charge density of the metal ion for the formation of chelation III in the present system.

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A Molecular Orbital Study of the Electronic Structure and the Ring Inversion Process in Cp_2TiS_3 Complex

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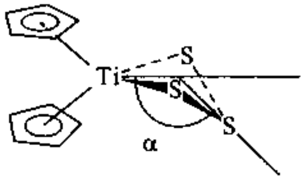
Ab initio and extended Hückel calculations have been applied to discuss the electronic structure, ring inversion barrier, and geometry of the Cp_2TiS_3 compound. The deformation of four membered ring in the planar geometry is originated from a second-order Jahn-Teller distortion due to the small energy gap between HOMO and LUMO on the basis of extended Hückel calculations. The puckered C_s geometry is stabilized by the interaction of the x^2-y^2 metal orbital with the hybrid orbital in sulfur. *Ab initio* calculations have been carried out to explore the ring inversion process for the model Cl_2TiS_3 compound. We have optimized C_s and C_{2v} structures of the model compound at the RHF level. The energy barriers for the ring inversion are sensitive to the used basis set. With 4-31G* for the Cl and S ligands, the barriers are computed to be 8.41 kcal/mol at MP2 and 8.02 kcal/mol at MP4 level.

Introduction

The factors that determine the ring size and chain lengths in elemental sulfur are poorly understood instead of intensive studies.[1] The versatility of sulfur atoms as a ligand has been recently established in transition metal complexes. The trend of sulfur to form metal complexes is probably due to its intrinsic nucleophilic property and electron donor ability. A number of metallacyclosulfanes, MS_x, where $x=2$ to 5, have been prepared.[2] The ring inversion barriers in these complexes have been measured by variable temperature NMR studies. The activation energy for the TiS_5 ring inversion in Cp_2TiS_5 complex has been measured to be 16.5 kcal/mol by Abel *et al.*[3] and the electronic structure and potential energy surface for the process of the six-membered ring have been studied by various methods including *ab initio* calculations.[4] $Cp_2^*TiS_3$ (Cp^* = pentamethylcylopentadienyl) complex has been reported to be its ground state geometry in a puckered four membered ring, and the angle α in **1** is 131°.[5] This complex has similar structure to the puckered cyclobutane. The interesting feature is the energy barrier for the ring flipping from one side to the other. It has been measured to be 9.6 kcal/mol by NMR technique.[5] This bar-



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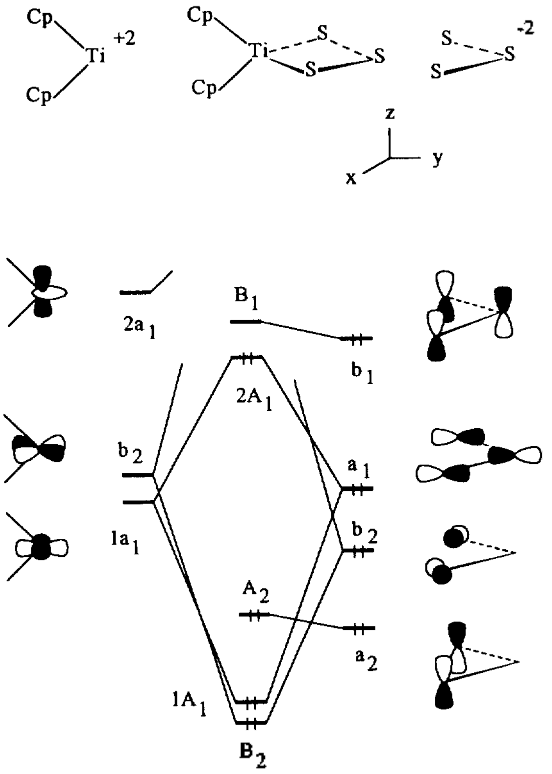


Figure 1. An orbital interaction diagram for Cp_2TiS_3 at a planar geometry

rier is unusually high when it is compared with that of cyclobutane of 1.5 kcal/mol.[6] In this paper, we discuss the analysis of the electronic structure and ring inversion process in Cp_2TiS_3 complex. We calculate the potential energy surface for the ring flipping process of the four membered TiS_3 unit at the semi-empirical extended Hückel[7] and *ab initio* levels.

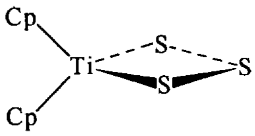
Computational Methods

The *ab initio* calculations were carried out with the GAUSSIAN 90[8] and GAMESS[9] packages. The basis set for Ti metal atom was of the form (4333/433/31) and has been described elsewhere.[10] Basically, it is of double-ξ quality for the metal *d* region. Standard 4-31G[11] and 4-31G*[12] were used for chlorine and sulfur atoms. All geometries were optimized at the restricted Hartree-Fock (RHF) level by the energy gradient technique. Second- and fourth-order Moller-Plesset perturbation (MP2 and MP4) calculations were carried out at the RHF optimized geometries to obtain improved energy comparisons for the energy barrier.

The extended Hückel calculations with the modified Wolfsberg-Helmholz formula[13] were performed for the qualitative analysis. The parameters were taken from previous work.[14,15] All Ti-S, S-S, Ti-C(Cp), and C-C distances were set at 2.41, 2.03, 2.39, and 1.41 Å, respectively. The S-Ti-S and Cp-Ti-Cp angles were kept at 84.4° and 136.9°.

Results and Discussion

Extended Hückel Calculations on Cp_2TiS_3. The ground state geometry of **1** is a puckered form. In order to describe the details of this geometry, it is necessary to describe the bonding in a planar form **2** in which the angle α is 180.0°. This is divided into two fragments, Cp_2Ti^{2+} and S_3^{2-}. The sulfur fragment **3** can be visualized as a diradical with two hybrid orbitals bearing the four electrons. The orbital interactioin diagram for the planar **2** is shown on Figure 1.



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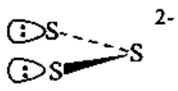

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On the left side of figure are displayed the important valence orbitals of Cp_2Ti^{2+} unit. This fragment has been extensively studied by several groups.[15] We shall briefly describe the salient features of the analysis. The orbitals are labeled with C_{2v} symmetry and used the coordinate system shown on the top of Figure 1. The $1a_1$ fragment orbital at the low energy level is predominantly x^2-y^2 metal *d* orbital pointed toward the vacant site by mixing of p_y orbital. The b_2 is mainly xy metal orbital. The z^2 metal orbital mixed with some metal x^2-y^2 and *s* characters is labeled $2a_1$ and lies at somewhat higher energy level. The $2a_1$ orbital is too high in energy to play an important role in interaction diagram. In Cp_2TiS_3, the Ti metal is formally d^0. Therefore, $1a_1$, b_2, and $2a_1$ fragmental orbitals are empty as shown on the left side of Figure 1. The four orbitals of the S_3^{2-} fragment are displayed on the right side of figure. There are two lone pair electrons (**3**) which are directed toward the metal fragment. Linear combinations produce two fragment orbitals of b_2 and a_1 symmetry. There are also two π type fragment orbitals, a_2 and b_1. The b_1 is an antisymmetric combination of p_z that is the highest occupied fragment orbital in S_3^{2-} unit. The $1a_1$ metal fragment orbital strongly interacts with the same symmetry orbital a_1 on S_3^{2-} unit to form bonding molecular orbital (MO) $1A_1$ and antibonding MO $2A_1$. The $2A_1$ MO is a highest occupied MO (HOMO) in the planar Cp_2TiS_3 geometry and the component of this MO is 68% of the $1a_1$ on metal and 20% of the a_1 on sulfur fragment. Another strong interaction is formed between b_2 orbitals on two fragments and it gives the stabilized B_2 MO and antibonding MO which is not displayed in figure. The A_2 MO comes from the a_2 fragment orbital in sulfur unit slightly destabilized by xz on the metal fragment not shown here. The b_1 in sulfur unit is also slightly destabilized by yz on the metal to produce LUMO, B_1. The component of LUMO is mainly sulfur fragment, 91% of the b_1. The HOMO and LUMO are represented by **4** and **5**, respectively.

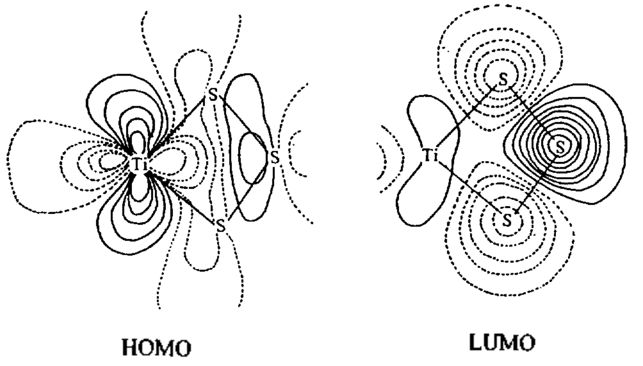
HOMO

4

LUMO

5

Contour plots of HOMO and LUMO are displayed in Figure 2. This figure clearly shows that the HOMO has appreciable density between metal and S_3 units in the antibonding



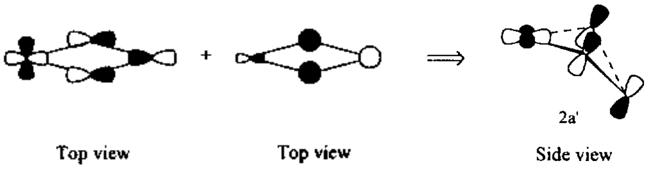
HOMO LUMO

Figure 2. Contour plots of HOMO ($2A_1$) and LUMO (B_1) in the planar Cp_2TiS_3 complex. The different phases of the wavefunction are represented by full and dashed lines. The orbitals were plotted in the *xy* plane defined in Figure 1. The LUMO which possess a node in the *xy* plane was plotted in this plane 1.0 in the *z* direction.

while the LUMO has large density in S_3 unit. The LUMO is almost nonbonding sulfur p_z orbital.

The energy gap between HOMO and LUMO is pretty small as 4.2 kcal/mol. This indicates a potential second-order Jahn-Teller distortion.[15b] The distortion will serve to mix the LUMO into HOMO, stabilizing the latter. One way to distort the geometry is lowering the point group from C_{2v} to C_s. That produces the same *a'* symmetry for the HOMO and LUMO and mixed together. We have changed the angle α defined in **1** to make C_s point group. An orbital correlation diagram is shown on Figure 3 along with the energy profile as a function of the angle α.

When the angle α is deviated from 180.0°, the system becomes C_s symmetry which is the puckered geometry. Therefore, $2A_1$ and B_1 are now able to interact with $1A_1$ with the identical *a'* symmetry that is shown on Figure 3(a). The effect is to provide three MO's-4 electron pattern for the interaction. Thus, the HOMO in the puckered geometry is produced by the combination of two MO's as shown in **6**.



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As the α is decreased, some interaction is formed between x^2-y^2 metal orbital and the hybrid orbital on the center sulfur atom in S_3 unit. The overlap population at α=130.0° is calculated to be 0.1679. Decreasing the α angle produces this stabilizing interaction and favors the puckered geometry. The *2a"* in Figure 3(a) is almost non-bonding MO and therefore not affected by the deformation of geometry. The *1a'* holds the system by strong interaction between the radical type hybrid orbital on S_3 unit and mainly x^2-y^2 metal orbital. The puckering of four membered ring affects this interaction. The overlap population between these orbitals decreases from 0.1371 to 0.0931 when the α angle is changed from 180.0° to 130.0°. At the planar geometry, the hybrid orbital on sulfur unit stays in the *xy* plane, whereas at the puckered geometry another orbital mixes in and hence the hybrids are tilted outward of the plane (**7**). It weakens the interaction with the x^2-y^2 metal orbital.

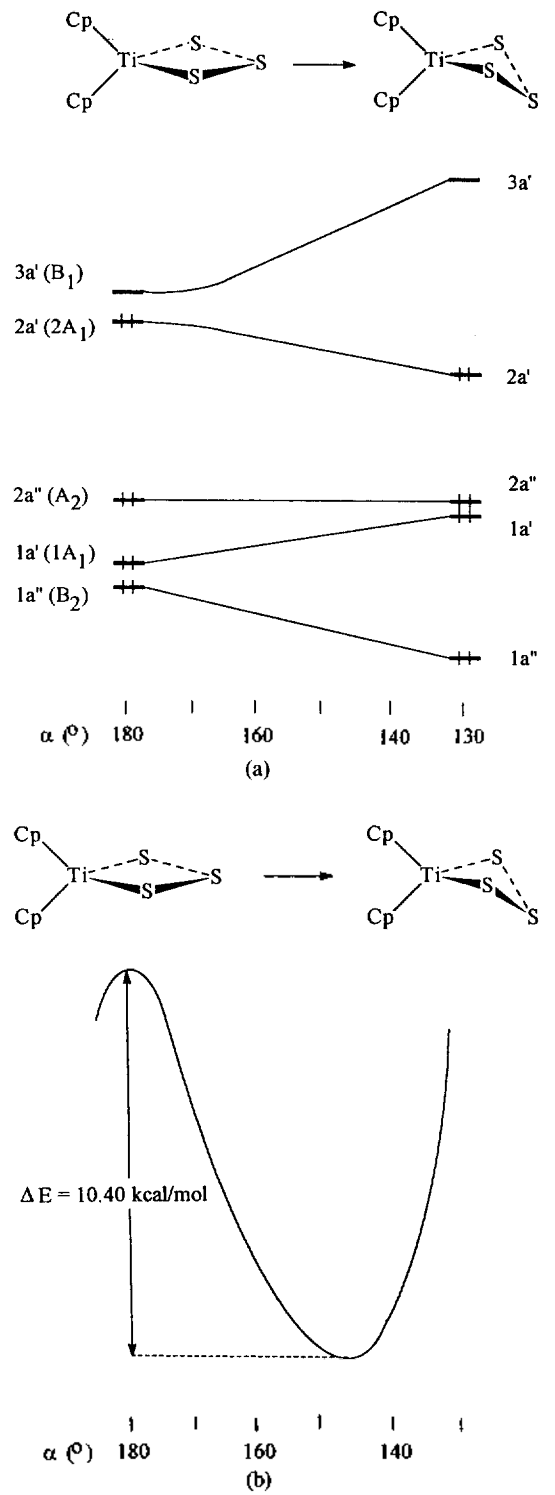


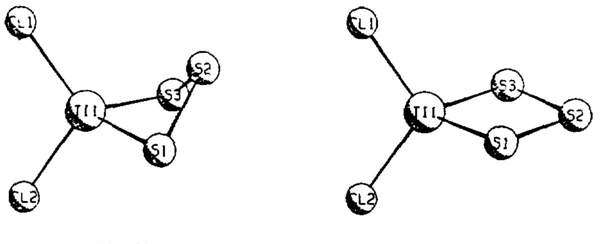
Figure 3. (a) Orbital correlation diagram for the distortion of Cp_2TiS_3 complex from the C_{2v} to C_s geometries. (b) The energy profile as a function of the angle defined in **1**.

As described, decreasing the α makes *2a'* to be stabilized and *1a'* destabilized. The optimum angle is resulted to be

Table 1. Optimized Geometries of C_s and C_{2v} Cl_2TiS_3 Complex at RHF Levels.[a] Basis Sets are for Cl and S Atoms. The Bond Distances are in Angstroms and the Angles in Degrees

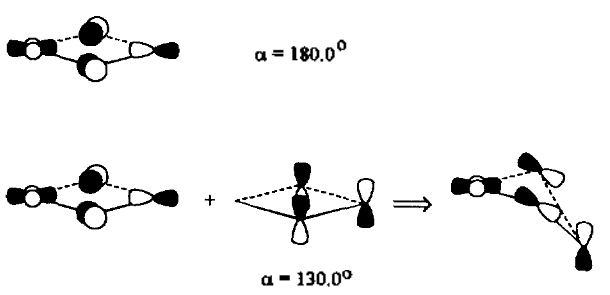
Basis	C_s		C_{2v}		X-ray of
sets	4-31G	4-31G*	4-31G	4-31G*	Cp_2TiS_3
Ti-S_1, S_3	2.30	2.30	2.31	2.27	2.41
Ti-S_2	2.76	2.53	3.03	2.94	2.77
S_1-S_2	2.32	2.12	2.33	2.14	2.04
Ti-Cl	2.23	2.21	2.23	2.20	
α	127.5	115.9	180.0	180.0	~131
θ	109.6	109.8	110.1	110.9	136.9
<S_1-Ti-S_3	97.2	90.1	99.0	92.7	84.4
<S-S-S	97.0	100.4	97.9	100.0	

[a] The atom numbering scheme and parameters are defined in **8**.



C_s Cl_2TiS_3 C_{2v} Cl_2TiS_3

Figure 4. Optimized geometries of C_s and C_{2v} Cl_2TiS_3.



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145.0° on the energy profile as a function of the α in Figure 3(b). The energy barrier for the four membered ring inversion is computed to be 10.4 kcal/mol that is pretty close to the experimental data of 9.6 kcal/mol.

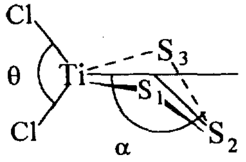
***Ab initio* Calculations on Model Cl_2TiS_3 Compound.** Using Cl in place of Cp is a good model to reduce computational complexity. Upton and Rappe used Cl ligand to replace Cp in a theoretical study of the isomerization of $Cp_2TiC_3H_6$ to $Cp_2TiCH_2(C_2H_4)$ and they found that this model system gives a reasonable result.[16] Also, several groups have used this kind of a simple model of Cl ligand to obtain good results in the quantitative calculations.[17] The important optimized bond distances and angles for the C_s and C_{2v} Cl_2TiS_3 are reported in Table 1 using the labeling shown in **8**; the molecular structures are illustrated in Figure 4.

The optimized α angles in C_s structure of Table 1 are 127.5° and 115.9° for 4-31G and 4-31G* basis sets, respectively. These values are consistent with the trend obtained in X-ray structure determination where the structure of four membered ring is puckered.[5] The optimized α angles are smaller than the experimentally observed one of 131° due to the less bulky Cl in place of Cp ligand. Generally, the 4-31G* basis set calculation reveals shorter bond distances than those of 4-31G. This is general trend at the basis set with polarization function.[18] The energy differences between the puckered C_s and the planar C_{2v} geometries are listed up to MP4 level in Table 2.

Table 2. The Energy Differences[a] between C_s and C_{2v} Geometries of Cl_2TiS_3. The Energies are Listed in kcal/mol

	4-31G	4-31G*
RHF	0.97	4.22
MP2	3.09	8.41
MP4	3.41	8.02
Exp.	9.6	

[a] The total energies of C_s at 4-31G* are −2957.09079 hartrees at RHF level, −2957.88306 hartrees at MP2 level, and −2958.03574 hartrees at MP4 level.



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With the 4-31G basis set, the energy barrier of ring inversion in Cl_2TiS_3 is computed to be 0.97 kcal/mol at the RHF level. Electron correlation effects increase it to 3.09 kcal/mol (MP2 level) or 3.41 kcal/mol (MP4 level). These barriers are far from the experimental measurement of 9.6 kcal/mol. We found out that the energy barrier is pretty sensitive to the basis set used. As given in Table 2, the puckered C_s geometry is computed to be 4.22 kcal/mol more stable than the planar C_{2v} at the RHF level with the polarization function 4-31G* basis set. It is also increased by electron correlation effects to 8.41 kcal/mol and 8.02 kcal/mol at MP2 and MP4 levels, respectively. We notice that the energy barrier is not much affected by the electron correlation beyond second-order Moller-Plesset perturbation theory. The full *ab initio* studies of Cp_2TiS_3 and its isoelectronic molecules will be forthcoming.

Conclusions

We have discussed the detailed computational studies of the electronic structure and ring inversion process in Cp_2TiS_3 compound at both the semi-empirical EHT and *ab initio* levels. The HOMO and LUMO in the planar geometry of Cp_2TiS_3 are very close in energy enough to deform the structure in terms of the 2nd order Jahn-Teller distortion. The puckered C_s form maximizes the stabilization to increase the interaction between the x^2-y^2 metal orbital and the hybrid orbital in sulfur. At the *ab initio* studies on the model compound, the optimized geometries are not much different in 4-31G and 4-31G* basis sets. The RHF optimizations give good structural accuracy. However, the relative energy is sensitive to the basis set. Our study indicates that the 4-31G* basis set is much better to calculate the energy barrier of the ring inversion in the model Cl_2TiS_3 compound. The electron correlation effect at MP2 level plays an important role to reproduce the energy barrier.

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