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REGULAR ARTICLE

The strength of the σ-, π- and δ-bonds in $Re_2Cl_8{}^{2-}$

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Abstract The geometry of $Re_2Cl_8{}^{2-}$ has been optimized for the eclipsed (D_{4h}) equilibrium conformation and for the staggered (D_{4d}) conformation at BP86/TZ2P. The nature of the Re–Re bond which has a formal bond order four has been studied with an energy decomposition analysis (EDA). The EDA investigation indicates that the contribution of the $b_2(\delta_{xy})$ orbitals to the Re–Re bond in the ${}^1A_{1g}(\delta^2\delta^{*0})$ ground state is negligibly small. The vertical excitation of one and two electrons from the bonding δ orbital into the antibonding δ* orbitals yielding the singly and doubly excited states ${}^1A_{1g}(\delta^1\delta^{*1})$ and ${}^1A_{1g}(\delta^0\delta^{*2})$ gives a destabilization of 17.5 and 36.1 kcal/mol, respectively, which is nearly the same as the total excitation energies. The preference for the D_{4h} geometry with eclipsing Re–Cl bonds is explained in terms of hyperconjugation rather than δ bonding. This is supported by the calculation of the triply bonded Re_2Cl_8 which also has an eclipsed energy minimum structure. The calculations also suggest that the Re–Re triple bond in Re_2Cl_8 is stronger than the Re–Re quadruple bond in $Re_2Cl_8{}^{2-}$. A negligible contribution of the δ orbital to the metal–metal bond strength is also calculated for Os_2Cl_8 which is isoelectronic with $Re_2Cl_8{}^{2-}$.

Keywords Bonding analysis · δ-bonding · Transition metal compounds · Metal-metal bond

1 Introduction

The synthesis and X-ray structure analysis of $K_2[Re_2Cl_8] \cdot 2H_2O$ which were reported in 1964 by Cotton et al. [1,2] opened a new era of inorganic chemistry. The hitherto limited spectrum of bonding multiplicity between two atoms exhibited by a triple bond was extended to four because the short rhenium–rhenium bond between two $ReCl_4^-$ moieties was convincingly interpreted in terms of one σ, one degenerate π and one δ bond. The work was the starting point for very active experimental research which led to the synthesis of a large number of homo- and heterodinuclear compounds with metal–metal quadruple bonds [3].

The experimental work about quadruply bonded compounds was later complemented by theoretical studies which addressed the electronic structure and nature of metal–metal multiple bonds. Two recent investigations by Gagliardi and Roos [4] and by Sakaki and co-workers [5] used high-level ab initio methods such as CASPT2, MCQDPT and CCSD(T) and others in order to understand the bonding situation in the archetypical compound $Re_2Cl_8{}^{2-}$. The paper by Gagliardi and Roos reported that the effective bond order using CASPT2 calculations of the σ bond is 0.92, the π bond has the value of 1.74 while the bond order of the δ-bond is only 0.54 [4]. This means that the δ bond should be rather weak. The strength of the δ bond in $Re_2Cl_8{}^{2-}$ was estimated in the work of Sasaki et al. by calculating the energy difference between the ${}^1A_{1g}$ ground state and the ${}^3A_{2u}$ excited state which is 12.1 kcal/mol [5]. The natural orbital populations of the δ and δ* orbitals in the ground state reported in the latter work are 1.52 and 0.48, respectively, while the ${}^3A_{2u}$

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excited state has nearly identical δ and δ* orbital populations of 1.01 and 0.99. It was suggested that the bonding and antibonding contributions of the δ and δ* orbitals in the $^3A_{2u}$ excited state cancel [5]. Therefore, the adiabatic excitation energy $^1A_{1g} \rightarrow {}^3A_{2u}$ = 12.1 kcal/mol should indicate the strength of the δ bond in $Re_2Cl_8^{2-}$.

We recently employed the energy decomposition analysis (EDA) [6–8] for systematically analysing the nature of the chemical bonds in a wide variety of main group and transition metal compounds [9,10]. The advantage of the EDA is that it directly reveals the strength of the various contributions to the intrinsic binding interaction in a molecule between two or more fragments without using other compounds as reference system. In particular, the breakdown of the orbital interactions ΔE_{orb} in multiple bonds into contributions coming from σ and π orbitals was found to be very useful for the bonding analysis [11–14]. We extended the EDA investigation of molecules with multiple bonds to compounds with metal–metal δ bonds. Here we report our results for $Re_2Cl_8{}^{2-}$.

2 Methods

The geometries of the molecules were optimized at the gradient corrected DFT level of theory using Becke's exchange functional [15] in conjunction with Perdew's correlation functional [16] (BP86). Uncontracted Slater-type orbitals (STOs) were employed as basis functions in SCF calculations [17]. Triple-ζ-quality basis sets were used, which were augmented by two sets of polarization functions, that is, p and d functions for the hydrogen atom and d and f functions for the other atoms. This level of theory is denoted as BP86/TZ2P. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle [18]. Scalar relativistic effects were considered using the zero-order regular approximation (ZORA) [19–23]. The vibrational frequencies of the molecules have been calculated using analytical derivatives. The calculations were carried out using the ADF(2005.1) program package [24]. Atomic partial charges have been estimated using the Hirshfeld method [25].

In the EDA, bond formation between the interacting fragments is divided into three steps, which can be interpreted in a plausible way. In the first step the fragments, which are calculated with the frozen geometry of the entire molecule, are superimposed without electronic relaxation yielding the quasiclassical electrostatic attraction $\Delta E_{\mathrm{elstat}}$. In the second step the product wave function becomes antisymmetrized and renormalized, which gives the repulsive term $\Delta E_{\mathrm{Pauli}}$, termed Pauli repulsion. In the third step the molecular orbitals relax to their final form to yield the stabilizing orbital interaction ΔE_{orb}. The latter term can be divided into contributions of orbitals having different symmetry. This latter step is crucial for the present study. The sum of the three terms $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}}$ gives the total interaction energy ΔE_{int}:

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}}$$

The EDA calculations involving open-shell fragments does, for technical reasons, neglect the spin-polarization in the fragments. This means that the interaction energies ΔE_{int} are slightly larger (in the order of a few kcal/mol per unpaired electron) than those using fully relaxed orbitals. This error has been neglected in the present study because the small differences are unimportant for the discussion in this paper. Further details about the EDA can be found in the literature [24,26].

3 Results

Figure 1 shows the optimized geometry of $Re_2Cl_8{}^{2-}$ at BP86/TZ2P. The equilibrium structure has an eclipsed conformation (D_{4h}) which is in agreement with the results of the X-ray structure analysis [1,2]. Geometry optimization of the staggered conformation with enforced D_{4d} symmetry using the broken-symmetry (BS) approach[1] yielded a transition state which is only 2.6 kcal/mol higher in energy than the D_{4h} energy minimum. The calculated Re–Re bond length (2.230 Å) of the equilibrium structure conforms with the experimental value of 2.24 Å. Theory and experiment are also in accord when it comes to the Re–Cl distance and the Cl–Re–Re angle. The Re–Re distance of the staggered transition state is 2.271 Å which is only slightly longer than the equilibrium bond length.

Figure 2 shows the contour line diagrams of the occupied valence orbitals for the Re–Re bond of $Re_2Cl_8{}^{2-}$. The Kohn–Sham orbitals agree with the qualitative model for a quadruple bond which has one Re–Re σ bond (HOMO-10), one degenerate π bond (HOMO-1) and one δ bond (HOMO). Figure 2 also shows the plot of the LUMO which corresponds to the Re–Re δ* orbitals. The calculated overlap of the valence orbitals between the $ReCl_4^-$ fragments suggests that the σ bond of HOMO-10 (S = 0.33) and the π bond of HOMO-1 (S = 0.21) should be much stronger than the δ bond of the HOMO (S = 0.04).

Table 1 gives the EDA results for the Re–Re bond of $Re_2Cl_8{}^{2-}$ in the $^1A_{1g}$ singlet ground state which has a $\sigma^2\pi^4\delta^2$

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[1] The BS approach for the D_{4d} form was employed in order to calculate the lowest lying singlet state for a degenerate wave function. The $d(\delta)$ orbitals of the rhenium atoms which yield the δ bond in the eclipsed (D_{4h}) conformation are orthogonal to each other in the staggered conformation.

Table 1 EDA results of $Re_2Cl_8{}^{2-}$ and Re_2Cl_8 at BP86/TZ2P at the Re–Re equilibrium distance of the dianion r(Re–Re) = 2.230 Å

	$Re_2Cl_8{}^{2-}$				$Re_2Cl_8^c$
	Closed-shell singlet		Open-shell singlet	Triplet	Singlet
	D_{4h} $\delta^{(2)}\delta^{*(0)}$	D_{4h} $\delta^{(0)}\delta^{*(2)}$	D_{4h} $\delta^{(1)}\delta^{*(1)}$	D_{4h} $\delta^{(1)}\delta^{*(1)}$	D_{4h} $\delta^{(0)}\delta^{*(0)}$
r(Re–Re)	2.230	2.230	2.230	2.230	2.230
ΔE_{int}	−54.2	−19.9	−37.3	−48.8	−117.8
ΔE_{pauli}	405.4	405.4	405.4	405.4	340.5
$\Delta E_{elstat}{}^a$	−244.5 (53.2%)	−244.5 (57.5%)	−244.5 (55.2%)	−244.5 (53.8%)	−222.3 (48.5%)
$\Delta E_{orb}{}^a$	−215.2 (46.8%)	−180.8 (42.5%)	−198.2 (44.8%)	−209.6 (46.2%)	−236.0 (51.5%)
$a_1(\sigma)^b$	−84.5 (39.3%)	−85.0 (47.0%)	−84.7 (42.7%)	−84.9 (40.5%)	−97.7 (41.4%)
a_2^b	−0.1 (0.1%)	−0.1 (0.1%)	−0.1 (0.1%)	−0.1(< 0.1%)	0.0 (<0.1%)
$b_1(\delta_{x^2-y^2})^b$	−1.5(0.7%)	−1.4 (0.8%)	−1.4 (0.7%)	−1.5 (0.7%)	−2.6 (1.1%)
$b_2(\delta_{xy})^b$	−0.5 (0.2%)	36.1(−20.0%)	17.5 (−8.8%)	6.2 (−3.0%)	−3.9 (1.7%)
$e(\pi)^b$	−128.6 (59.8%)	−130.4 (72.1%)	−129.5 (65.3%)	−129.3 (61.7%)	−131.8 (55.8%)
E_{rel}	0.0	34.3	16.8	5.4	

Energy values in kcal/mol. The interacting fragments for the dianion are $ReCl_4^-$ ($^5B_2$) and for the neutral compound they are $ReCl_4$($^4A_1$)

[a] Values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$

[b] Values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}

[c] EDA calculation using the frozen geometry of $Re_2Cl_8{}^{2-}$

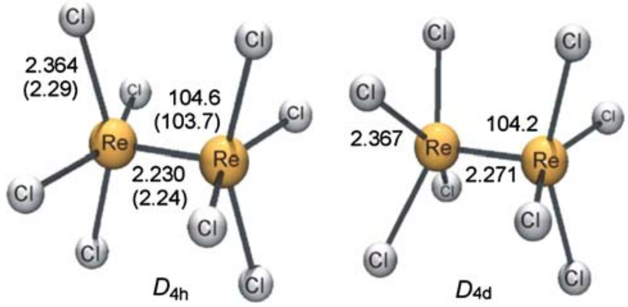

Fig. 1 Optimized geometries at BP86/TZ2P for the D_{4h} and D_{4d} forms of $Re_2Cl_8{}^{2-}$. Bond lengths are given in Å, angles in degrees. Experimental values are shown in parentheses

δ^{*0} electron configuration. EDA calculations have also been carried out for the doubly excited singlet state with the configuration $\sigma^2\pi^4\delta^0\delta^{*2}$, for the singly excited singlet state with the configuration $\sigma^2\pi^4\delta^1\delta^{*1}$ and for the $^3A_{2u}$ triplet state ($\sigma^2\pi^4\delta^1\delta^{*1}$) of $Re_2Cl_8{}^{2-}$ using the frozen geometry of the $^1A_{1g}$ singlet ground state. Since the occupation of the σ and π valence orbitals is the same in the three electronic states we use in the following only the occupation numbers of the δ and δ* orbitals as indicators of the electron configuration. Please note that the symmetry notation of the orbitals which is used in the EDA agrees with C_{4v} symmetry because the $ReCl_4^-$ fragments have only C_{4v} symmetry and not D_{4h} or D_{4d}. The electronic state of the latter fragment is $^5B_2$ where the four unpaired electrons are in the d(σ), degenerate d(π) and d(δ) orbitals.

The EDA data give an intrinsic Re–Re interaction energy for the energy minimum structure of $\Delta E_{int} = -54.2$ kcal/mol. Breakdown of the energy terms of the EDA indicates that the orbital (covalent) contribution to ΔE_{int} amounts to 46.8% of the attractive Re–Re interactions while the electrostatic attraction ΔE_{elstat} contributes 53.2%. Intuitively it is puzzling that the electrostatic interactions between two negatively charged $ReCl_4^-$ fragments are strongly attractive. The explanation for the attraction can be given if one realizes that the charge distribution in $ReCl_4^-$ and in $Re_2Cl_8{}^{2-}$ is highly anisotropic. The negative charge is located at the chlorine atoms which carry a negative partial charge in $Re_2Cl_8{}^{2-}$ of −0.29e while the Re atoms have a positive charge of +0.16e. The electrostatic stabilization comes mainly from the attraction between the electron density in the occupied d_{z^2} orbital of Re with the nucleus of the other Re atom. A thorough discussion of the electrostatic interaction in nonpolar molecules has been given by Frenking and co-workers [27,28].

The attractive orbital interactions in $Re_2Cl_8{}^{2-}$ come mainly from the π bond. Table 1 shows that the e(π) orbitals provide 59.8% of the ΔE_{orb} term while 39.3% comes from σ interactions. Note that there are two π bonding components in the $e(\pi)$ orbital while there is only one component in $a_1(\sigma)$. The most surprising EDA result is the negligible contribution of the $b_2(\delta_{xy})$ orbitals to the ΔE_{orb} term. The calculated data suggest that the Re–Re δ orbital shown in Fig. 2 (HOMO) provides only −0.5 kcal/mol which are just 0.2% of the attractive orbital interactions. The contribution of the $b_1(\delta_{x^2-y^2})$ orbitals which come from the metal $d_{x^2-y^2}$

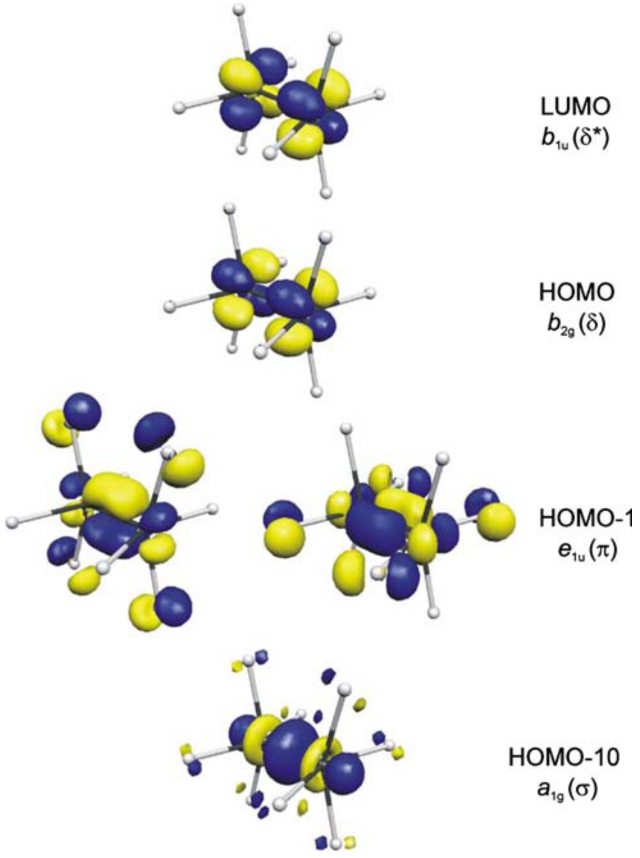

Fig. 2 Plot of the vacant LUMO and the occupied valence orbitals of $Re_2Cl_8{}^{2-}$ showing the Re–Re bonding orbitals possessing σ, π and δ symmetry

AOs is even slightly higher (−1.5 kcal/mol, 0.7%). The latter $b_1(\delta_{x^2-y^2})$ orbitals of $Re_2Cl_8{}^{2-}$ correspond to the Re–Cl ligand bonds. The EDA results suggest that there is practically nil stabilization of the electrons in the $5d_{xy}$ AO of Re through Re–Re interactions.

It may be argued that the EDA result is questionable because it is obtained using a single determinant method. High level calculations show that the first excited configuration makes a significant contribution to the CASSCF wave function of the $^1A_{1g}$ ground state of $Re_2Cl_8{}^{2-}$ [4,5]. We want to point out that mixing of the first excited state yields a population of the δ* orbital which further weakens the contribution of the δ bond to the stabilizing interactions. Furthermore, the EDA method actually overestimates the strength of the stabilizing orbital interactions because the ΔE_{orb} term includes the contribution due to polarization of the fragment orbitals.

We calculated the doubly excited $^1A_{1g}$ singlet state of $Re_2Cl_8{}^{2-}(\delta^0\delta^{*2})$ where the two electrons of the HOMO are excited into the LUMO (Fig. 2). The EDA calculation of the excited state at the equilibrium geometry of the ground state now gives a destabilizing contribution of the $b_2(\delta_{xy})$ orbitals to the ΔE_{orb} term of 36.1 kcal/mol. Since all other energy terms of the excited state have nearly the same values as in the ground state the repulsive contribution of the $b_2(\delta_{xy})$ orbital is very close to the calculated vertical excitation energy $^1A_{1g}(\delta^2\delta^{*0}) \rightarrow {}^1A_{1g}(\delta^0\delta^{*2})$ at BP86/TZ2P of 34.3 kcal/mol (Table 1).

Table 1 also gives the EDA results for the singly excited $^1A_{2u}(\delta^1\delta^{*1})$ state of $Re_2Cl_8{}^{2-}$ where one electron is excited from the HOMO into the LUMO. The calculations at BP86/TZ2P give a vertical excitation energy $^1A_{1g}(\delta^2\delta^{*0}) \rightarrow {}^1A_{2u}(\delta^1\delta^{*1})$ of 16.8 kcal/mol which is smaller than the experimental value (42.0 kcal/mol) [29,30]. It is also smaller than the theoretical values of previous high-level calculations using CASPT2 including spin–orbit coupling (45.4 kcal/mol) [4] and MRMP2 (45.0 kcal/mol) [5]. The EDA calculations indicate that the excitation energy is directly related to the destabilizing contribution of the $b_2(\delta_{xy})$ orbital which amounts to 17.5 kcal/mol because the values for all other energy terms change very little upon excitation of one electron. Thus, the $^1A_{1g}(\delta^2\delta^{*0}) \rightarrow {}^1A_{2u}(\delta^1\delta^{*1})$ vertical excitation energy and the repulsive energy contribution of the δ* orbital which come from exciting one electron are nearly half the value which is calculated for exciting two electrons yielding the $^1A_{1g}(\delta^0\delta^{*2})$ state.

We also analyzed the Re–Re bonding in the $^3A_{2u}(\delta^1\delta^{*1})$ excited state of $Re_2Cl_8{}^{2-}$ at the frozen D_{4h} geometry of the singlet ground state with the EDA. The results are given in Table 1. The calculations at BP86/TZ2P give a vertical excitation energy $^1A_{1g}(\delta^2\delta^{*0}) \rightarrow {}^3A_{2u}(\delta^1\delta^{*1})$ of 5.4 kcal/mol which is in remarkable agreement with previous high-level calculations at CASPT2 including spin–orbit coupling (9.9 kcal/mol) [4] and MRMP2 (12.0 kcal/mol) [5]. The latter value has been suggested by Sakaki et al. to be an estimate of the strength of the Re–Re δ bond in $Re_2Cl_8{}^{2-}$ because the natural orbital populations of the δ and δ* orbitals in the $^3A_{2u}(\delta^1\delta^{*1})$ state have nearly identical values [5]. This is a reasonable approach which is only valid, however, if the strength of δ and δ* interactions cancel. The EDA results indicate that this is not the case. The contribution of the $b_2(\delta_{xy})$ orbital in the $^3A_{2u}(\delta^1\delta^{*1})$ state is destabilizing by 6.2 kcal/mol (Table 1) which is nearly the same as the overall $^1A_{1g}(\delta^2\delta^{*0}) \rightarrow {}^3A_{2u}(\delta^1\delta^{*1})$ excitation energy. The reader may wonder why the contribution of the $b_2(\delta_{xy})$ orbital in the $^3A_{2u}(\delta^1\delta^{*1})$ state is clearly lower than in the $^1A_{2u}(\delta^1\delta^{*1})$ state while the other energy terms of the EDA have essentially the same values. This is because we used the same fragments for the EDA calculations of the $^1A_{2u}(\delta^1\delta^{*1})$ and $^3A_{2u}(\delta^1\delta^{*1})$ states. It is not possible to construct $^3A_{2u}(\delta^1\delta^{*1})$ from two $ReCl_4^-$ fragments possessing the same spin without reversing

Table 2 EDA results of $Re_2Cl_8{}^{2-}$ and Re_2Cl_8 at BP86/TZ2P at the optimized geometries

	$Re_2Cl_8^{2-}$					Re_2Cl_8	
	Closed-Shell Singlet		Open-Shell Singlet	Triplet		Singlet	
	D_{4h} $\delta^{(2)}\delta^{*(0)}$	D_{4h} $\delta^{(0)}\delta^{*(2)}$	D_{4h} $\delta^{(1)}\delta^{*(1)}$	D_{4h} $\delta^{(1)}\delta^{*(1)}$	D_{4d} $\delta^{(1)}\delta^{*(1)}$	D_{4h} $\delta^{(0)}\delta^{*(0)}$	D_{4d} $\delta^{(0)}\delta^{*(0)}$
r(Re–Re)	2.230	2.345	2.287	2.289	2.266	2.326	2.301
ΔE_{int}	−54.2	−21.5	−36.8	−48.5	−63.5	−109.7	−108.2
ΔE_{pauli}	405.4	294.5	345.8	343.9	360.1	272.7	282.8
$\Delta E_{\text{elstat}}{}^{a}$	−244.5 (53.2%)	−170.0 (53.9%)	−204.9 (53.6%)	−203.8 (51.9%)	−214.2 (50.6%)	−181.3 (47.4%)	−188.1 (48.1%)
$\Delta E_{\text{orb}}{}^{a}$	−215.2 (46.8%)	−145.5 (46.1%)	−177.7 (46.4%)	−188.6 (48.1%)	−209.4 (49.4%)	−201.1 (52.6%)	−203.1 (51.9%)
$a_1(\sigma)^{b}$	−84.5 (39.3%)	−74.3 (51.1%)	−79.2 (44.6%)	−79.2 (42.0%)	−82.7 (39.5%)	−89.9 (44.7%)	−91.3 (45.0%)
$a_2{}^{b}$	−0.1 (0.1%)	−0.1 (0.1%)	−0.1 (0.1%)	−0.1 (0.1%)	−0.1 (0.0%)	−0.1 (0.0%)	−0.1 (0.0%)
$b_1(\delta_{x2-y2})^{b}$	−1.5 (0.7%)	−1.0 (0.7%)	−1.2 (0.7%)	−1.2 (0.6%)	−1.6 (0.7%)	−1.9 (1.0%)	−2.3 (1.1%)
$b_2(\delta_{xy})^{b}$	−0.5 (0.2%)	31.8 (−21.9%)	17.6 (−9.9%)	6.2 (−3.3%)	−1.6 (0.8%)	−2.0 (1.0%)	−2.3 (1.1%)
$e(\pi)^{b}$	−128.6 (59.8%)	−101.9 (70.0%)	−114.8 (64.6%)	−114.3 (60.6%)	−123.4 (58.9%)	−107.2 (53.3%)	−107.1 (52.7%)
E_{rel}	0.00	30.0	15.8	4.4	3.5	0.0	1.5

Energy values in kcal/mol. The interacting fragments for the dianion are $ReCl_4^-$ ($^5B_2$) and for the neutral compound they are $ReCl_4$($^4A_1$)

[a] Values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$

[b] Values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}

the spin in one fragment. We used the quintet state of $ReCl_4^-$ for constructing the $^1A_{2u}(\delta^1\delta^{*1})$ and $^3A_{2u}(\delta^1\delta^{*1})$. For the latter triplet state, the spin reversal of one electron takes place in the orbital relaxation step of the EDA which gives a smaller value for the repulsive $b_2(\delta_{xy})$ orbital contribution than in the singlet state.

Because the EDA calculations suggest that the contribution of the δ-bonding orbital to the Re–Re bond in $Re_2Cl_8{}^{2-}$ is negligible we were interested to investigate the change in the metal–metal interactions when the highest lying $b_2(\delta_{xy})$ orbital is empty. Table 1 gives the EDA results for the neutral molecule Re_2Cl_8 which have been calculated using the equilibrium geometry of $Re_2Cl_8{}^{2-}$. It is interesting to note that the total Re–Re interaction energy in the neutral compound $\Delta E_{\text{int}} = -117.8$ kcal/mol is twice as high as in the dianion. This means that a Re–Re triple bond should be stronger than a Re–Re quadruple bond! Inspection of the EDA results shows that the increase in the Re–Re attraction in Re_2Cl_8 comes mainly from the weaker Pauli repulsion which is much smaller ($\Delta E_{\text{Pauli}} = 340.5$ kcal/mol) than in $Re_2Cl_8{}^{2-}$($\Delta E_{\text{Pauli}} = 405.4$ kcal/mol). This is reasonable because the dianion should exhibit larger Pauli repulsion than the neutral system. The electrostatic attraction in the neutral compound ($\Delta E_{\text{elstat}} = -222.3$ kcal/mol) is slightly weaker than in the dianion ($\Delta E_{\text{elstat}} = -244.5$ kcal/mol) but the orbital interaction in the former system is stronger ($\Delta E_{\text{orb}} = -215.2$ kcal/mol) than in the latter ($\Delta E_{\text{orb}} = -236.0$ kcal/mol) which roughly cancels the change in the ΔE_{elstat} term. It is interesting to note that in the formally triply bonded Re_2Cl_8 the Re–Re σ-bonding contribution ($a_1 = -97.7$ kcal/mol) and the Re–Re π-bonding contribution (e = −131.8 kcal/mol) are slightly stronger than in the formally quadruply bonded $Re_2Cl_8{}^{2-}$($a_1 = -84.5$ kcal/mol; $e = -128.6$ kcal/mol). The stabilizing orbital interactions in the formally triply bonded Re_2Cl_8 are stronger than the orbital interactions in the formally quadruply bonded $Re_2Cl_8{}^{2-}$! The small stabilizing contribution of the $b_2(\delta_{xy})$ orbital in Re_2Cl_8(−3.9 kcal/mol) comes from the relaxation of ligand orbitals.

The D_{4h} form of the $^3A_{2u}(\delta^1\delta^{*1})$ excited triplet state of $Re_2Cl_8{}^{2-}$ is not an energy minimum. Rotation about the Re–Re axis by 45° yields a D_{4d} geometry where the Re–Cl bonds are in a staggered conformation which is slightly more stable than the eclipsed structure. Table 2 gives the EDA results for the compounds at optimized geometries which may be compared with the results using frozen geometries given in Table 1. The D_{4d} energy minimum form of the $^3A_{2u}(\delta^1\delta^{*1})$ triplet state of $Re_2Cl_8{}^{2-}$ is 0.9 kcal/mol lower in energy than the triplet species which is optimized with D_{4h} symmetry constraint. The $^3A_{2u}(\delta^1\delta^{*1})$ triplet state is 3.5 kcal/mol less stable than the $^1A_{1g}(\delta^2\delta^{*0})$ global energy minimum of $Re_2Cl_8{}^{2-}$.

The EDA results of the eclipsed structures for the electronic states $^1A_{1g}(\delta^2\delta^{*0})$, $^1A_{2u}(\delta^1\delta^{*1})$ and $^3A_{2u}(\delta^1\delta^{*1})$ with optimized bond lengths and bond angles are quite interesting because they show that the orbital contributions of the stabilizing $a_1(\sigma)$ and $e(\pi)$ interactions become clearly weaker at the longer Re–Re distances while the destabilizing $b_2(\delta_{xy})$ orbital contributions change only little. The smaller values of the attractive terms ΔE_{orb} and $\Delta E_{\mathrm{elstat}}$ at the optimized Re–Re distances are compensated by the weaker Pauli repulsion $\Delta E_{\mathrm{Pauli}}$ which yields an overall stabilization. This is a further example which shows that the equilibrium distance of a covalent bond is not determined by the maximum overlap but by the interplay of attractive and repulsive interactions [28].

The EDA results for the D_{4d} energy minimum form of the $^3A_{2u}(\delta^1\delta^{*1})$ triplet state of $Re_2Cl_8^{2-}$ indicates that the contribution of the $b_2(\delta_{xy})$ orbital is negligible. As noted above, the triplet state is calculated to be 3.5 kcal/mol higher in energy than the D_{4h} global energy minimum of the $^1A_{1g}(\delta^2\delta^{*0})$ singlet. The lower energy of the latter species than the D_{4d} form has been taken as evidence for the stabilization due to Re–Re δ bonding [31]. This is because the d_{xy} metal AOs may only overlap in a bonding fashion yielding a $b_2(\delta_{xy})$ MO when the Re–Cl bonds are eclipsing each other. The results presented here suggest that the preference for the eclipsed conformation of $Re_2Cl_8^{2-}$ is not related to Re–Re δ bonding. The barrier for rotation about the Re–Re bond is very low. The calculation of the twisted (D_{4d}) structure at the open-shell singlet state using the BS approach gives a barrier of only 2.6 kcal/mol. We did not carry out an EDA of the open-shell transition state because the calculations collapse to a broken-symmetry solution. A possible explanation for the lower energy of the eclipsed conformation can be given in terms of hyperconjugation of the Re–Cl orbitals. It has been shown in recent theoretical studies that hyperconjugation may play a very important role for the conformation of molecules [32,33 see also 35]. The strength of the hyperconjugation in $^1A_{1g}(\delta^2\delta^{*0})$ cannot be determined with the EDA because the stabilizing interactions between the occupied Re–Cl and vacant Re–Cl* orbitals may have the same symmetry as the Re–Re bonding orbitals.

The value of the destabilizing contribution of the $b_2(\delta_{xy})$ orbitals changes only slightly from the frozen geometry (Table 1) to the energy minimum structure of the $^1A_{1g}(\delta^0\delta^{*2})$ excited state of $Re_2Cl_8^{2-}$ (Table 2). The optimization of the latter species at BP86/TZ2P gives a Re–Re bond length of 2.345 Å which is as expected longer than the equilibrium distance in the $^1A_{1g}(\delta^2\delta^{*0})$ ground state. Table 2 shows that the value for the destabilizing contribution of the $b_2(\delta_{xy})$ orbitals is now 31.8 kcal/mol which is slightly less than that at the shorter Re–Re distance. The other energy terms encounter larger changes but the overall value for the adiabatic excitation energy $^1A_{1g}(\delta^2\delta^{*0}) \rightarrow {}^1A_{1g}(\delta^0\delta^{*2})$ is again very close (30.0 kcal/mol) to the calculated data for the $b_2(\delta_{xy})$ orbital term.

The strongest argument against the role of Re–Re δ-bonding favouring the D_{4h} geometry of $Re_2Cl_8^{2-}$ comes from the geometry optimizations of the D_{4h} and D_{4d} structures of singlet Re_2Cl_8. Table 2 shows that the eclipsed structure of the latter species which has a Re–Re triple bond is 1.5 kcal/mol lower in energy than the staggered species which is a transition state. Calculations at the CCSD(T) level using a TZ2P quality basis set gave a difference of 0.2 kcal/mol in favor of the D_{4h} form. The weakly stabilizing contributions of the $b_2(\delta_{xy})$ orbitals in both forms which have nearly the same strength (−2.0 kcal/mol in the eclipsed form and −2.3 kcal/mol in the staggered form) come from the relaxation of the metal-ligand orbitals. The finding that the D_{4h} geometry with eclipsing Re–Cl bonds is lower in energy than the D_{4d} form which has a staggered conformation both in of $Re_2Cl_8^{2-}$ where the Re–Re $b_2(\delta_{xy})$ orbital is occupied and in Re_2Cl_8 where it is vacant supports the conclusion that the lower energy of the eclipsed conformation comes from hyperconjugation.

The comparison of the EDA results for $Re_2Cl_8^{2-}$ and Re_2Cl_8 at the equilibrium geometry of the singlet states reveals interesting details. The calculated Re–Re bond becomes longer when two electrons are removed from the dianion which is in agreement with the formal reduction of the bond order from four to three. However, the calculations also show that the Re–Re triple bond in Re_2Cl_8 is indeed significantly *stronger* ($\Delta E_{\mathrm{int}} = -109.7$ kcal/mol) than the Re–Re quadruple bond in $Re_2Cl_8^{2-}$ ($\Delta E_{\mathrm{int}} = -54.2$ kcal/mol). There is no correlation between bond multiplicity and bond strength and neither is there a correlation between bond strength and bond length. The same conclusion has recently been made in a thorough theoretical study about metal–metal multiple bond by Roos, Borin and Gagliardi [35]. Since the Re–Re δ bond is according to the EDA negligible for the bonding interactions, there must be other factors responsible for the change in the bond length and bond energy. The data in Table 2 clearly show that it is the weaker Pauli repulsion which leads to the overall stronger bond in neutral Re_2Cl_8, because the attractive terms ΔE_{orb} and $\Delta E_{\mathrm{elstat}}$ are weaker than in $Re_2Cl_8^{2-}$. The conclusion is that the population of the $b_2(\delta_{xy})$ orbital in $Re_2Cl_8^{2-}$ actually weakens the metal–metal bond because of the stronger Pauli repulsion which is induced in the dianion.

In order to analyse the change of the energy terms in $Re_2Cl_8^{2-}$ and Re_2Cl_8 at different Re–Re bond lengths we carried out EDA calculations using the longer bond of the neutral compound (2.326 Å) for the dianion and the shorter bond of the dianion (2.230 Å) while the rest of the geometries was optimized. The results are shown in Table 3. The comparison of the EDA values for $Re_2Cl_8^{2-}$ with the calculated data at the equilibrium geometry (Table 1) shows that the increase in the Pauli repulsion at the shorter distance by 95.5 kcal/mol is compensated by stronger orbital interactions of 37.1 kcal/mol and particularly by enhanced electrostatic attraction of 63.6 kcal/mol. Note that the contribution of the $b_2(\delta_{xy})$ orbital in $Re_2Cl_8^{2-}$ at the longer distance is now even slightly repulsiv. We want to point out

Table 3 EDA of $Re_2Cl_8^q$(q= 2−, 0) and $Os_2Cl_8^q$(q= 0, 2+) at BP86/TZ2P. Energies in kcal/mol

	$Re_2Cl_8^{2-a,b}$ D_{4h} $\delta^{(2)}\delta^{*(0)}$	$Re_2Cl_8^{c,d}$ D_{4h} $\delta^{(0)}\delta^{*(0)}$	$Re_2Cl_8^{2-b}$ D_{4h} $\delta^{(2)}\delta^{*(0)}$	$Re_2Cl_8^{d}$ D_{4h} $\delta^{(0)}\delta^{*(0)}$	$Os_2Cl_8^{e}$ D_{4h} $\delta^{(2)}\delta^{*(0)}$	$Os_2Cl_8^{2+f}$ D_{4h} $\delta^{(0)}\delta^{*(0)}$
r(M-M)	2.326	2.230	2.230	2.326	2.273	2.403
ΔE_{int}	−49.1	−110.0	−54.2	−109.7	−92.7	−10.1
$\Delta E_{\mathrm{pauli}}$	309.9	360.2	405.4	272.7	256.8	162.4
$\Delta E_{\mathrm{elstat}}{}^{g}$	−180.9 (50.4%)	−234.2 (49.8%)	−244.5 (53.2%)	−181.3 (47.4%)	−151.7 (43.4%)	+15.5
$\Delta E_{\mathrm{orb}}{}^{g}$	−178.1 (49.6%)	−236.0 (50.2%)	−215.2 (46.8%)	−201.1 (52.6%)	−197.9 (56.6%)	−188.0
$a_1(\sigma)^h$	−75.3 (42.3%)	−98.6 (41.8)	−84.5 (39.3%)	−89.9 (44.7%)	−97.6 (49.3%)	−102.5 (54.5%)
$a_2{}^h$	−0.1 (0.1%)	−0.1(< 0.1%)	−0.1(< 0.1%)	−0.1(< 0.1%)	−0.1(< 0.1%)	−0.3(0.2%)
$b_1(\delta_{x2-y2})^h$	−1.1 (0.6%)	−2.7 (1.1%)	−1.5 (0.7%)	−1.9 (1.0%)	−2.9 (1.5%)	−3.6 (1.9%)
$b_2(\delta_{xy})^h$	3.3 (−1.9%)	−3.1 (1.3%)	−0.5 (0.2%)	−2.0 (1.0%)	0.9 (−0.5%)	−2.9 (1.5%)
$e(\pi)^h$	−104.9 (58.9%)	−131.5 (55.7%)	−128.6 (59.8%)	−107.2 (53.3%)	−98.2 (49.6%)	−78.7 (41.9%)

[a] Optimized geometry with a frozen longer Re–Re distance

[b] The interacting fragments are $ReCl_4^-$ ($^5B_2$)

[c] Optimized geometry with a shorter longer Re–Re distance

[d] The interacting fragments are $ReCl_4$($^4A_1$)

[e] The interacting fragments are $OsCl_4$($^5B_2$)

[f] The interacting fragments are $OsCl_4^+$($^4A_1$)

[g] Values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$

[h] Values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}

that the overall attraction in neutral Re_2Cl_8 at the shorter Re–Re distance of 2.230 Å is actually slightly stronger ($\Delta E_{\mathrm{int}} = -110.0$ kcal/mol) than at the equilibrium distance of 2.326 Å ($\Delta E_{\mathrm{int}} = -109.7$ kcal/mol). The reason for the longer bond is the geometry relaxation of the $ReCl_4$ fragments at the equilibrium which compensate for the small decrease of the metal–metal attraction. The analysis of the Re–Re interactions in $Re_2Cl_8{}^{2-}$ and Re_2Cl_8 are another striking example that it is not justified to use the bond length as indicator for the strength of the bond.

We finally analysed the complexes Os_2Cl_8 and $Os_2Cl_8^{2+}$ which are isoelectronic with $Re_2Cl_8{}^{2-}$ and Re_2Cl_8 in order to address the question whether the negative charge in the rhenium complex has an influence on the negligible contribution of the $b_2(\delta_{xy})$ orbital to the metal–metal interactions. Table 3 gives the EDA data for the four complexes at the equilibrium geometries. The orbital interactions in the osmium complexes are slightly stronger than in the rhenium species but the trend of the σ and π contributions when one goes from the formally quadruply bonded species to the triply bonded complexes is the same. The metal–metal σ bonds become stronger and the π bonds become weaker when the metal–metal δ orbital is vacant. The calculated metal–metal bond in both systems becomes longer when two electrons are removed which is in agreement with the formal reduction of the bond order from four to three. The total orbital contribution ΔE_{orb} to the metal–metal bonding also decreases for both systems when one goes from the occupation $\delta^2\delta^{*0}$ to $\delta^0\delta^{*0}$ but the decrease is not related to the loss of the $b_2(\delta_{xy})$ contribution to the metal–metal bonding which is negligible in all cases. The results clearly show that the very weak stabilization which comes from the metal–metal δ bond is not an artefact of the negative charge in $Re_2Cl_8{}^{2-}$. It is interesting to note that the Os-Os interaction in $Os_2Cl_8^{2+}$ is much weaker ($\Delta E_{\mathrm{int}} = -10.0$ kcal/mol) than in Os_2Cl_8 ($\Delta E_{\mathrm{int}} = -92.8$ kcal/mol). This comes from the dramatic loss of the electrostatic term which in the latter compound is strongly attractive ($\Delta E_{\mathrm{elstat}} = -151.7$ kcal/mol) while it is even repulsive in the dication ($\Delta E_{\mathrm{elstat}} = +15.5$ kcal/mol).

4 Summary and conclusion

The EDA investigation of the metal–metal interactions in $Re_2Cl_8{}^{2-}$ indicates that the strength of the δ bonding is nil. The contribution of the $b_2(\delta_{xy})$ orbitals to the Re–Re bond in the $^1A_{1g}(\delta^2\delta^{*0})$ ground state is negligibly small. The vertical excitation of one and two electrons from the bonding δ orbital into the antibonding δ* orbitals yielding the singly and doubly excited states $^1A_{1g}(\delta^1\delta^{*1})$ and $^1A_{1g}(\delta^0\delta^{*2})$ gives a destabilization of 17.5 and 36.1 kcal/mol, respectively, which is nearly the same as the total excitation energies. The preference for the D_{4h} geometry with eclipsing Re–Cl bonds is explained in terms of hyperconjugation rather than δ bonding. This is supported by the calculation of the triply bonded Re_2Cl_8 which also has an eclipsed energy minimum structure. The calculations also suggest that the Re–Re triple bond in Re_2Cl_8 is stronger than the Re–Re quadruple bond in $Re_2Cl_8{}^{2-}$. A negligible contribution of the δ orbital to the metal–metal bond strength is also calculated for Os_2Cl_8 which is isoelectronic with $Re_2Cl_8{}^{2-}$.

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