A DFT and NBO Analysis of the Bonding in Titanocenyl Complexes containing a Five-membered L,L'-cyclic Ligand: L,L' = O,O'; S,S' or Se,Se'

Jeanet Conradie*

Department of Chemistry, University of the Free State, Bloemfontein 9301, South Africa

Received 4 August 2009, revised 2 February 2010, accepted 29 May 2010

ABSTRACT
An NBO analysis of the electron distribution in the DFT-optimized geometries of different Cp₂TiIV(L,L'-BID) complexes with L,L'-BID = dioxolene, dithiolene or diselenolene, showed that a large degree of folding along the L···L axis is needed for sufficient Ti←L π-donation. The out of plane folding for maximum Ti←L π-donation increases with larger Ti–L bond lengths: Cp₂TiIV(O,O'-BID) (–35 °) < Cp₂TiIV(S,S'-BID) (47 ° average) < Cp₂TiIV(Se,Se'-BID) (50 ° average).

KEYWORDS
Gaussian, NBO, titanocene.

1. Introduction
Titanocenyl dichloride, Cp₂TiICl₂ (Cp = cyclopentadienyl, η⁵-C₅H₅), is widely used in organometallic and organic synthesis both as a reagent and as a catalyst.¹ Free titanocene, Cp₂Ti, is a 14 electron species and is not isolable. However, a wide range of stable 16 electron Ti(IV) complexes of the type Cp₂TiIV(BID) where BID is a potentially bidentate ligand, exists.² The chemical reactivity of these complexes is largely determined by the relative frontier orbital energies.³ The frontier molecular orbitals (MOs) of the bent Cp₂TiIV² fragment are described by Lauher and Hoffmann⁴ as 1a (LUMO), b₁ (LUMO+1), 2a₁ (LUMO+2), b₂ (LUMO+3) and a₁ (LUMO+4) under C₂ᵥ symmetry (see Fig. 1).

Folding along the S···S hinge of the metallacycle in Cp₂Ti(dithiolene) complexes resulted in a stabilizing interaction between the empty acceptor LUMO 1a₁ orbital of the Cp₂TiIV² fragment and the HOMO (a π orbital of b₁ symmetry) of the dithiolene ligand.⁴ This stabilizing interaction is only possible if there is a symmetry lowering of the Cp₂Ti(dithiolene) complex and associated folding of the TiC₅ metallocycle with bending values θ well above 40 ° , as illustrated in Fig. 2. Similar folding is observed in Cp₂Ti(dioxolene)⁵ and Cp₂Ti(diselenolene)⁶ complexes.

Density functional theory (DFT) has become the method of choice for computational studies of medium-sized molecules.⁷ In this study we use the DFT approach to further understand the Ti-ligand bond and orbital mixing in a series of Cp₂TiIV(L,L'-BID) complexes with L,L'-BID = dianionic bidentate ligand with donor atoms L and L' containing different donor/acceptor properties, viz. L,L' = O,O'; S,S' or Se,Se'. An NBO analysis quantifies the degree of the Ti←ligand π-charge transfer.

2. Theoretical Approach
Density functional theory (DFT) calculations were carried out using the GAUSSIAN 03 program⁸ with the PW91 exchange and correlation functional.⁹ Optimizations were done in the gas phase with the 6-311G(d,p) basis set on all atoms. A spin-restricted formalism was used. The accuracy of the computational method was evaluated by comparing the root-mean-square (RMS) deviation between the optimized molecular structure and the crystal structure, using the non-hydrogen atoms in the molecule. RMS deviation values were calculated using the ‘RMS Compare Structures’ utility in ChemCraft Version 1.5.¹⁰ Whether artificially generated atomic coordinates, or coordinates obtained from X-ray crystal data were used in the input files, optimizations for each compound resulted in the same minimum energy optimized geometry. Optimized structures were verified as a minimum through frequency calculations. Unless indicated, no symmetry limitations were imposed on the calculations. Geometries obtained from DFT calculations were used to perform an NBO analysis by using the NBO 3.1 module¹² in GAUSSIAN 03.³

3. Results and Discussion
Density functional theory (DFT) calculations were carried out on the series of d⁶ Cp₂TiIV⁷(L,L'-BID) complexes containing a five-membered L,L'-cyclic ligand with L,L' = O,O'; S,S' or Se,Se', with known crystal structures in order to validate the reliability of the computational method used. Selected calculated and experimental geometrical parameters of these Cp₂TiIV⁷(L,L'-BID) complexes are presented in Table 1. The validity of the density functional method is obtained by comparing the calculated data with the known single crystal X-ray diffraction structural data of these complexes. The root-mean-square distance (RMSD) values calculated for non-hydrogen atoms for the best three-dimensional superposition of calculated structures on experimental structures give a qualitative measurement of the accuracy of the ground state geometries of the calculated structures. Excellent agreement between experimental and theoretical structures was obtained as reflected by the RMSD values less than 0.02 Å, except for the Cp₂TiIV⁷(benzil-O,O') complex with a RMSD value of 0.46 Å. The large RMSD value of Cp₂TiIV⁷(benzil-O,O') is a result of the rotation of the Cp rings in the optimized complex relative to the experimental structure. All the bonds in the Ti-L,L' ring structure of the different Cp₂TiIV⁷(L,L'-BID) complexes in Table 1 were reproduced by DFT calculations within 0.02 Å for Ti-L bonds, within 0.03 Å for L-C bonds and within 0.01–0.04 Å for C-C bonds from the experimental values. Since comparisons of
experimental metal-ligand bond lengths with calculated bond lengths below a threshold of 0.02 Å are considered as meaningful, the computational method used therefore gives an excellent account of experimental bond lengths. The L-Ti-L' angles were calculated accurately within 1.1°. DFT-optimized structures containing titanocene with the Cp rings in the staggered or in the eclipsed conformation are approximately equi-energetic, with no preference for either conformation. Especially pleasing is the fact that all the models optimized spontaneously to C2v symmetry around the metal centre in agreement with the experimental crystal structures. The folding around the L-L'-axis, measured by the angle θ between the plane through the Ti-L-L' atoms and the plane through the L'-L-C-C' atoms (Fig. 2), is reproduced by the DFT calculations within 1.1°. The increasing order of experimental bending angle θ goes from Cp2Ti(μ-O,O'-BID) (~35°) to Cp2Ti(μ-S,S'-BID) (48° average) to Cp2Ti(μ-Se,Se'-BID) (50° average) also is well reproduced by the DFT calculations.

The Cp2Ti(μ-L,L'-BID) complexes are formally 16-electron d8 complexes if only Ti-Lα-bonding is considered. The Kohn-Sham molecular orbitals (MOs) of simplified Cp2Ti(d8)(L,L'-BID) models, viz., Cp2Ti(η2-L(CH3)=C(CH3)L) (L = O, S, Se) with C2v symmetry constraint were constructed to investigate how the orbital mixing looks for these complexes. The ordering and character of the frontier MOs of the simplified models 1–3 are very similar. Figures S1 and S2 of the supplementary material give presentations of a number of MOs of 1–3, including the MOs of the free ligands (optimized geometries) associated with these complexes. The MOs are stabilized by the expected σ-type interactions between the Cp2Ti(μ) complex and the L,L'-BID fragment. For example for Cp2Ti(η2-SeC(CH3)=C(CH3)Se), the filled HOMO-2 of the ligand of symmetry a1 donates electron density into the empty 2a1 LUMO+2 fragment MO of Cp2Ti(μ) to form the α HOMO-4 of the complex. The filled HOMO-1 of the ligand of symmetry b2 donates electron density into the empty b1 LUMO+1 fragment MO of Cp2Ti(μ) to form the α HOMO-3 of the complex. A presentation of the MOs involved in these Ti-L σ interactions is illustrated schematically in Fig. 3.

Out of plane π-type interactions involving the a1, LUMO of the Cp2Ti2+ fragment and the b1, HOMO of the ligand, as illustrated schematically in Fig. 2, are observed in the HOMO of all three complexes. The electron count for these formally 16-electron complexes is increased by Ti-Lπ donation (see Fig. 3 for the HOMO of 3 to visualize the Ti-Lπ interaction). This interaction in Cp2Ti(dioxolene) and Cp2Ti(diene) calculated with DFT in this study, is similar to the interaction described earlier on the basis of EH calculations, for 5-membered metallacycle Cp2Ti(μ-dithiolene) complexes.53

The bond energies, ΔE, of the Ti-L bond lengths provide a good approximation to bond strength values. ΔE is the energy associated with the interaction between the two fragments Cp2Ti(μ) and (L,L'-BID)−, which both possess the local equilibrium geometry of the final molecule, and which both have an electronic structure suitable for bond formation. The bond energy values of the Ti-L bonds of the different Cp2Ti(μ) complexes calculated with DFT in this study are tabulated in Table 1. The calculated values show that for the simplified models:

\[
\Delta E = \begin{cases} 
\text{Cp2Ti(η2-OC(CH3)=C(CH3)O)} & \text{(–2571 kJ mol}^{-1}) < \\
\text{Cp2Ti(η2-SC(CH3)=C(CH3)S)} & \text{(~–2204 kJ mol}^{-1}) < \\
\text{Cp2Ti(η2-SeC(CH3)=C(CH3)Se)} & \text{(~–2179 kJ mol}^{-1}) \\
\end{cases}
\]

\[d(\text{Ti-O})(1.966 \text{ Å}) < d(\text{Ti-S})(2.415 \text{ Å}) < d(\text{Ti-Se})(2.557 \text{ Å});\]

\[\theta \text{ Cp2Ti(η2-OC(CH3)=C(CH3)O)(40.5°) < } \]

\[\theta \text{ Cp2Ti(η2-SC(CH3)=C(CH3)S)(44.9°) < } \]

\[\theta \text{ Cp2Ti(η2-SeC(CH3)=C(CH3)Se)(48.6°).} \]

Thus the bond energy, ΔE, is the strongest for 1, which has the shortest Ti-L bond length. More folding is possible for 2 and 3 with longer Ti-L bond lengths in order to get the largest bond strength possible for these complexes. The experimental systems show the same trend.

The Ti-L bond energy, ΔE, the total energy and the corresponding Ti-L bond length as functions of the folding angle, θ, around the L-L'-axis for the simplified models 1–3, are illustrated in Fig. 4. For both complexes Cp2Ti(η2-SC(CH3)=C(CH3)S)(2, and...
Table 1. Selected NPA charge, bond energy of the Ti-L bond and geometrical parameters for the indicated experimental Cp₃Ti(L₂BID) compounds (optimized with no symmetry constraint) as well as the simplified models 1−3 (optimized with C₃ symmetry constraint).

<table>
<thead>
<tr>
<th></th>
<th>d(Ti-L) Å</th>
<th>d(Ti-L) Å</th>
<th>d(L-C) Å</th>
<th>d(L-C') Å</th>
<th>d(C-C') Å</th>
<th>&lt;L−Ti−L(^{-})</th>
<th>θ°</th>
<th>RMSD Å</th>
<th>ΔE[kJ mol(^{-1})]</th>
<th>q(Ti) e (^{-})</th>
<th>q(L) e (^{-})</th>
<th>q(L') e (^{-})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exp</td>
<td>calc</td>
<td>exp</td>
<td>calc</td>
<td>exp</td>
<td>calc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.967</td>
<td>1.966</td>
<td>1.349</td>
<td>1.349</td>
<td>1.385</td>
<td>82.6</td>
<td></td>
<td>40.5</td>
<td>-2571</td>
<td>1.312</td>
<td>-0.627</td>
<td>-0.627</td>
<td>this study</td>
</tr>
<tr>
<td></td>
<td>1.965</td>
<td>1.967</td>
<td>1.960</td>
<td>1.954</td>
<td>1.361</td>
<td>1.341</td>
<td>1.337</td>
<td>1.349</td>
<td>1.370</td>
<td>1.407</td>
<td>81.8</td>
<td>81.2</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2.415</td>
<td>2.415</td>
<td>1.758</td>
<td>1.758</td>
<td>1.380</td>
<td>81.9</td>
<td></td>
<td>44.9</td>
<td>-2268</td>
<td>1.274</td>
<td>-0.622</td>
<td>-0.620</td>
<td>this study</td>
</tr>
<tr>
<td></td>
<td>2.418</td>
<td>2.428</td>
<td>2.411</td>
<td>2.417</td>
<td>1.736</td>
<td>1.766</td>
<td>1.766</td>
<td>1.410</td>
<td>1.431</td>
<td>81.9</td>
<td>83.0</td>
<td>47.3</td>
<td>46.4</td>
</tr>
<tr>
<td></td>
<td>2.433</td>
<td>2.453</td>
<td>2.430</td>
<td>2.446</td>
<td>1.735</td>
<td>1.757</td>
<td>1.717</td>
<td>1.736</td>
<td>1.357</td>
<td>84.4</td>
<td>84.4</td>
<td>47.5</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>2.412</td>
<td>2.428</td>
<td>2.416</td>
<td>2.438</td>
<td>1.733</td>
<td>1.751</td>
<td>1.735</td>
<td>1.743</td>
<td>1.374</td>
<td>82.5</td>
<td>82.9</td>
<td>49.3</td>
<td>49.0</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>2.424</td>
<td>2.438</td>
<td>2.415</td>
<td>2.432</td>
<td>1.735</td>
<td>1.749</td>
<td>1.739</td>
<td>1.747</td>
<td>1.371</td>
<td>83.0</td>
<td>83.6</td>
<td>47.5</td>
<td>46.6</td>
</tr>
<tr>
<td></td>
<td>2.557</td>
<td>2.557</td>
<td>1.929</td>
<td>1.929</td>
<td>1.369</td>
<td>82.5</td>
<td></td>
<td>48.6</td>
<td>-2197</td>
<td>1.003</td>
<td>-0.046</td>
<td>-0.046</td>
<td>this study</td>
</tr>
<tr>
<td></td>
<td>2.546</td>
<td>2.552</td>
<td>2.564</td>
<td>2.560</td>
<td>1.908</td>
<td>1.919</td>
<td>1.909</td>
<td>1.920</td>
<td>1.407</td>
<td>82.1</td>
<td>82.9</td>
<td>50.0</td>
<td>48.7</td>
</tr>
<tr>
<td></td>
<td>2.568</td>
<td>2.579</td>
<td>2.533</td>
<td>2.528</td>
<td>1.879</td>
<td>1.893</td>
<td>1.898</td>
<td>1.911</td>
<td>1.363</td>
<td>82.6</td>
<td>83.1</td>
<td>47.8</td>
<td>47.8</td>
</tr>
<tr>
<td></td>
<td>2.548</td>
<td>2.576</td>
<td>2.543</td>
<td>2.555</td>
<td>1.895</td>
<td>1.901</td>
<td>1.902</td>
<td>1.909</td>
<td>1.369</td>
<td>82.6</td>
<td>82.4</td>
<td>52.7</td>
<td>51.0</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>2.554</td>
<td>2.569</td>
<td>2.546</td>
<td>2.548</td>
<td>1.894</td>
<td>1.904</td>
<td>1.903</td>
<td>1.913</td>
<td>1.380</td>
<td>82.4</td>
<td>82.8</td>
<td>50.1</td>
<td>49.2</td>
</tr>
</tbody>
</table>

\(^a\) RMSD values, in Å, are root mean square atom positional deviations, calculated for non-hydrogen atoms for the best three-dimensional superposition of calculated structures on experimental structures.

\(^b\) ΔE is the calculated bond energy of the Ti-L bonds in kJ mol\(^{-1}\).

\(^c\) Simplified molecules not included in the calculation of the average values.
CP₂Ti(L=O, S or Se) complexes. The natural atomic charge on Ti and the minimum degree of folding was observed experimentally for the real complexes (see Table 1).

To explore the electron density of the NBO from a single complex perspective to eliminate steric effects of the coordinating atom L, the natural charges as a function of folding angle for complexes 1–3 are given in Table 2. For both complexes 2 and 3, the minimum (positive) natural charge on Ti and the minimum (negative) natural charge on L correspond to the minimum energy geometry. This implies that the bending of complexes 2 and 3 is optimal for maximum $\pi$-bonding from the lone pairs on L to the empty Ti-d orbitals. Complex 1 did not follow this trend.

The basic parameters of the natural orbitals of bonds and lone electron pairs (LPs) which involve the L (L = O, S or Se) and titanium atoms for 1–3 are listed in Table 3. For each O atom in 1 one natural O-C bond orbital and three lone pair orbitals were detected. For each L atom in 2 (L=S) and 3 (L=Se) one natural L-C bond orbital, one natural Ti-L bond orbital and two lone pair orbitals were detected. Due to $C_{3v}$ symmetry the NBOs on L and L' have the same character.

Each L-C NBO is a 2-centre bond (BD) with a population of 1.983, 1.972 and 1.965 $e$ for 1–3, respectively, showing small deviations from an ideal Lewis structure. The O-C NBO of 1 has ca. 66 $%$ O character and 34 $%$ C character and is polarized towards the oxygen atom because O has a higher electronegativity.

The S-C and Se-C NBOs of 2 and 3 are less polarized, which is in agreement with the similar electronegativities of S, Se and C. Figure 5 (middle row) gives a visualization of the bonding and antibonding O-C and Se-C NBOs.

No natural Ti-O bond orbital was detected for 1. The natural bond length allows for a greater folding before the L,L'-BID ligand collides with the cyclopentadienyl ligand. It is expected that complexes with a larger degree of folding need a larger degree of $\pi$-bonding. This order is the same as the increasing order of the folding of complexes 1–3. A longer Ti-L bond length allows for a greater folding before the L,L'-BID ligand collides with the cyclopentadienyl ligand. It is expected that complexes with a larger degree of folding need a larger degree of $\pi$-bonding between the empty acceptor LUMO 1a orbital of the CP₂Ti²⁻ fragment and the HOMO b$_1$ orbital of the L,L'-BID ligand for the same Ti-L bond energy. Exactly the same degree of folding was observed experimentally for the real complexes (see Table 1).

To explore the electron density of the NBO from a single complex perspective to eliminate steric effects of the coordinating atom L, the natural charges as a function of folding angle for complexes 1–3 are given in Table 2. For both complexes 2 and 3, the minimum (positive) natural charge on Ti and the minimum (negative) natural charge on L correspond to the minimum energy geometry. This implies that the bending of complexes 2 and 3 is optimal for maximum $\pi$-bonding from the lone pairs on L to the empty Ti-d orbitals. Complex 1 did not follow this trend.

The basic parameters of the natural orbitals of bonds and lone electron pairs (LPs) which involve the L (L = O, S or Se) and titanium atoms for 1–3 are listed in Table 3. For each O atom in 1 one natural O-C bond orbital and three lone pair orbitals were detected. For each L atom in 2 (L=S) and 3 (L=Se) one natural L-C bond orbital, one natural Ti-L bond orbital and two lone pair orbitals were detected. Due to $C_{3v}$ symmetry the NBOs on L and L' have the same character.

Each L-C NBO is a 2-centre bond (BD) with a population of 1.983, 1.972 and 1.965 $e$ for 1–3, respectively, showing small deviations from an ideal Lewis structure. The O-C NBO of 1 has ca. 66 $%$ O character and 34 $%$ C character and is polarized towards the oxygen atom because O has a higher electronegativity. The S-C and Se-C NBOs of 2 and 3 are less polarized, which is in agreement with the similar electronegativities of S, Se and C. Figure 5 (middle row) gives a visualization of the bonding and antibonding O-C and Se-C NBOs.

No natural Ti-O bond orbital was detected for 1. The natural
The orbitals of the three lone pairs of each oxygen atom differ essentially in the nature of hybridization, energy and population (see Table 3). The lone electron pair LP1(O), with minimum energy, corresponds to the hybrid orbital of approximately 54% s and 46% p character. LP3(O) with 8% s and 92% p character is oriented along the Ti-O axis (see Fig. 5, top left). This indicates a σ-bond between Ti and O. LP3(L) was not detected for 2 and 3, having a natural Ti-L bond orbital instead. The energies of LP2(O) and LP3(O) on O, with a p electron character of 92–96%, are ca. 0.3 a.u. higher than that of LP1(O). The populations of the LP2(O) and LP3(O) orbitals are noticeably lower than that of the LP1(O) orbital. Electron density from the three LP orbitals of oxygen is strongly delocalized into the LP*: Ti-d orbitals – the occupancy of the oxygen LP orbitals is between 1.62 and 1.95 e.

Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>Dihedral angle Ti-L-C'/°</th>
<th>Folding angle, θ'/°</th>
<th>d(Ti-L)/Å</th>
<th>q(Ti)/e</th>
<th>q(L)/e</th>
<th>Bond energy/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (L = O)</td>
<td>0.0</td>
<td>0.0</td>
<td>1.918</td>
<td>1.453</td>
<td>-0.645</td>
<td>-2587</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>12.4</td>
<td>1.934</td>
<td>1.415</td>
<td>-0.643</td>
<td>-2576</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>27.0</td>
<td>1.955</td>
<td>1.347</td>
<td>-0.636</td>
<td>-2568</td>
</tr>
<tr>
<td></td>
<td>29.9</td>
<td>40.5</td>
<td>1.966</td>
<td>1.312</td>
<td>-0.627</td>
<td>-2571</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>40.6</td>
<td>1.966</td>
<td>1.312</td>
<td>-0.627</td>
<td>-2571</td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>57.0</td>
<td>1.986</td>
<td>1.293</td>
<td>-0.616</td>
<td>-2572</td>
</tr>
<tr>
<td></td>
<td>47.0</td>
<td>68.1</td>
<td>2.019</td>
<td>1.286</td>
<td>-0.608</td>
<td>-2568</td>
</tr>
<tr>
<td>2 (L = S)</td>
<td>0.0</td>
<td>0.0</td>
<td>2.486</td>
<td>1.103</td>
<td>-0.144</td>
<td>-2127</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>13.3</td>
<td>2.442</td>
<td>1.062</td>
<td>-0.129</td>
<td>-2149</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>26.9</td>
<td>2.422</td>
<td>1.017</td>
<td>-0.104</td>
<td>-2176</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>41.2</td>
<td>2.414</td>
<td>1.002</td>
<td>-0.094</td>
<td>-2197</td>
</tr>
<tr>
<td></td>
<td>32.5</td>
<td>44.9</td>
<td>2.415</td>
<td>0.999</td>
<td>-0.089</td>
<td>-2204</td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>56.9</td>
<td>2.424</td>
<td>1.021</td>
<td>-0.096</td>
<td>-2201</td>
</tr>
<tr>
<td></td>
<td>47.0</td>
<td>69.1</td>
<td>2.457</td>
<td>1.060</td>
<td>-0.103</td>
<td>-2190</td>
</tr>
<tr>
<td>3 (L = Se)</td>
<td>0.0</td>
<td>0.0</td>
<td>2.634</td>
<td>1.105</td>
<td>-0.104</td>
<td>-2102</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>13.4</td>
<td>2.582</td>
<td>1.014</td>
<td>-0.066</td>
<td>-2124</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>27.5</td>
<td>2.562</td>
<td>1.018</td>
<td>-0.062</td>
<td>-2149</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>42.0</td>
<td>2.554</td>
<td>1.002</td>
<td>-0.051</td>
<td>-2170</td>
</tr>
<tr>
<td></td>
<td>34.5</td>
<td>48.6</td>
<td>2.557</td>
<td>1.003</td>
<td>-0.046</td>
<td>-2179</td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>57.2</td>
<td>2.569</td>
<td>1.021</td>
<td>-0.052</td>
<td>-2179</td>
</tr>
<tr>
<td></td>
<td>47.0</td>
<td>68.7</td>
<td>2.605</td>
<td>1.065</td>
<td>-0.065</td>
<td>-2167</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>NBO type</th>
<th>1 (L = O)</th>
<th>2 (L = S)</th>
<th>3 (L = Se)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD(Ti - L)</td>
<td>–</td>
<td>–</td>
<td>1.9301⁻¹</td>
</tr>
<tr>
<td>BD*(Ti - L)</td>
<td>–</td>
<td>–</td>
<td>0.1784</td>
</tr>
<tr>
<td>LP*1(Ti)</td>
<td>0.5589</td>
<td>-0.0862</td>
<td>0.5132</td>
</tr>
<tr>
<td>LP*2(Ti)</td>
<td>0.5137</td>
<td>-0.0706</td>
<td>0.5058</td>
</tr>
<tr>
<td>LP*3(Ti)</td>
<td>0.5096</td>
<td>-0.0661</td>
<td>0.4518</td>
</tr>
<tr>
<td>LP*4(Ti)</td>
<td>0.5009</td>
<td>-0.0807</td>
<td>–</td>
</tr>
<tr>
<td>LP*5(Ti)</td>
<td>0.4068</td>
<td>-0.0752</td>
<td>–</td>
</tr>
<tr>
<td>LP*6(Ti)</td>
<td>0.1559</td>
<td>0.7136</td>
<td>0.2473</td>
</tr>
<tr>
<td>LP1(L)</td>
<td>1.9476</td>
<td>-0.5639</td>
<td>1.9665</td>
</tr>
<tr>
<td>LP2(L)</td>
<td>1.7234</td>
<td>-0.2585</td>
<td>1.6807</td>
</tr>
<tr>
<td>LP3(L)</td>
<td>1.6247</td>
<td>-0.3040</td>
<td>–</td>
</tr>
<tr>
<td>BD(L - C)</td>
<td>1.9826</td>
<td>-0.8206</td>
<td>1.9712⁻²</td>
</tr>
<tr>
<td>BD*(L - C)</td>
<td>0.0275</td>
<td>0.3524</td>
<td>0.0383</td>
</tr>
</tbody>
</table>

a 25.1% Ti and 74.9% S.

b 26.5% Ti and 73.5% Se.
c 66.4% O and 33.6% C.
d 46.5% S and 53.5% C.
e 43.6% Se and 56.4% C.
only 46% p character. The natural bond orbitals BD*(Ti – S) and BD*(Ti – Se) in \(2\) and \(3\) interact with a lone pair NBO on Ti of 62–64% s and 34–37% p character and electron occupation of \(0.25\) e.

These interactions and the occupancy of the Ti-d orbitals of complexes \(1\)–\(3\) reflect the increase in the electron count of the formal 16-electron \(d^0\) Cp2TiIV(L,L'-BID) complexes.

4. Conclusions

Cp2TiIV(L,L'-BID) 16-electron \(d^0\) complexes all exhibit a striking structural flexibility in such a way as to increase the electron count by Ti\(\cdots\)L\(\pi\) donation by symmetry lowering and folding of the L,L'-BID ligand around the L \(\cdots\) L' axis. Computational evidence of the \(\pi\)-bonding is determined by a natural bond orbital (NBO) analysis. The out of plane folding angle for maximum Ti\(\cdots\)L\(\pi\) donation increases with larger Ti–L bond lengths: CpTiIV(O,O'-BID) \((\sim 35°)\) < CpTiIV(S,S'-BID) \((47° \text{ average})\) < CpTiIV(Se,Se'-BID) \((50° \text{ average})\). The bond energies, \(\Delta E\), of the Ti–L bonds of complexes CpTiIV(\(\eta^2\)-SC(CH3)=C(CH3)S), \(2\), and CpTiIV(\(\eta^2\)-SeC(CH3)=C(CH3)Se), \(3\), become stronger (more negative) with increased folding until the point where a steric repulsion between the L,L'-BID and the cyclopentadienyl ligand leads to a weakening in \(\Delta E\). The most stable geometries of \(2\) and \(3\) have the shortest Ti–L bond lengths and the strongest bonding energies, \(\Delta E\), of the Ti–L bond. \(\Delta E\) as well as the total energy of complex \(1\) is not very sensitive to the folding angle, \(\theta\), between the plane through the Ti–L–L' atoms and the plane through the L'–L–C–C' atoms.

Table 4 Interaction energy, \(E\), between donor and acceptor orbitals for the simplified models \(1\)–\(3\) under a \(C_s\) symmetry constraint. Only values \(>65\) kJ mol\(^{-1}\) are tabulated.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Donor NBO</th>
<th>Acceptor NBO</th>
<th>(E/\text{kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>LP3(O)</td>
<td>LP*2(Ti)</td>
<td>214.6</td>
</tr>
<tr>
<td></td>
<td>LP3(O)</td>
<td>LP*3(Ti)</td>
<td>97.3</td>
</tr>
<tr>
<td></td>
<td>LP2(O)</td>
<td>LP*3(Ti)</td>
<td>69.1</td>
</tr>
<tr>
<td></td>
<td>LP*6(Ti)</td>
<td>RY*3(O)</td>
<td>68.1</td>
</tr>
<tr>
<td>(2)</td>
<td>BD*(Ti-S)</td>
<td>LP*6(Ti)</td>
<td>292.7</td>
</tr>
<tr>
<td>(3)</td>
<td>BD*(Ti-Se)</td>
<td>LP*6(Ti)</td>
<td>328.1</td>
</tr>
</tbody>
</table>

**Figure 5** Selected NBOs of the simplified models Cp2Ti(dioxolene) (1), Cp2Ti(dithiolene) (2) and Cp2Ti(diselenolene) (3). A contour of \(0.1\) e Å\(^{-3}\) has been used for the orbital plots. Colour code for atoms: Ti (lime green), C (black), H (white), S (green-yellow), Se (bright yellow) and O (red).

**Supplementary Material**

A presentation of a number of MOs of the simplified models \(1\)–\(3\), including the ligand MOs associated with these complexes, and a summary of the optimized Cartesian coordinates of the studied molecules are provided in the supplementary material.

**Acknowledgements**

Financial assistance by the South African National Research Foundation, under grant number 2067416, and the Central Research Fund of the University of the Free State is gratefully acknowledged.

**References and Notes**

RESEARCH ARTICLE

J. Conradie,


<http://journals.sabinet.co.za/sajchem/>.

(a) A. Kuhn, A. Muller and J. Conradie, Polyhedron, 2009, 28, 966–974;

2

16

In order to access the extent of donated and/or backdonated charges, single point calculations for the ligand and the metallic fragment with their frozen geometry in the complex were done. The increase in the natural charge on L and the decrease of the natural charge on Ti gave the same results as above: increase in the natural charge on L: 0.227 $e$ (O) < 0.555 $e$ (S) < 0.586 $e$ (Se), decrease in the natural charge on Ti: 0.230 $e$ on Ti: 0.230 $e$ (O) < 0.555 $e$ (S) < 0.586 $e$ (Se).

17


18


19


20

**Supplementary Material to:**


![Figure S1](image1.png)

*Fig. S1* The frontier MOs of [Cp₂Ti³⁺]²⁺. Colour code for atoms: Ti (lime green), C (black) and H (white).
Fig. S2 The frontier MOs of simplified \([\text{Cp}_2\ce{Ti}^\sigma(L,L'-\text{BID})]\) models, \(L,L'-\text{BID} = \text{dioxolene, dithiolene or diselenolene}\). Colour code for atoms: Ti (lime green), C (black), H (white), S (green-yellow), Se (bright yellow) and O (red). A \(C_2\) symmetry constraint was imposed.
Optimized Cartesian coordinates/Å
All compounds were optimized with Gaussian/PW91/6-311G(d,p).

1. \( \text{Cp}_2\text{Ti}(\eta^2-\text{OC(CH}_3)=\text{C(CH}_3)\text{O}) \)

<table>
<thead>
<tr>
<th>Atom</th>
<th>X(Å)</th>
<th>Y(Å)</th>
<th>Z(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>-0.000626000</td>
<td>-0.473026000</td>
<td>0.000000000</td>
</tr>
<tr>
<td>O</td>
<td>-0.741253000</td>
<td>0.799931000</td>
<td>1.286531000</td>
</tr>
<tr>
<td>O</td>
<td>-0.741253000</td>
<td>0.799931000</td>
<td>-1.286531000</td>
</tr>
<tr>
<td>C</td>
<td>-0.580075000</td>
<td>1.999171000</td>
<td>0.694059000</td>
</tr>
<tr>
<td>C</td>
<td>-0.580075000</td>
<td>1.999171000</td>
<td>-0.694059000</td>
</tr>
<tr>
<td>C</td>
<td>2.116221000</td>
<td>-0.744718000</td>
<td>-1.151447000</td>
</tr>
<tr>
<td>H</td>
<td>2.110844000</td>
<td>-1.075524000</td>
<td>-2.186170000</td>
</tr>
<tr>
<td>C</td>
<td>2.117500000</td>
<td>0.605825000</td>
<td>0.704946000</td>
</tr>
<tr>
<td>H</td>
<td>2.079103000</td>
<td>1.483280000</td>
<td>1.542743000</td>
</tr>
<tr>
<td>C</td>
<td>2.112621000</td>
<td>-0.744718000</td>
<td>1.151447000</td>
</tr>
<tr>
<td>H</td>
<td>2.110844000</td>
<td>-1.075524000</td>
<td>2.186170000</td>
</tr>
<tr>
<td>C</td>
<td>2.117500000</td>
<td>0.605825000</td>
<td>-0.704946000</td>
</tr>
<tr>
<td>H</td>
<td>2.079103000</td>
<td>1.483280000</td>
<td>-1.542743000</td>
</tr>
<tr>
<td>C</td>
<td>2.140036000</td>
<td>0.658250000</td>
<td>0.704946000</td>
</tr>
<tr>
<td>H</td>
<td>2.108440000</td>
<td>1.483280000</td>
<td>1.542743000</td>
</tr>
<tr>
<td>C</td>
<td>2.140036000</td>
<td>0.658250000</td>
<td>-0.704946000</td>
</tr>
<tr>
<td>H</td>
<td>2.108440000</td>
<td>1.483280000</td>
<td>-1.542743000</td>
</tr>
<tr>
<td>C</td>
<td>2.108440000</td>
<td>0.658250000</td>
<td>0.704946000</td>
</tr>
<tr>
<td>H</td>
<td>2.108440000</td>
<td>1.483280000</td>
<td>1.542743000</td>
</tr>
<tr>
<td>C</td>
<td>2.108440000</td>
<td>0.658250000</td>
<td>-0.704946000</td>
</tr>
<tr>
<td>H</td>
<td>2.108440000</td>
<td>1.483280000</td>
<td>-1.542743000</td>
</tr>
<tr>
<td>C</td>
<td>2.140036000</td>
<td>0.658250000</td>
<td>0.704946000</td>
</tr>
<tr>
<td>H</td>
<td>2.108440000</td>
<td>1.483280000</td>
<td>1.542743000</td>
</tr>
<tr>
<td>C</td>
<td>2.140036000</td>
<td>0.658250000</td>
<td>-0.704946000</td>
</tr>
<tr>
<td>H</td>
<td>2.108440000</td>
<td>1.483280000</td>
<td>-1.542743000</td>
</tr>
<tr>
<td>C</td>
<td>2.140036000</td>
<td>0.658250000</td>
<td>0.704946000</td>
</tr>
<tr>
<td>H</td>
<td>2.108440000</td>
<td>1.483280000</td>
<td>1.542743000</td>
</tr>
<tr>
<td>C</td>
<td>2.140036000</td>
<td>0.658250000</td>
<td>-0.704946000</td>
</tr>
<tr>
<td>H</td>
<td>2.108440000</td>
<td>1.483280000</td>
<td>-1.542743000</td>
</tr>
</tbody>
</table>

2. \( \text{Cp}_2\text{Ti}^{IV}(O,O'-\text{BID}) \)

<table>
<thead>
<tr>
<th>Atom</th>
<th>X(Å)</th>
<th>Y(Å)</th>
<th>Z(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>-0.000626000</td>
<td>-0.473026000</td>
<td>0.000000000</td>
</tr>
<tr>
<td>O</td>
<td>0.438262000</td>
<td>4.146894000</td>
<td>2.963736000</td>
</tr>
<tr>
<td>O</td>
<td>0.438262000</td>
<td>4.146894000</td>
<td>-2.963736000</td>
</tr>
<tr>
<td>C</td>
<td>1.671146000</td>
<td>4.877002000</td>
<td>2.687044000</td>
</tr>
<tr>
<td>C</td>
<td>2.835352000</td>
<td>5.218573000</td>
<td>1.853002000</td>
</tr>
<tr>
<td>C</td>
<td>1.622403000</td>
<td>4.584466000</td>
<td>0.057139000</td>
</tr>
<tr>
<td>C</td>
<td>2.662044000</td>
<td>4.796401000</td>
<td>5.085207000</td>
</tr>
<tr>
<td>C</td>
<td>2.640146000</td>
<td>6.010509000</td>
<td>0.701533000</td>
</tr>
<tr>
<td>C</td>
<td>1.309042000</td>
<td>1.886461000</td>
<td>2.700469000</td>
</tr>
<tr>
<td>C</td>
<td>3.596555000</td>
<td>5.847933000</td>
<td>5.014907000</td>
</tr>
<tr>
<td>C</td>
<td>3.589372000</td>
<td>4.176507000</td>
<td>7.252890000</td>
</tr>
<tr>
<td>C</td>
<td>4.128148000</td>
<td>4.713230000</td>
<td>2.104423000</td>
</tr>
<tr>
<td>C</td>
<td>5.191160000</td>
<td>5.021978000</td>
<td>1.255784000</td>
</tr>
<tr>
<td>C</td>
<td>-2.218557000</td>
<td>4.672147000</td>
<td>4.229858000</td>
</tr>
<tr>
<td>C</td>
<td>4.524741000</td>
<td>6.043951000</td>
<td>6.038957000</td>
</tr>
<tr>
<td>C</td>
<td>0.354248000</td>
<td>1.301927000</td>
<td>3.580808000</td>
</tr>
<tr>
<td>C</td>
<td>-2.907440000</td>
<td>3.232690000</td>
<td>2.573167000</td>
</tr>
<tr>
<td>C</td>
<td>3.706877000</td>
<td>6.320570000</td>
<td>-0.141330000</td>
</tr>
<tr>
<td>C</td>
<td>0.705622000</td>
<td>2.032435000</td>
<td>1.425554000</td>
</tr>
<tr>
<td>C</td>
<td>-0.829194000</td>
<td>1.064546000</td>
<td>2.840316000</td>
</tr>
<tr>
<td>C</td>
<td>-0.617248000</td>
<td>1.531585000</td>
<td>1.508188000</td>
</tr>
<tr>
<td>C</td>
<td>-2.475222000</td>
<td>4.440882000</td>
<td>1.958392000</td>
</tr>
<tr>
<td>C</td>
<td>4.530189000</td>
<td>5.206339000</td>
<td>7.161350000</td>
</tr>
<tr>
<td>C</td>
<td>-2.085911000</td>
<td>5.332641000</td>
<td>2.987544000</td>
</tr>
<tr>
<td>C</td>
<td>-2.719990000</td>
<td>3.367375000</td>
<td>3.978151000</td>
</tr>
<tr>
<td>C</td>
<td>4.980094000</td>
<td>5.831517000</td>
<td>0.132244000</td>
</tr>
<tr>
<td>H</td>
<td>-1.911423000</td>
<td>3.189791000</td>
<td>6.309462000</td>
</tr>
<tr>
<td>C</td>
<td>1.635438000</td>
<td>6.372215000</td>
<td>0.484100000</td>
</tr>
<tr>
<td>C</td>
<td>2.320179000</td>
<td>2.177885000</td>
<td>2.961991000</td>
</tr>
<tr>
<td>Atoms</td>
<td>x</td>
<td>y</td>
<td>z</td>
</tr>
<tr>
<td>---------------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td>H</td>
<td>3.58771500</td>
<td>6.52321400</td>
<td>4.16002800</td>
</tr>
<tr>
<td>H</td>
<td>3.57631700</td>
<td>3.52667400</td>
<td>8.13164000</td>
</tr>
<tr>
<td>H</td>
<td>4.29785800</td>
<td>4.07130500</td>
<td>2.96875800</td>
</tr>
<tr>
<td>H</td>
<td>6.18217800</td>
<td>4.61711800</td>
<td>1.46616400</td>
</tr>
<tr>
<td>H</td>
<td>–1.91562000</td>
<td>5.06313400</td>
<td>5.19509600</td>
</tr>
<tr>
<td>H</td>
<td>5.23738200</td>
<td>6.86705700</td>
<td>5.96893700</td>
</tr>
<tr>
<td>H</td>
<td>0.51125500</td>
<td>1.06899400</td>
<td>4.62975200</td>
</tr>
<tr>
<td>C</td>
<td>–3.29396700</td>
<td>2.36073300</td>
<td>2.06137600</td>
</tr>
<tr>
<td>H</td>
<td>3.53698100</td>
<td>6.94436000</td>
<td>–1.02032900</td>
</tr>
<tr>
<td>H</td>
<td>1.16457000</td>
<td>2.48642600</td>
<td>0.55185900</td>
</tr>
<tr>
<td>H</td>
<td>–1.74112600</td>
<td>0.61554200</td>
<td>3.22247100</td>
</tr>
<tr>
<td>H</td>
<td>–1.33867000</td>
<td>1.50068000</td>
<td>0.69647800</td>
</tr>
<tr>
<td>H</td>
<td>–2.45409300</td>
<td>4.64653700</td>
<td>0.89175100</td>
</tr>
<tr>
<td>H</td>
<td>5.25463200</td>
<td>5.36476000</td>
<td>7.96114100</td>
</tr>
<tr>
<td>H</td>
<td>–1.63122100</td>
<td>6.31508800</td>
<td>2.84041700</td>
</tr>
<tr>
<td>H</td>
<td>–2.93242800</td>
<td>2.61061400</td>
<td>4.72798400</td>
</tr>
<tr>
<td>H</td>
<td>5.82192700</td>
<td>6.06889100</td>
<td>–0.53078300</td>
</tr>
</tbody>
</table>

3 \( \text{Cp}_3\text{Ti}(\eta^2-\text{SC}(\text{CH}_3)\text{S}) \) complex 2

| Ti          | 0.03727300 | –0.74114400 | 0.00000000 |
| S           | –0.81402500| 0.86363200  | 1.58795600 |
| S           | –0.81402500| 0.86363200  | –1.58795600|
| C           | –0.34948900| 2.30754700  | 0.69105300 |
| C           | –0.34948900| 2.30754700  | –0.69105300|
| C           | 2.12114800 | –1.06782900 | –1.15041000|
| C           | 2.11111800 | –1.39850300 | 2.18500400 |
| C           | 2.15467000 | –1.89890700 | 0.00000000 |
| C           | 2.17568200 | –2.98418400 | 0.00000000 |
| C           | –1.59662500| –2.05122600 | –1.15049300|
| H           | –1.84986700| –1.82273300 | –2.18178500|
| C           | –0.57087200| –2.92674000 | –0.71143500|
| H           | 0.09630000 | –3.49421600 | –1.35305600|
| C           | –0.57087200| –2.92674000 | 0.71143500  |
| H           | 0.09630000 | –3.49421600 | 1.35305600 |
| C           | –1.59662500| –2.05122600 | 1.15049300 |
| H           | –1.84986700| –1.82273300 | 2.18178500 |
| C           | –2.23302000| –1.50268800 | 0.00000000 |
| H           | –3.03571400| –0.78103300 | 0.00000000 |
| C           | –0.03789300| 3.51577000  | –1.53739800|
| H           | –0.70566900| 3.54578100  | –2.40968300|
| C           | –0.14552400| 4.45922100  | –0.98691100|
| H           | 0.99264600 | 3.47499700  | –1.92752500|
| C           | –0.03789300| 3.51577000  | 1.53739800 |
| H           | –0.14552400| 4.45922100  | 0.98691100 |
| C           | –0.70566900| 3.54578100  | 2.40968300 |
| H           | 0.99264600 | 3.47499700  | 1.92752500 |

4 \( \text{Cp}_3\text{Ti}(S,S'–\text{BID}) \) complex: \( \text{Cp}_3\text{Ti}^v(1,2–\text{benzene–dithionato}) \)

| C            | 1.66631000 | 2.75968000 | –0.27701600|
| C            | 3.29366900 | –1.41080000| –0.54362200|
| C            | 2.22789500 | –0.58821000| –0.09533900|
| C            | 5.52315300 | 2.06562400 | –2.05089900|
| C            | 5.18041400 | 1.43745600 | –3.27755200|
| C            | 5.34738400 | 0.03730700 | –3.11598400|
| C            | 5.80113300 | –0.20033900| –1.78966600|
| C            | 5.90134400 | 1.05136800 | –1.12788300|
| C            | 0.78230000 | 3.18678000 | 0.73494500 |
| C            | –0.50488000| 3.61332200  | 0.42434000 |
| C            | –0.94290100| 3.61373600  | –0.91057600|
| C            | –0.09257300| 3.18533500  | –1.92498400|
| C            | 1.21973900 | 2.75663600 | –1.63624300|
| C            | 1.40587900 | –0.28979100| –1.20708600|
| C            | 1.95490700 | –0.93465000| –2.35271200|
| C            | 3.10619400 | –1.64451900| –1.93976200|
| S            | 2.32021400 | 2.29217000 | –2.93702000|
5  Cp₂Ti⁺(S,S'–BID) complex: Cp₂Ti⁺(ethylene–1,2–dithiolato)

6  Cp₂Ti⁺(S,S'–BID) complex: Cp₂Ti⁺(1,3–dithiole–2–thione–4,5–dithiolato)
7 Cp$_2$Ti(S,S'–BID) complex: Cp$_2$Ti(5,6–dihydro–1,4–dithiine–2,3–dithiolato)

8 Cp$_2$Ti($\eta^2$–SeC(CH$_3$)=C(CH$_3$)Se) complex 3
C 0.390946000 3.450043000 1.537789000
H 0.380496000 4.399504000 0.985735000
H –0.277159000 3.549976000 2.405155000
H 1.408989000 3.310690000 1.937079000

Cp₂Ti²⁺(Se,Se’–BID) complex: Cp₂TiIV(1,2–benzene–diselenato)

9

Ti 0.694089000 10.156462000 14.509038000
Se 0.315115000 8.282767000 12.778293000
Se –0.422154000 8.515940000 16.071600000
C 0.721950000 6.897505000 14.002724000
C 0.445993000 6.976490000 15.350031000
C 1.330453000 5.683147000 13.357719000
C 3.319480000 4.443814000 13.112011000
H 4.379857000 4.575361000 13.346624000
H 3.162847000 4.363223000 12.028799000
H 2.920666000 3.548190000 13.605852000
C 0.695629000 5.795953000 16.217058000
C 0.694337000 4.956362000 18.418901000
H 0.519007000 5.348774000 19.424836000
H 1.709744000 4.548180000 18.330027000
H –0.027141000 4.164520000 18.178077000
C 2.468024000 10.995997000 15.844971000
H 2.245205000 11.665061000 16.671190000
C 2.577909000 9.580174000 15.921693000
H 2.432426000 8.978850000 16.812618000
C 2.885260000 9.092465000 14.631267000
H 3.027477000 8.051591000 14.359888000
C 2.980319000 10.206829000 13.746338000
H 3.199741000 10.156165000 12.681476000
C 2.754900000 11.381035000 13.685034000
H 2.776520000 12.398126000 14.122086000
C –1.077439000 11.559190000 15.300000000
H –1.387058000 11.532465000 16.341166000
C –0.069264000 12.389922000 14.746608000
H 0.527055000 13.114418000 15.291963000
C 0.022428000 12.107164000 13.355262000
H 0.696179000 12.579299000 12.646828000
C –0.941557000 11.106922000 13.046879000
H –1.147602000 10.696030000 12.064597000
C –1.624038000 10.773337000 14.247258000
H –2.409288000 10.031557000 14.342134000
O 0.741587000 4.923536000 12.618549000
C 0.022428000 4.956362000 18.418901000
O 0.022428000 4.956362000 18.418901000
O 0.022428000 4.956362000 18.418901000
O 0.022428000 4.956362000 18.418901000

C 0.741587000 4.925356000 12.618549000

10

Cp₂Ti²⁺(Se,Se’–BID) complex: Cp₂TiIV(1,2-bis(methoxycarbonyl)ethylene–1,2–diselenolato–Se,Se’)

Se 1.789115000 2.886524000 3.882402000
Se 4.409720000 5.148610000 3.997125000
Ti 4.296345000 2.673688000 3.297119000
S 0.208079000 5.210338000 2.403273000
S –0.213665000 7.994254000 1.299653000
S 2.425748000 7.115511000 2.484466000
C 1.695313000 4.620510000 3.146441000
C 0.738385000 6.856106000 2.015829000
C 2.744106000 5.530297000 3.183215000
C 0.444754000 1.268911000 5.214910000
H 3.470304700 0.909253000 5.547033000
C 4.692544000 2.446181000 5.661568000
H 4.283092000 3.168347000 6.359467000
C 5.955101000 2.528644000 5.009923000
H 6.692019000 3.316298000 5.146808000
C 6.088648000 1.392618000 4.170718000
H 6.947565000 1.157192000 3.550823000
C 4.390165500 0.614196000 4.289436000
C 4.695662000 –0.326291000 3.781823000
C 4.818420000 3.701166000 1.163184000
H 5.099140000 4.746604000 1.096599000
C 3.506480000 3.181966000 1.038978000
H 2.604726000 3.758236000 0.888432000
C 3.574871000 1.764540000 1.196641000
11 Cp₂Ti²(Se,Se'–BID) complex: Cp₂Ti²(5,6–dihydro–1,4–dithiine–2,3–diselenolato–Se,Se')

C 4.934104000 1.413888000 1.372678000
H 5.323763000 0.407006000 1.485864000
C 5.705022000 2.614535000 1.384285000
H 6.782650000 2.685307000 1.498390000
C 3.616851000 3.438768000 15.558652000
C 2.288343000 3.798469000 15.637604000
S 1.397740000 4.638716000 14.356220000
S 4.779709000 3.817235000 14.274190000
C 2.350514000 4.106134000 12.879390000
C 3.790843000 4.588303000 12.915976000
C 3.511199000 5.762953000 17.733133000
C 2.687928000 5.949759000 18.880960000
C 4.786506000 5.325921000 18.167439000
C 4.755680000 5.223864000 19.382272000
C 3.461257000 5.634835000 20.023186000
C 3.602142000 2.766540000 20.976639000
H 4.266201000 3.297685000 21.650698000
C 2.808705000 1.300622000 19.394959000
C 3.981152000 1.741474000 20.071037000
C 2.289767000 2.973178000 20.849954000
H 1.653651000 3.686825000 21.406960000
C 1.710699000 2.063016000 19.877250000
H 2.758650000 0.534010000 18.629689000
H 0.676267000 1.945837000 19.568136000
H 5.581701000 4.916373000 20.216971000
H 1.653651000 6.275229000 18.872726000
H 3.212624000 5.929298000 16.704695000
H 3.127600000 5.688598000 21.055025000
H 5.633044000 5.094947000 17.530089000
H 2.289767000 3.013181000 12.796799000
H 1.818949000 4.552672000 12.025987000
H 4.322933000 4.298500000 11.997301000
H 4.985251000 1.352638000 19.925684000
H 3.830413000 5.677395000 13.016980000