positive charge increases with the electronegativity of the ligands and with the number of electronegative ligands. There is very little direct Ti-Ti bonding based on natural orbital occupation numbers (NOON’s).4

Singlet-Triplet Splitting

Dynamic electron correlation is required for calculating accurate energy gaps. Without correlation, some triplet states lie below the singlet states. With correlation, all
singlets are lowest in energy. As the basis set size is increased, the singlet-triplet splitting increases by up to 0.3 kcal/mol on going from TZV(p) to TZVP(f) and 0.6 kcal/mol from TZVP(f) to TZVP(fg).4,6

**Isotropic Interaction/Magnetic Properties**

Isotropic interaction follows the same trends as singlet-triplet splitting. The isotropic interaction parameters determined are much larger than experimental J values for compound with halide bridges.4 Magnetic properties of dinuclear complexes depend on the intramolecular interaction between the two metal centers and this is affected by both the bridging ligands and the terminal ligands. As the bridging ligand changes from H to Br to Cl to F, the interaction becomes more ferromagnetic (J becomes less negative). As the terminal ligand changes from H to Br to Cl to F, the interactions becomes more antiferromagnetic (J becomes more negative).6

**Reproducing Calculations**

I started out trying to reproduce the Geometry Parameters for the Lowest-Energy Singlet and Triplet States, the Mulliken Charges on Ti, and the calculated singlet-triplet energy gap. First I started off by trying to reproduce the titanium molecules with fluorine as ligands. I used GAMESS to reproduce my calculations and the molecules were visualized using PCMODEL.

**Determining Method**

For the singlet geometry optimizations the paper used the method TCSCF. I started out using this as my method but GAMESS does not recognize TCSCF as a keyword. I then found out that the Method GVB is equivalent to the TCSCF. I then learned after more trial and error that if you are using SCFTYP = GVB the $SCF group is
required in the input file. The GVB wave function assumes orbitals are in the order core, open pairs. So the $SCF$ line in the input file requires $NCO$, $NSETO$, and $NPAIR$. The $NCO$ is the number of closed shell orbitals, the $NSETO$ is the number of open shells in the function and the $NPAIR$ is the number of geminal pairs in the GVB functions. I determined the $NCO$ by adding up the number of electrons in each titanium molecule, dividing by two and then subtracting one. I set $NSETO=0$ because there are not any open shells. I set $NPAIR=1$ so I would have one open shell for the electrons to move to.\textsuperscript{12}

For the triplet geometry optimizations the paper uses the ROHF method. GAMESS recognized this keyword and I was able to use this method for my triplet geometry optimizations.

**Determining Basis Set**

The basis set that the article used for their Geometry optimizations was the TZV (p). The basis set I used was TZV. GAMESS did not recognize the TZV(p). Apparently there is a different keyword for the polarization of the TZV basis group. I tried adding a polarized function by using the keyword $NFFUNC=1$ to add an F group to the titanium but this did not work.\textsuperscript{12} I then found a paper about GAMESS Basis Sets that told me that if polarization functions are to be added to the basis set that for $GBASIS=TZV$ the keyword $POLAR=HONDO7$ must be added. I added the keyword $POLAR=HONDO7$ in the $Basis$ group input file but this did not change anything in my output file.\textsuperscript{13} I also tried $POLAR=POPLE$ but this did not change anything either.\textsuperscript{12} I then went back to my paper and saw that the polarization (14s11p6d/10s8p3d) basis set was used for titanium and for fluorine (10s6p/5s3p) basis set was used. I compared these basis sets to the
atomic basis sets in the raw output of a GAMESS job run with the TZV basis set. Below is the atomic basis set of Ti$_2$F$_6$.

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<table>
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<td>22 S 32</td>
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<td>22 S 33</td>
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<tr>
<td>24</td>
<td>31</td>
<td>29 P 48</td>
</tr>
</tbody>
</table>

Since the atomic basis set in my GAMESS output is equivalent to the polarization set of titanium and fluorine, I assumed that the TZV basis set was polarized and close enough to the TZV(p) basis set used in the article.

Another problem I then had when running GAMESS was in some of my geometry optimizations $SCF$ was not converging. The reason the geometry was not converging was it need more than the standard 30 convergences of the energy. In order to fix this I added the keyword MAXIT=100 to the $CONTROL$ line of the input.\textsuperscript{12}

**Input File**

The following is the input I used for each molecule:

**Ti$_2$F$_6$**

```
$CONTRL SCFTYP=GVB RUNTY=OPTIMIZE MAXIT=100 ICHARG=0 MULT=1
   COORD=ZMTMPC $END
$BASIS GBASIS=TZV $END
$SCF NCO=48 NSETO=0 NPAIR=1 $END
$DATA
```
For the Ti\textsubscript{2}F\textsubscript{2}H\textsubscript{4} singlet I was unable to use the GVB method. When I used the GVG method the GAMESS file would fail. The reason it would fail is the rotation angle vector had a huge norm. I tried making the angles of Ti\textsubscript{2}F\textsubscript{2}H\textsubscript{4} smaller but my GAMESS file would still fail. So in order to get the geometry optimization of the singlet I tried the ROHF method and this worked. I thought this would be acceptable since both GVB and ROHF are TCSCF methods. What I discovered was that the GVB method gives the orbital occupation numbers but the ROHF method does not. This might have occurred
since the ROHF method does not require the SCF in the input file. I then tried to run the
ROHF method with the SCF input in attempt to calculate the orbital occupation numbers
for the Ti₂F₂H₄ singlet. The result of this is the following non-linear geometry:

* Ti₂F₂H₄ with ROHF method and SCF input

Even though the geometry is non-linear, I still looked for the occupation numbers in the
output file. I was unable to find any in the output file so apparently the occupation
numbers are exclusive to the GVB method.

I tried to create a geometry optimization for the Cl molecules using the same type
of input as above but all of my GAMESS runs failed. All of the input files failed because
the SCF did not converge. It was suggested that if there were convergence problems to
try SOCF=.FALSE., so I went back and added to this and SHIFT=.TRUE. to $BASIS
input line. Unfortunately, this did not work so I was unable to complete any geometry
calculations for chlorine.

I tried geometry optimizations for the Br molecules but they did not run because
an illegal basis function was requested. Apparently in the article some other basis set was
used for the Br but it was not discussed so I was unable to do any Br geometry
optimizations.
Results for Geometry Optimizations

Geometrical Parameters for the Lowest-Energy Singlet and Triplet States

<table>
<thead>
<tr>
<th></th>
<th>Distances (Å)</th>
<th>Bond Angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Singlet States</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti$_2$F$_6$</td>
<td>3.3912159</td>
<td>2.0435902</td>
</tr>
<tr>
<td>Ti$_2$H$_2$F$_4$</td>
<td>3.4098845</td>
<td>2.0408796</td>
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<tr>
<td>Ti$_2$F$_2$H$_4$</td>
<td>3.2496930</td>
<td>2.0047870</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triplet States</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti$_2$F$_6$</td>
<td>3.3895321</td>
<td>2.0509800</td>
</tr>
<tr>
<td>Ti$_2$H$_2$F$_4$</td>
<td>3.4191389</td>
<td>2.0782698</td>
</tr>
<tr>
<td>Ti$_2$F$_2$H$_4$</td>
<td>3.4178666</td>
<td>2.0657595</td>
</tr>
</tbody>
</table>

The distances from my GAMESS runs were similar to the distances produced in the article for the Ti-Ti, Ti-X, and Ti-Y and the angles for the X-Ti-X. Just as in the paper the differences in the geometries between the singlet and triplet states is slight. The difference between my GAMESS calculations and the article’s was the bond angle of the Y-Ti-Y and the distance of Y-Y. When I was doing my calculations GAMESS seemed to dislike the large Y-Ti-Y bond angle. Originally the input structure had larger angles than the geometry optimized structure. This difference in my calculations could be accounted for by the basis set that I used.
Geometries of Singlets and Triplets

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Singlet</th>
<th>Triplet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₂F₆</td>
<td>1.748585</td>
<td>1.779150</td>
</tr>
<tr>
<td>Ti₂H₂F₄</td>
<td>1.403886</td>
<td>1.420853</td>
</tr>
<tr>
<td>Ti₂F₂H₄</td>
<td>0.924213</td>
<td>1.049474</td>
</tr>
</tbody>
</table>

*Mulliken populations and charges are the simplest division of the electron density between orbitals*
The Mulliken charges for Ti that I calculated are slightly similar to the ones in the article for Ti$_2$F$_6$ and Ti$_2$H$_2$F$_4$. In the article the Mulliken charges are the same for both the triplet and the singlet for Ti$_2$F$_6$ and Ti$_2$H$_2$F$_4$ but my results show them as being different. Again these slight variations could be the result of my basis set being different or an input that the article used but chose not to mention.

Natural Orbital Coefficients

<table>
<thead>
<tr>
<th>Molecule</th>
<th>ORB 1 (a$_g$)</th>
<th>ORB 2 (b$_{1u}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$F$_6$</td>
<td>1.00990</td>
<td>0.99010</td>
</tr>
<tr>
<td>Ti$_2$H$_2$F$_4$</td>
<td>1.01968</td>
<td>0.98032</td>
</tr>
</tbody>
</table>

*NOON’s were not determined for Ti$_2$F$_2$H$_4$ since the ROHF method was used instead of the GVB.

The natural orbital coefficients I calculated for Ti$_2$F$_6$ were almost the same as the NOON’s in the article. The NOON’s for Ti$_2$H$_2$F$_4$ were similar but slightly different. Since all of the NOON’s for each molecule were so close to each other in value this could be considered a noticeable difference.

**Calculated Singlet – Triplet Gap (E(triplet) – E(singlet))**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Singlet</th>
<th>Triplet</th>
<th>Difference (Hartree)</th>
<th>Kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$F$_6$</td>
<td>-2294.1212</td>
<td>-2294.0669</td>
<td>.05429</td>
<td>34.07137</td>
</tr>
<tr>
<td>Ti$_2$H$_2$F$_4$</td>
<td>-2094.2705</td>
<td>-2096.1629</td>
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<td>-1187.5607</td>
</tr>
<tr>
<td>Ti$_2$F$_2$H$_4$</td>
<td>-1897.8599</td>
<td>-1898.1688</td>
<td>-.30332</td>
<td>-190.3360</td>
</tr>
</tbody>
</table>

The energy I calculated wasn’t even close to the values that were presented in the paper. First, the Ti$_2$F$_6$ energy gap was negative while I got a positive result. The Ti$_2$H$_2$F$_4$ and Ti$_2$F$_2$H$_4$ energy gaps should have been positive while I calculated positive results. The numerical results of the energy were not near the values presented in the paper. I assumed that the energy given in the GAMESS output was in Hartree and I then
converted it to kcal/mol by multiplying by 627.5095. Possibly I used the wrong energy for this calculation or this energy difference is a result of the basis set I used.

**Frequencies**

The article showed theoretical vibrational frequencies of the titanium molecules. I performed a vibrational frequency job but the job failed because there was not enough memory.

**Gaussian**

I performed a geometry optimization of Ti$_2$F$_6$ to compare to GAMESS. I used the method B3LYP and the basis set LanL2DZ. The geometry that it calculated was not linear.

So apparently this method and basis set in Gaussian does not perform the same geometry optimization as GAMESS.
**Evaluation**

By doing this paper I learned a lot about the computer program GAMESS. To me GAMESS is not as user friendly as Gaussian. Lots of additional keywords have to be added to the GAMESS input in order for it to run properly. I had difficulties in reproducing the calculations in the article because the article did not really explain what basis sets and methods were used to perform each calculation. I found it most frustrating trying to figure out the keywords to add to the input file to make the GAMESS run. The article could have been improved upon by providing more details about keywords used in the input for each GAMESS file. In the paper, the method TCSCF was used but when I tried to use this as my method my run failed and the output data told me that TCSCF was an illegal keyword. Many of the other methods and basis sets that were used in the paper are generic terms and not the keywords accepted in the GAMESS input file. Even in the GAMESS input description I was unable to find the methods and basis sets. If the scientists in the article used some special type of input in GAMESS, I feel that they should have made a note of it so others could try to reproduce the data. The scientists in the article just assumed that most people would be proficient in GAMESS.

In the computational details there is no mention about vibrational frequencies but vibrational frequencies of the titanium molecules are presented in the paper. It would have been helpful if in the computational details more emphasis was put on this. Especially since my vibrational frequency calculations failed because there was not enough memory. If excess memory was needed this should have been mentioned. Since I have tried to recalculate the results, I think it would have been interesting if the scientists had added any computational difficulties they had.
In the article I was unsure about why certain calculations were performed. The point of the paper was to show the magnetic properties of the interactions between the two metal centers. The article demonstrated this by showing how the bridging ligand changes from H to Br to Cl to F, the interactions becomes more ferromagnetic and they were able to determine this because the J became less negative. Since this is how the ferromagneticism is determined I thought that this aspect would have been discussed more. I feel it would have been more helpful also if more representations of the molecules were presented in the paper. It is helpful when there are visuals of what is happening.

Overall, I feel that the article benefited me by I learn about GAMESS. I feel that I might like Gaussian better because it is easier to add methods and basis sets. Although, GAMESS appeared to be better for the titanium molecule because when I tried to do a geometry optimization in Gaussian my molecule lost the linear planar structure. I wish I had been more familiar with GAMESS or that it had friendlier input so I would have been able to reproduce more of the calculations in the article.
References


(9) Basic EPR Theory. [http://mch3w.ch.man.ac.uk/services/epresr/EPRprecip2.htm](http://mch3w.ch.man.ac.uk/services/epresr/EPRprecip2.htm) (accessed 04/29/04).


