A multiconfigurational approach to the electronic structure of electro-generated species of the Re₂(µ-Ph₂PCH₂PPh₂)(S₂CNEt₂)₄ complex

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Abstract

Studies electronic structure of transition metal complexes containing metal-metal multiple bond offer insight into the nature of metal-metal bonding and facilitate predictions of the physical properties and the reactivities. In this computational study, we have explored the electronic structure of the neutral and two oxidized species of the Re₂(µ-Ph₂PCH₂PPh₂)(S₂CNEt₂)₄ (1⁰, 1⁺, and 1²⁺) complex using state-of-the-art quantum chemical methodologies including DFT and CASSCF. In particular, we focused on the nature of the Re-Re bonding in those species. Our results show that the ground state electron configuration of the 1⁰ is σ²π⁴δ²δ−² with an effective bond order of 2.73 computed with CASSCF. The two oxidized processes of the 1⁰ remove electrons from metal-based orbital as suggested by DFT to produce 1⁺ and 1²⁺ with an effective bond order of 2.71 and 2.64, respectively, calculated by CASSCF. Those values very similar to that of the neutral molecule suggesting that the oxidation process has almost no effect on the Re-Re bond strength even though it remove electrons from metal-based orbitals. However, the wavefunction is different which explain the similarity of effective bond order of all three species. The electrons of the δ components of the Re-Re bond is localized on two Re ions in the 1⁺ and 1²⁺ which are excluded from bond order evaluation. In another words, the σ and π and their antibonding counterparts are determined the nature of the Re-Re bonding of the oxidized species (1⁺ and 1²⁺).

Introduction

The Re₂Cl₄(µ-dppm)₂ complex where dppm is Ph₂PCH₂PPh₂ have firstly synthesis in 1976 and the solid-state structure was determined later in 1985.¹,² The two Re ions are bridged by two dppm ligands while two of the four chlorine ions bound to one of Re atoms. Since then several complexes have been synthesis based on this molecule for carrying out an extensive reaction chemistry involving Re-Re multiple bonds. For example, the reaction of Re₂Cl₄(µ-dppm)₂ with a cyanotrihydroborate ligands replace all the four chlorine ions by [BH₃CN].³ The four chlorine ions were also replaced by CH₃ by reacting Re₂Cl₄(µ-dppm)₂ with CH₃Li to form Re₂(µ-dppm)₂(CH₃)₄.⁴ The Re₂Cl₄(µ-dppm)₂ complex react with different ligands to produce a variety of molecules, those ligands are, for example, dioxygen,⁵ PhSeSePh⁶ 2-mercaptoquinoline,⁷ 2-hydroxypyridine,⁸ carbon disulfide,⁹ sulfur dioxide,¹⁰ triphenylguanidine,¹¹ and acetylacetone,¹² carbon monoxide, isocyanides, and nitriles.¹³,¹⁴,¹⁵,¹⁶ Recently, Chattopadhyay and co-worker¹⁷ have synthesised Re₂(µ-dppm)(S₂CNEt₂)₄ (1⁰) complex (Fig.1a) starting from the Re₂Cl₄(µ-dppm)₂. The cyclic voltammetry measurements of the Re₂(µ-dppm)(S₂CNEt₂)₄ complexes display two quasi-reversible one-electron oxidation processes, the two oxidation processes in the ranges -0.022 V to -0.070 V and +1.22 V to +1.196 V are assigned to the Re₂⁵⁺/Re₂⁴⁺ and Re₂⁴⁺/Re₂³⁺ couples, respectively. The X-ray data is available just for the neutral structure (1⁰). Thus, there is no information regarding the electronic structure of the two oxidized species (1⁺ and 1²⁺). Therefore, exploring the electronic structure of the 1⁰, 1⁺, and 1²⁺ complexes computationally is needed to shed light on the electronic structure of those species. The structure of 1⁰ shows that each rhenium ion is bonded to the ligand through four atoms in equatorial position and one atom in axial position. There is a great similarity between the structure of 1⁰ to the landmark [Re₂Cl₄]²⁻ molecule¹⁸,¹⁹, if we consider just the bonded ligand in the equatorial position. Therefore, the molecular orbital diagram of [Re₂Cl₄]²⁻ can be provide
a great help in understanding the nature of Re-Re bonding of $^{10}$ as illustrated systematically in Fig.1b. Four d-orbitals on each metal centres overlap to form eight molecular orbitals, populating those orbitals with ten electrons give electron configuration of $\sigma^2\pi^4\delta^2\delta^*2$. The oxidation processes can remove electrons from metal-based and/or ligand-based orbitals, however, these cannot be predicted based on simple molecular diagram. High level computational calculations offer fundamental insight into the nature of metal-metal bonding in the neutral and oxidized species of the Re$_2$(μ-dppm)(S$_2$CNET$_2$)$_4$ complex. However, analysing the nature of metal-metal bonding introduce a challenge to the theory.$^{20}$ Density Functional Theory (DFT) is widely used to deal with large systems, particularly, those that contain transition metals in their structures. However, DFT in some cases fails to give clear description of the nature of the metal-metal bonding because a single determinant in nature and the accuracy of the available exchange-correlation functionals is still open to debate. Alternatively, the complete active space self-consistent field (CASSCF) can be used for an accurate discretion of the metal-metal bonding because it takes into account the different contributions of the component of the metal-metal bonding to the overall bond strength.

![Diagram](image)

**Fig.1:** (a) The crystallographic structure of the Re$_2$(μ-dppm)(S$_2$CNET$_2$)$_4$ complex and (b) systematic representation of the molecular orbital diagram of [Re$_2$Cl$_6$]$^2-$. Hydrogen atoms were omitted for clarity, the colour code is green for Re, yellow for S, orang.

Recently, we were interested in understanding the nature of metal-metal bonding in oxidized and reduced species of dimeric transition metal complexes by means of state-of-the-art quantum chemistry methods including density functional theory and complete active space self-consistent field (CASSCF).$^{21}$ Our results showed that removing or addition of electrons to the metal-based orbitals or ligand-based orbitals determine the nature of the metal-metal bonding. However, in this report we showed that removing electrons from metal-based orbitals giving electron configurations that need to be looked at very carefully. In this report, we have studied the electronic structure of Re$_2$(μ-dppm)(S$_2$CNET$_2$)$_4$ complex in neutral and two oxidized forms by means of DFT and CASSCF methodologies. Our results show that the oxidation processes remove electrons mainly from metal-based orbitals of $^{10}$ giving $^{1+}$ and $^{12+}$ species. The ground state wavefunction is dramatically changed, going from $\pi^4\sigma^2\delta^2\delta^*2$ electron configuration in $^{10}$ to $\pi^4\sigma^2\delta^2\delta^*1$ configuration in $^{1+}$ and $\pi^4\sigma^2\delta^2$ in $^{12+}$, surprisingly, giving the same bond order and Re-Re bond distances. These interested features explained by CASSCF as shown that the electrons of the $\delta$ component of Re-Re bond of $^{1+}$ and $^{12+}$ is localized on the two Re centres, thus, have no effect on the bond strength.

**Results and discussion**

In this computational study, the geometries of the natural ($^{10}$) and two oxidized species ($^{1+}$ and $^{12+}$) of the Re$_2$(μ-dppm)(S$_2$CNET$_2$)$_4$ complexes have been optimized with BP86 exchange-correlation functional with applying the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ). All geometry optimization
were started from the crystallographic structure of 1⁰ without imposing any simplification. Then, the complete active space self-consistent (CASSCF) calculations were carried out on those optimized structures. Therefore, we firstly will introduce the DFT results and then we will present the CASSCF.

**DFT results:** Table 1 shows the optimized structure parameters of the 1⁰, 1⁺ and 1²⁺ molecules along with the experimental crystallographic data. The experimental structure is available just for the neutral form (1⁰), therefore, we will compare the optimized structure parameters of the 1⁰ with the X-ray data to validate our methodology. Then we discuss the optimized structures of the two oxidized species (1⁺ and 1²⁺). For 1⁰, the optimized Re-Re bond distance of 2.30 Å in excellent agreement with the X-ray value (2.3196(8) Å). The averaged Re-P and Re-Saxial bond distances is well predicted to be both shorter than the X-ray value by only 0.01 Å. The Re-S bond length is also in excellent agreement with the X-ray counterpart. These results are also in agreement with previous DFT calculations. Those results proved that our DFT methodology valid to analyses the electronic structure of 1⁰ and it is oxidized forms (1⁺ and 1²⁺).

<table>
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<tr>
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<th>1⁺</th>
<th>1²⁺</th>
<th>X-ray</th>
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<tr>
<td>Re-Re</td>
<td>2.30</td>
<td>2.30</td>
<td>2.31</td>
<td>2.3196(8)</td>
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<tr>
<td>Avg. Re-P</td>
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<td>2.40</td>
<td>2.45</td>
<td>2.36</td>
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<tr>
<td>Avg. Re-S</td>
<td>2.44</td>
<td>2.43</td>
<td>2.43</td>
<td>2.44</td>
</tr>
<tr>
<td>Avg. Re-Saxial</td>
<td>2.74</td>
<td>2.67</td>
<td>2.56</td>
<td>2.75</td>
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Kohn-sham molecular orbital diagram of 1⁰ is shown in Fig.2 similar to that of [Re₂Cl₄]²⁻ in Fig.1. Populating these orbitals with ten electrons give a ground state electron configuration of π₄σ²δ²δ*² with a formal bond order of 3.0 (sum of electrons of bonding orbitals minus sum of electrons in antibonding orbitals and the results divided by two). Mayer bond order and natural bond orbital were found to be 1.85 and 2.00, respectively, as shown in Table 2, these are very diverged from the formal bond order of 3.0. The first oxidation process removes one electron from metal-based orbital or ligand-based orbit or from both.

For 1⁺, the first oxidation process removes one electron from mainly metal-based orbital. The electron removal from anti-bonding δ⁻ orbital gives an π₄σ²δ²δ⁻¹ electron configuration with a formal bond order of 3.5. The Mulliken spin density of 0.47 one Re1 and 0.27 on Re2 shows some localization of the unpaired electron on one rhenium centre. This oxidation process has no effect on the Re-Re bond distance where it is predicted to be 2.30 Å same to that of 1⁰. However, the Re-P distance increased from 2.35 Å in 1⁰ to 2.40 Å in 1⁺ and Re-Saxial reduced from 2.74 Å in 1⁰ to 2.67 Å in 1⁺. The calculated Mayer bond order and natural bond orbital are 1.92 and 1.96, respectively (Table 2). These results very similar to that of 1⁰ confirming that removing one electron has almost no effect on the Re-Re bond strength. Even though the electron left the weakly bonded δ⁺ orbital, it should have some effect on the Re-Re bond strength. The explanation of this unexpected behaviour is found by CASSCF calculations as we will see shortly.
Table 2: Comparison of Re-Re bond orders of the $1^0$, $1^+$, and $1^{2+}$ calculated by different methods, Mayer bond order (MBO) and Natural bond orbitals (NBO) from DFT, and effective bond order (EBO) from CASSCF.

<table>
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<tr>
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<th>NBO</th>
<th>EBO</th>
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<tr>
<td>$1^0$</td>
<td>1.85</td>
<td>2.00</td>
<td>2.73</td>
</tr>
<tr>
<td>$1^+$</td>
<td>1.92</td>
<td>1.96</td>
<td>2.71</td>
</tr>
<tr>
<td>$1^{2+}$</td>
<td>1.82</td>
<td>2.00</td>
<td>2.64</td>
</tr>
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Fig. 2: Kohn-Sham molecular orbital diagram of $1^0$ calculated with BP86 functional. Only occupied orbitals are shown, the energy scaled arbitrarily, and the isosurface value is 0.06.

The second oxidation process removes another unpaired electron occupied the $\delta^*$ orbital giving $\pi^4\sigma^2\delta^2$ ground state electron configuration of $1^{2+}$ with a Re-Re formal bond order of 4.0. That is confirmed by the DFT calculations, the Mulliken spin density of zero on both rhenium centres. If the unpaired electron were removed from the ligand-based orbitals, the Mulliken spin density would be the same to the $1^+$. Again, this process has almost no effect on the Re-Re bond length (2.30 Å in $1^0$ vs. 2.31 Å in $1^{2+}$). The calculated Mayer bond order and natural bond orbital are 1.82 and 2.00, respectively (Table 2) similar to that found in the $1^0$ and $1^+$ molecules. However, The Re-P distance increased from 2.35 Å in $1^0$ to 2.45 Å in $1^{2+}$ and Re-Saxial reduced from 2.74 Å in $1^0$ to 2.56 Å in $1^{2+}$. These results need further explanation as we will see in the CASSCF section.

To understand the nature of the Re-Re bonding under oxidation processes by deeper insight into the nature of the Re-Re bonding we will turn our attention the multiconfigurational methodology, particularly, CASSCF methodology.
**CASSCF results:** for $1^0$, an active space of CAS(10,8) were adopted that includes ten electrons in eight orbitals. The eight orbitals are the metal-based orbitals that participate in the Re-Re bonding, one $\sigma$, two $\pi$, and one $\delta$ orbitals and their antibonding counterparts (Fig.2). The DFT geometry with Re-Re bond distance of 2.30 Å were used in the single point CASSCF calculations. Fig.3a shows the active space natural orbitals with their occupations. The CASSCF results show that the $\pi^4\sigma^2\delta^2\delta^*$ configuration makes 88% of the total wavefunction. The effective Re-Re bond order of $1^0$ is 2.73 which is smaller than the formal bond order of 3.0 that could be expected from a simple molecular orbital diagram. However, the effective bond order of 2.73 is very diverged from the calculated values by Mayer bond order and natural bond orbitals that are 1.85 and 2.00, respectively.

For $1^+$, the active space of CAS(9,8) were used as shown in Fig.3b, the DFT geometry with Re-Re bond distance of 2.30 Å were used. The $\pi^4\sigma^2\delta^2\delta^*$ configuration makes 85% of the total wavefunction, this configuration is better described as shown in Fig.4. Notably, the $\delta$ components of the Re-Re bonds is localized on two metal centres. Therefore, they excluded from effective bond order estimation, this gives an effective bond order of 2.71 very similar to that of $1^0$ (2.73). This value is also diverged from a formal bond order of 3.5 and also from MBO and NBO (Table 2). For $1^{2+}$, the CAS(8,8) was applied using DFT geometry with Re-Re bond distance of 2.31 Å (the active space natural orbitals with occupations shown in Fig.ESI1). The ground state wavefunction of this molecule is much
multiconfigurational compared to that of $1^0$ and $1^\ast$. The $\pi^4\delta^2$ configuration makes 34% of the total wavefunction. However, the dominant configuration weighted 40% of the total wavefunction is shown in Fig.4, the two electrons in the $\delta$ component is localized on the Re centres antiferromagnetically. Thus, the effective bond order is 2.64 slightly lower than that of $1^0$ and $1^{2+}$ by only 0.06.

![Diagram](Fig.3: Systematic representation of the Re-Re bonding in $1^0$, $1^\ast$ and $1^{2+}$ species.)

In summary, DFT calculations show that the Re-Re bond distances of all there $1^0$, $1^\ast$, and $1^{2+}$ complexes are the same. In addition, the bond order calculated by different methodologies including MBO, NBO, and EBO shows the same trend (Table 2). However, an unpaired electron was removed from metal-based orbital in each oxidation process. The explanation of that come from the CASSCF calculations, in all systems, the $\delta$ components of the Re-Re bonds are not included in count of bond order. They cancel each out in $1^0$ while in $1^\ast$ and $1^{2+}$ they localized on each Re centres. Therefore, in $1^\ast$ and $1^{2+}$ species the Re-Re bonds form from six electrons that occupied the $\sigma$ and $\pi$ orbitals with localized $\delta$ component as shown in Fig.4.

**Computational details**

The crystallographic coordinates for $1^0$ were obtained from the structure deposited at the Cambridge Structure Database with Refcode NUDDIC, which corresponds to Re$_2$(μ-dppm)(S$_2$CNEt$_2$)$_4$. All calculations present in this paper were performed using Orca 5.0 package, otherwise mentioned. The BP86 functional were used in this work. SARC-ZORA-TZVP basis set to describe the Re ions, and def2-SVP basis set to describe S, P, N, C, and H in combination with SARC/J auxiliary basis set. The atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ) were applied. The resolution of the identity (RI) approximation was employed for fitting the Coulomb integrals. The TIGHTSCF keyword were used for all geometry optimization. Single point gas-phase CASSCF calculations was carried out using def2-TZVP basis set to describe the Re and def2-svp/c to describe S, P, N, C, and H with def2/J auxiliary basis set of Weigend. To speed up the CASSCF calculations we have used RIJCOSX approximation. The natural bond orbitals (NBO) were calculated using Gaussian 16 package.

**Conclusions**

The electronic structure of $1^0$, $1^\ast$, and $1^{2+}$ molecules were studied using DFT and CASSCF. The nature of the Re-Re bonding in those complexes were analysis in details. For the neutral molecule, the effective bond order is 2.73 which is very diverged from a formal bond order of 3.0 that would be expected from a simple molecular orbital diagram. It is also diverged from DFT calculated bond order by means of Mayer bond order and natural bond orbitals (Table 2). The two oxidation processes remove electrons from mainly metal-based orbitals of $1^0$ generated $1^\ast$ and $1^{2+}$ species with no effect on the Re-Re bond lengths (2.30 Å in $1^0$ vs 2.30 Å in $1^\ast$ and 2.31 Å in $1^{2+}$). The effective bond order of 2.71 and 2.64 of $1^\ast$ and $1^{2+}$, respectively, showing that these two processes have almost no effect on
the Re-Re bond strength. That because the electrons that occupied the $\delta$ component localized on the two Re ions, thus, they excluded from bond order calculation. These results show that carefully investigate the electronic structure of the Re$_2$($\mu$-dppm)(S$_2$CNEt$_2$)$_4$ and related molecules highly recommended for both theory and experimental.

Notes and references