Theoretical and Experimental Characterization of Cr–L Multiple Bonds (L = O, N, and C)

Chih-Chieh Wang, Ting-Hua Tang, and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China, and Department of Chemistry, Soochow University, Taipei, Taiwan, Republic of China

Received: March 27, 2000; In Final Form: August 4, 2000

A combined experimental and theoretical study on the bond characterization of Cr–L (L = O, N, C) multiple bonds is applied to a series of Cr-complexes: [(CO)2(Cl)Cr(V)(CPh)] 1; [Cr(V)(N)(bpb)] 2, and [Cr(V)(N-t-Bu)-(bpb)(Cl)] 3, where [bpb2− = (1,2-bis(pyridine-2-carboxamido)benzene)]; and [(TPPOMe)CrIVO] 4, where [TPPOMe = (5,10,15,20-p-methoxyphenyl)porphyrin]. Compounds 1 and 2 were investigated by accurate single-crystal X-ray diffraction. Detailed descriptions of Cr–C°carbyne, Cr–N°nitrido, Cr–N°imido, and Cr–O°oxo bonds will be given based on the natural bonding orbital (NBO) analyses and Fermi hole function. The bonding feature of all these multiple bonds is essentially a triple bond character consisting of one σ and two π bonds. The σ character of the Cr–L multiple bonds is a highly polarized one with the electron density strongly polarized toward L (O, N, C) ligands. The π character of the Cr–L multiple bonds depends on the nature of L ligand, i.e., with electron density polarized toward the Cr and O center for Cr–C°carbyne and Cr–O°oxo bond, respectively, whereas electron density is roughly equally distributed at both Cr and N for the Cr–N°nitrido and Cr–N°imido bonds. Bond characterizations are also shown in terms of Laplacian of electron density where the inner valence shell charge concentration (i-VSCC) is embedded. The isovalue surface of zero Laplacian of electron density reveals the shape of such i-VSCC at each chromium atom. Shapes around the Cr atom are a pressed disklike for 1 and 3 and inverted square pyramid for 2 and 4. The topological properties associated with the bond critical point (BCP) of Cr–L multiple bonds in these compounds indicate a strong covalent bond character. The order of the binding interaction is Cr–N°nitrido > Cr–O°oxo > Cr–N°imido > Cr–C°carbyne. The combined study of experiment and theory on 1 and 2 demonstrates good agreement between experiment and theory.

Introduction

Chemical bonding is a very important concept in understanding molecular behavior. Bond characterization is therefore becoming ever needed for predicting the physical and chemical properties of molecules. Combined experimental and theoretical studies1–6 has been used for such a purpose in terms of deformation density distribution and natural bond orbital analysis. Such studies do provide qualitative description of bonding type. However, the drawback in this method is the bias7–10 on the definition of the promolecule. The topological analysis of “Atoms in Molecules” theory11 brings in new insight on chemical bonding characterization. The bias on how to treat properly the promolecule model is no longer a problem since the topological properties analysis is based entirely on the total electron density of the molecule. Deformation density studies of Cr-complexes12–14 have revealed important aspects on the bonding features of various types of Cr–L multiple bonds. To give a quantitative description of the Cr–L multiple bond, four Cr-complexes, [(CO)2(Cl)Cr(V)(CPh)] 1,12 [Cr(V)(N)(bpb)] 2,13 [Cr(V)(N-t-Bu)-(bpb)(Cl)] 3,14 and [(TPPOMe)CrIVO] 4,14 with the Cr–C°carbyne, Cr–N°nitrido, Cr–N°imido, and Cr–O°oxo bond are chosen to be investigated by the topological analysis of the electron density distribution,11 natural bond orbital (NBO)13 analysis, and Fermi hole distribution.16–18 The topological properties associated with the BCP for various types of Cr–ligand bond are compared and discussed in detail between experiment and theory. The inner valence shell charge concentrations (i-VSCCs)19,20 of Cr atoms associated with their geometrical conformation are also investigated.

Computational Details

The geometries of compound 1, 2, 3, and 4 used for the theoretical calculations are taken from the diffraction data.12–14 Simplified model compound 3 [(Cl)(bpb)Cr(NCH3)] and 4 [(porphyrin)CrO] are used for the theoretical calculations. All computations are performed using the B3LYP hybrid HF/DFT method21 with the G98 program package.22 The basis set contraction used for Cr atom is (62111111)/5112/411).23,24 The (14s, 9p) primitive Gaussian functions are taken from Wachters23 and (6d) basis set are taken from Goddard.24 The 6-31G* basis set was used for Cl, N, O, C, and H. The importance of electron correlation of transition metal system has been reported.25–27 The DFT includes electron correlation effect empirically and is claimed to have comparable accuracy as post-Hartree–Fock methods. However, it was reported that the topological properties of the electron density are not qualitatively affected by the inclusion of electron correlation. The quantitative changes at the critical points in both ρ(r) and...
$V^2 \rho(r)$ induced by correlation are found to be small in magnitude.

The topological property analysis on electron density is based on Bader's "Atoms in Molecules (AIM)" theory. Total electron density obtained from the experiment is calculated according to the multipole model and the multipole coefficients ($P_{lm}$'s) and the single kappa values of $\kappa_1$ and $\kappa_2$ are taken from the literature. The multipole terms of Cr atom are up to hexadecapole (total number of 25) for both $\kappa_1$ and $\kappa_2$. Total electron density from the theory is calculated on the basis of the DFT calculation. Maps of Laplacian, charge distribution, and the other topological properties are obtained using the PROP and AIMPAC programs for experiment and theory, respectively.

Result and Discussion

Structures. The crystal structures and deformation density distribution of 1, 2, 3, and 4 have been reported. The coordination spheres of Cr center are either in an octahedral (1 and 3) or in a square pyramidal (2 and 4) geometry. The molecular structure and the local coordinates of Cr atom for compound 1, 2, 3, and 4 are shown in Figure 1. Compound 1 is a typical low-valent carbyne complex with the Cr–C(carbyne) distance of 1.724(1) Å. Compounds 2 and 3 are both high-valent Cr complexes with Cr–N distance of 1.555(2) and 1.63(1) Å for nitrido 2 and imido 3 complexes. The Cr atom is located at 0.519 and 0.173 Å above the equatorial plane of the tetradeionate of bph$^{2-}$ ligand for 2 and 3, respectively. Compound 4 is a five-coordinated complex with Cr–O(oxo) bond of 1.588(4) Å. The Cr atom is located 0.434 Å above the plane of porphyrin ligand. Selected bond distances of various Cr–L bond are listed in Table 1. There are various types of Cr–N bonds in these four complexes, where the bond length is in the order of Cr–N nitrido < Cr–N imido < Cr–N amido < Cr–N pyridine ≈ Cr–N pyrole.

NBO Analysis. The natural bond orbital analyses (NBO) of four types of Cr–L multiple bonds (Cr–C(carbyne), Cr–N nitrido, Cr–N imido, and Cr–O(oxo)) are listed in Table 2. Each one is described in terms of bond type ($\sigma$, $\pi$), natural hybrid orbital (NHO) at each bonded atomic center as well as the electron occupancy of the bond. It is clear that all of the Cr–L multiple bonds are a triple bond character with one $\sigma$ and two $\pi$ bonds. The calculated bond orders are 2.44, 2.72, 2.40, and 2.65 for Cr–C(carbyne), Cr–N nitrido, Cr–N imido, and Cr–O(oxo) bonds, respectively. The $\sigma$ bond of Cr–L multiple bond is formed by a sd$_z^2$ hybrid orbital of Cr and a sp$_z$ hybrid of L with major contribution (60–80%) from L. The $\pi$ bonds of Cr–L are formed by d$_x$ (d$_{xy}$, d$_{xz}$) orbitals of Cr and p$_x$ (p$_x$, p$_y$) orbitals of L. In the cases of Cr–N nitrido and Cr–N imido bonds in 2 and 3, both $\pi$ bonds are formed with equal contribution from p$_x$ orbital of N nitrido/imido and d$_z$ orbitals of Cr, though p$_x$ of N imido does contribute slightly more than d$_z$ of Cr in 3. In the case of Cr–O(oxo) bond in 4, the p$_x$ orbital of O contributes much more than the d$_z$ orbitals of Cr on Cr–O(oxo) $\pi$ bond. But, in the case of

Figure 1. Molecular structures of compound (a) 1, (b) 2, (c) 3, and (d) 4.
Properties Associated with BCP of 1, 2, 3, and 4 (for 1 and 2, first line from experiment, second line from theory)
Cr–Cl direction in experiment (Figure 3b) but not in theory (Figure 3d) of compound 1. The feature around Cr at the projection of Cr–N nitrido in 2 is different in experiment (Figure 4b) and theory (Figure 4d). The effect of the size of the basis set on the metal i-VSCC was discussed on the metal carbonyls (Cr, Fe, and Ni). But the discrepancies observed here are unlikely to be fully rationalized by the weakly pronounced feature mentioned therein. The Laplacian, $r^2 F(r)$ around the Cr center and Cr–O oxo bond of 3 and 4 from DFT calculation are shown in Figures 5 and 6, respectively. The feature at the horizontal plane ($xy$) are roughly the same for all four complexes; however, along the Cr–L bond, the local CC is only found around Cr toward the O$_{max}$ ligand. The Laplacian at C$_{carbonyl}$, N$_{nitrido}$, and N$_{imido}$ atoms shows local CC toward the Cr. It is worth noticing that the i-VSCC of the Cr atom is in its third quantum shell, and is topologically affected by the population of the 3d orbitals. To show the shape of such i-VSCC around Cr, the isovalue surface of zero Laplacian ($\nabla^2 \rho(r) = 0$) around Cr atom is displayed in Figures 7–10, respectively, for complexes 1, 2, 3, and 4. These surfaces simply give the relative description of the interfaces between the local charge concentrations and local charge depletions. In complex 1, the surface around the chromium atom can be described as a pressed disk with four bumps located at the bisection of four carbonyl ligands both from experiment (Figure 7a) and theory (Figure 7b), there are six concaves toward each ligand. In complex 2, a square pyramidal shape is observed where four bumps are located at the bisection of four ligands both from experiment (Figure 8a) and theory (Figure 8b), there are six concaves toward each ligand.

Figure 3. Laplacian maps of the $xy$ plane (a,c) and $xz$ plane (b,d) around the Cr center for compound 1: (a), (b) from experiment; (c), (d) from DFT. The contour changes in steps of $(-1)^{l+m+n} 10^l$ ($l = 1, 0; m = 1−3; n = −2$ to $+2$).

Figure 4. Laplacian maps of the $xy$ plane (a,c) and $xz$ plane (b,d) around the Cr center for compound 2: (a), (b) from experiment; (c), (d) from DFT. The contours and plot sizes are as in Figure 3.

Figure 5. Laplacian maps of the $xy$ plane (a) and $xz$ plane (b) around the Cr center for compound 3 from DFT. The contours and plot sizes are as in Figure 3.

Figure 6. Laplacian maps of the $xy$ plane (a), $xz$ plane (b), and $yz$ plane (c) around the Cr center for compound 4 from DFT. The contours and plot sizes are as in Figure 3.

Figure 7-10. Laplacian maps of the $xy$ plane (a) and $xz$ plane (b) around the Cr center for compounds 1 through 4 from DFT. The contours and plot sizes are as in Figure 3.
The surface in complex 3 shown in Figure 9 is similar to that of complex 1. The surface in complex 4 shown in Figure 10 is somewhat peculiar. From the geometry of the coordination, it ought to be similar to that of 2. However, there is an extra bump toward the O oxo. This makes Cr–O oxo bond insert into a bump on this surface, whether this has anything to do with the high polarity of the bond is unclear at the moment. The same feature along V–O oxo bond was also observed in VOCl 3.

The structure of the Laplacian of charge density for atoms in molecules is most easily visualized in terms of the minimum in $\nabla^2 \rho(r)$, a polyhedron whose numbers of vertices (V), edges (E), faces (F) and the only cage critical point within the sphere obey the Poincaré–Hopf relationship. As a peculiar case, this is easily transformed into Euler’s polyhedral formula: $V - E + F = 2$. The local minimum (charge concentration, CC) in the valence shell of an atom defines the vertexes, V. The unique pair of trajectories of the gradient of $\nabla^2 \rho(r)$ that originate at a (3, −1) critical point or saddle point between two minima and terminate at neighboring vertexes define the edges E of the polyhedron. The set of trajectories that arise at a (3, +1) critical point define the faces F of the polyhedron. The face critical points are where $\nabla^2 \rho(r)$ attains a local maximum (charge depletion). This is called an atomic graph. Generally, the ligands avoid the vertexes formed by CCs in the valence shell of a metal but are inserted in the faces of the polyhedron. Take 1 as an example, shown in Figure 7, there are four vertexes, eight edges, and six faces in chromium’s i-VSCC, therefore satisfies the Euler’s rule of 4 − 8 + 6 = 2. It is understandable that each CC of six ligand atoms inserts toward one of the six faces. In the case of 2, there are five vertexes, eight edges, and five faces. In the case of 3, it is the same as in 1. In the case of 4, there are six vertexes, eight edges, and four faces. All the CCs of ligands are inserted toward the face, therefore the number of faces is the coordination number of the metal ion. As mentioned above, one exception is Cr–O oxo in 4 where the ligand O oxo is toward a vertex instead of a face. We have not yet a good explanation for this, except the density polarization in this bond is highly polarized toward O oxo.

**Topological Properties of Bond Critical Points.** Topological properties associated with BCPs of some typical covalent bonds of 1 and 2 are given in Table 3 from both experiment and theory. Those of Cr–L bonds are given in Table 1. The experimental $\rho(r_c)$ and $\nabla^2 \rho(r_c)$ values are in good agreement with the theoretical ones, where $r_c$ is the BCP. All C=C, C=O, and C=N bonds are definitely of covalent bond character (shared interaction), having negative value of $\nabla^2 \rho(r_c)$ and a greater than 1.0 of $\rho(r_c)$ value at the BCP, $r_c$. The positive value of $\nabla^2 \rho(r_c)$ of the C=O bond found from the MO calculation in 1 can be rationalized by the highly polarized electron density on an extremely short bond since the BCP is only 0.37 Å away from C nucleus. In view of the complications to various bonding analyses based on the total electron density, it is also advantageous to use the local properties of the energy to analyze the bonding character. For this purpose, the total energy density $H(r)$ is defined as $H(r) = G(r) + V(r)$, where $G(r)$ is a local
Investigation of a variety of chemical bonds revealed 44 that at a point \( r \) field experienced by one electron in a many-particle system bonds. The larger the minus \( c \)-

**TABLE 4: Topological Properties Analysis at the BCP of the M–L Multiple Bonds (first line from experiment, second line from theory)**

<table>
<thead>
<tr>
<th>bond</th>
<th>B.L. (Å)</th>
<th>( d_1 ) (Å)</th>
<th>( \rho (r_{bc}) ) (e Å(^{-3}))</th>
<th>( \nabla^2 \rho (r_{bc}) ) (e Å(^{-5}))</th>
<th>( H_b ) (Hartree/Å(^3))</th>
<th>B.O.(^{a})</th>
<th>BDE (kcal/mol)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr–C(_{\text{carbonyl}})</td>
<td>1.725</td>
<td>0.895</td>
<td>0.86</td>
<td>15.82</td>
<td>-0.618</td>
<td>4.49</td>
<td>115.2(^{b})</td>
<td>29</td>
</tr>
<tr>
<td>W–C(_{\text{carbonyl}})</td>
<td>1.843</td>
<td>1.015</td>
<td>1.22</td>
<td>13.88</td>
<td>-0.699</td>
<td>155</td>
<td>45</td>
<td>29</td>
</tr>
<tr>
<td>Cr–C(_{\text{carbene}})</td>
<td>1.999</td>
<td>0.998</td>
<td>0.68</td>
<td>9.41</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W–C(_{\text{carbene}})</td>
<td>2.088</td>
<td>1.065</td>
<td>0.77</td>
<td>7.46</td>
<td>-0.272</td>
<td>75.0</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>Cr–N(_{\text{amido}})</td>
<td>1.555</td>
<td>0.846</td>
<td>1.87</td>
<td>26.94</td>
<td>-1.782</td>
<td>2.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo–N(_{\text{amido}})</td>
<td>1.728</td>
<td>0.959</td>
<td>2.49</td>
<td>10.14</td>
<td>-2.557</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W–N(_{\text{amido}})</td>
<td>1.727</td>
<td>0.934</td>
<td>2.27</td>
<td>14.45</td>
<td>-2.286</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr–N(_{\text{mido}})</td>
<td>1.630</td>
<td>0.847</td>
<td>1.48</td>
<td>23.92</td>
<td>-0.82</td>
<td>2.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr–O(_{\text{oxo}})</td>
<td>1.582</td>
<td>0.815</td>
<td>1.83</td>
<td>23.54</td>
<td>-1.239</td>
<td>2.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo–O(_{\text{oxo}})</td>
<td>1.755</td>
<td>0.932</td>
<td>2.15</td>
<td>21.07</td>
<td>-1.936</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W–O(_{\text{oxo}})</td>
<td>1.732</td>
<td>0.914</td>
<td>2.02</td>
<td>25.48</td>
<td>-1.741</td>
<td>30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) B.O. (bond order) = 1/2(occupancy of bonding orbitals – occupancy of antibonding orbitals) based on NBO analysis. \(^{b}\) Ref 7, [(CO)\(_5\)Cr(C\(_2\)H\(_5\))]
Acknowledgment. The authors thank the National Science Council of the Republic of China for the financial support. The authors also thank Dr. Anne Spasojevic-de Bire of Laboratoire de Chimie et Physico-Chimie Moléculaires, ERS 0070 du CNRS, Ecole Centrale Paris, France, for her supply of multipole coefficients and atomic parameters of chromium carbyne complex 1 (ref 12).

Supporting Information Available: Complete lists of topological properties at BCP of compound 1, 2, 3, and 4. Fermi hole distribution of compounds 1, 3, and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(23) (a) Reed, A. E.; Weinhold, F.; Menning, C. In The Challenge of d and f electrons: Theory and Computation; Eds.: ACA Symposium Series 94; American Chemical Society; Washington, DC, 1989; p 165.