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THE CHEMICAL BONDING OF Re_3Cl_9 AND $Re_3Cl_9^{2-}$ REVEALED BY THE ADAPTIVE NATURAL DENSITY PARTITIONING ANALYSES

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Chemical bonding of neutral rhenium trichloride Re_3Cl_9 and doubly charged $Re_3Cl_9^{2-}$ has been brought into question in the current work. Despite recently reported propositions of π-aromaticity of neutral Re_3Cl_9 based on negative nuclear independent chemical shift (NICS) values[1,2] to the contrary, it is shown to be a purely classical chemical molecule, according to the results of the recently developed Adaptive Natural Density Partitioning (AdNDP) analysis.[3–5] The formation of three consecutive double bonds in a triatomic cycle formed by rhenium atoms that was initially predicted by Cotton et al.[6–8] is confirmed. The chemical bonding picture changes dramatically upon addition of two excess electrons to Re_3Cl_9. The rhenium atoms of the resulting doubly charged cluster are shown to be held together via three single Re-Re σ-bonds, three Re-Cl-Re σ-bonds, and a totally delocalized π-bond based on valence d atomic orbitals (d-AO) of rhenium atoms with minor contributions coming from the density associated with six apical chlorine atoms, which makes $Re_3Cl_9^{2-}$ π-aromatic.

Keywords: AdNDP, chemical bonding, Re_3Cl_9, $Re_3Cl_9^{2-}$, transition metal aromaticity

The polymeric rhenium chloride $[Re_3(\mu\text{-}Cl)_3Cl_6]$ when dissolved[6] or in the gas phase[9] features a Re_3Cl_9 metal cluster in which three rhenium

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atoms form an equilateral triangle with three chlorine atoms (μ) acting as bridging groups along the edges of the triangle and the remaining six apical chlorine atoms out of the plane forming a trigonal prism. Cotton and co-workers[6–8] proposed that each rhenium atom in Re_3Cl_9 possessed homophilicity, or a tendency to form bonds to one or more other atoms of the same chemical identity, based on a valence bond approach by use of certain limiting, generally quite symmetrical, hybridization schemes. There exist two different chemical bonding languages in contemporary chemistry. The first is the well-known Lewis chemical bonding model,[10] which he had developed as a generalization of numerous experimental data well before the formulation of quantum mechanics. It's a "pencil and paper" approach based on the octet rule to predict structure of a given system knowing its chemical formula, where chemical bonding objects are thought to be comprised of two electrons localized over one (a lone pair, or *one*-center—*two*-electron (*1*c-*2*e) bond), or two atoms (*two*-center—*two*-electron (*2*c-*2*e) bond). The second language was introduced by quantum chemistry on the basis of canonical Hartree–Fock or Kohn–Sham molecular orbitals. The key difference of the second language is that *two*-electron chemical bonding objects called canonical molecular orbitals (CMOs) are now delocalized over the entire molecule. Since the 1960s, a few schemes have been proposed for obtaining localized orbitals from completely delocalized ones,[11–15] with the Natural Bonding Orbital (NBO) procedure being the most popular, and incorporated into most of the computational chemistry software packages such as Gaussian. While reproducing intuitively expected Lewis bonding pictures for classical chemical molecules in terms of *1*c-*2*e (lone pairs) and *2*c-*2*e bonds, and a single resonance Kekule structure, when it comes to typical aromatic organic systems,[4] the NBO analysis gives a non-interpretive chemical bonding picture for non-classical systems with delocalized bonding such as boron clusters.[3] This issue arises due to the fact that NBO is restricted for dividing the total electron density into two electron objects delocalized over no more than three atoms. To reconcile this problem the AdNDP analysis was developed,[3–5] which represents the electronic structure in terms of *n*-center–*two*-electron (*n*c-*2*e) bonds, with *n* spanning from one to the total number of atoms of the system of interest (see detailed description of the method elsewhere). The development of such a unified chemical bonding theory tool was most essential for deciphering chemical bonding in metal clusters, which often feature both localized Lewis bonding elements and delocalized bonding objects,

with the latter being interpreted from the view of aromaticity concepts since 2001.[16]

In the present study, we performed the AdNDP analysis of the molecular orbital (MO) wave function of both neutral and doubly charged rhenium chloride species. All the calculations were carried out using the hybrid density functional method, known in the literature as B3LYP,[17–19] with a pseudo core LANL2DZ potential and basis-set.[20] In order to test if the obtained results depend on the method used, we repeated all the calculations at Hartree-Fock, BPW91,[21–24] and PBE1PBE[25–26] levels with the same LANL2DZ potential and basis-set. All the calculations were performed using the Gaussian 03 software package.[27] It is shown that the results of the AdNDP analysis, similar to those of NBO, do not depend on the quality of the basis set used,[3,4] so the choice of the level of theory for the AdNDP application is adequate. The visualization of the AdNDP results are done using MOLEKEL 4.3 program.[28] The experimental X-ray parameters of Re_3Cl_9 were reported by Cotton and co-workers,[29] whereas the theoretical structural parameters of Re_3Cl_9, and $Re_3Cl_9^{2-}$ calculated using Amsterdam Density Functional with spin orbit and scalar relativistic effects incorporated via the zero order regular approximation were reported by Alvarado-Soto et al.[1,2]

The results of the AdNDP analysis of Re_3Cl_9 and $Re_3Cl_9^{2-}$ clusters are presented in Figure 1(a) and (b), respectively. The occupation numbers and the visualized AdNDP-obtained bonds do not depend on the choice of the theoretical method. Occupation numbers for all the bonds are given at B3LYP/LANL2DZ, HF/LANL2DZ (in parenthesis), BPW91/LANL2DZ (in square brackets), PBE1PBE/LANL2DZ (in squiggle brackets) levels (see Figure 1), and differ by no more than 0.1 |e|.

There are 84 and 86 valence electrons, which form 42 and 43 *two*-electron elements in Re_3Cl_9 and $Re_3Cl_9^{2-}$, respectively. In both cases, 27 lone pairs (three on each of the chlorine atoms) are deleted from Figure 1, thus leaving only 15 and 16 chemical bonding objects in (a) and (b), respectively. According to the AdNDP analyses, both neutral and doubly charged anion have six *2*c-*2*e p-d-hybridized σ-bonds between each apical chlorine atom and the neighboring rhenium atom; bridging chlorine atoms are bound to the triangular Re_3 core via *3*c-*2*e p-d-hybridized Re-Cl-Re σ-bonds with the major electron density contribution of 74% coming from lone pairs on bridging μ-chlorine atoms (in other words, if these three *3*c-*2*e p-d-hybridized Re-Cl-Re σ-bonds

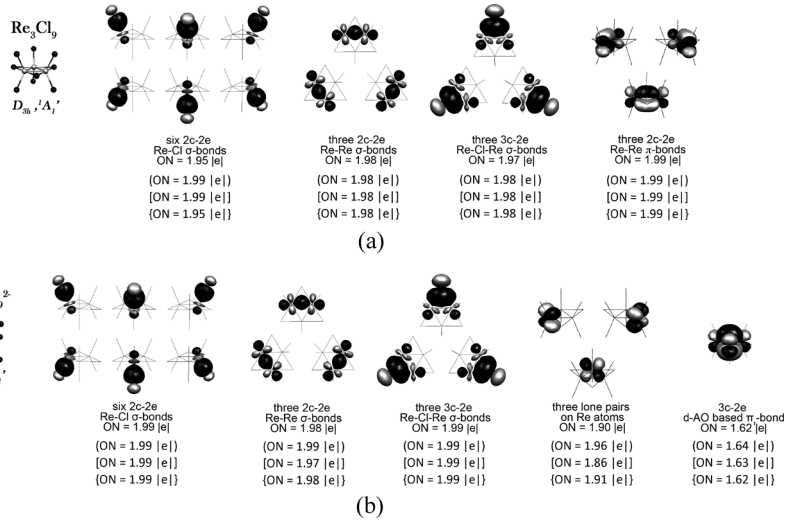

Figure 1. Chemical bonding elements recovered by the AdNDP analyses of (a) neutral Re_3Cl_9 and (b) doubly charged $Re_3Cl_9^{2-}$. Occupation numbers (ON) are given at B3LYP/LANL2DZ, HF/LANL2DZ (in parenthesis), BPW91/LANL2DZ (in square brackets), PBE1PBE/LANL2DZ (in squiggle brackets) levels.

are reduced to just lone pairs on the three bridging μ-chlorine atoms their occupation number drops to 1.46 |e|); and, finally, there are three *2*c-*2*e Re-Re d-AO based σ-bonds. For all the recovered chemical bonding elements the occupation numbers (ON), which indicate how many electrons there are per bond, are close to the ideal limit of 2.00 |e|. The difference in the chemical bonding picture of Re_3Cl_9 and $Re_3Cl_9^{2-}$ is rooted in the AdNDP bonds formed out of d-AO based canonical π-MOs. There are six symmetry-adapted combinations of d-AOs that one can construct to form π-MOs in a model triatomic system: totally bonding radial, totally antibonding tangential, and two sets of doubly degenerate π-MOs of bonding-antibonding characters built out of both tangential and radial d-AOs (Figure 2).

In the case of Re_3Cl_9, there are three occupied π-CMOs with the main electron density contribution coming from d-AOs of rhenium atoms, namely highest occupied doubly degenerate MO (HOMO) of e$''$ symmetry and a totally bonding radial HOMO-1 of a_2'' symmetry (Figure 2a). If one were to exclude the contribution of electron density associated with chlorine atoms, the resulting MOs would resemble

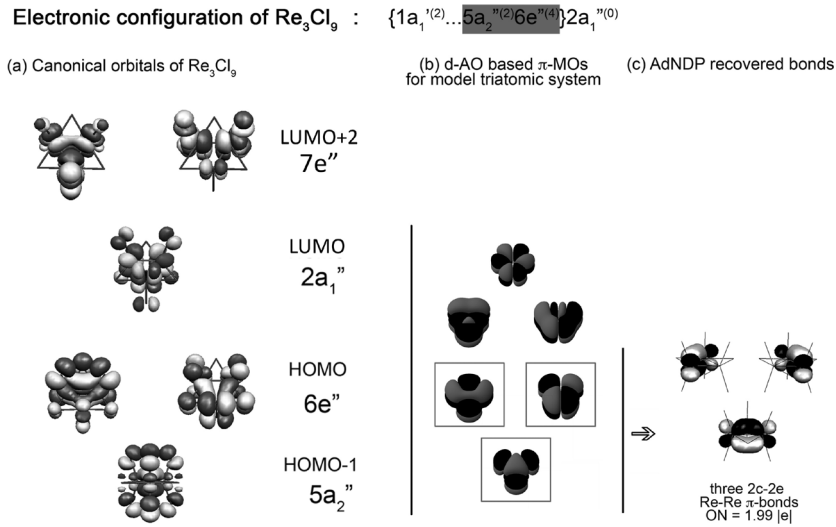

Figure 2. (a) Canonical molecular orbitals (CMOs) of Re_3Cl_9; (b) d-AO based π-molecular orbitals for model triatomic system with the occupied ones being marked in green in case of neutral Re_3Cl_9; and (c) three Re-Re π-bonds recovered by the AdNDP analysis.

a model triatomic system (Figure 2b). According to the AdNDP analysis, the occupation of $6e''$ HOMO, and $5a_2''$ HOMO-1 results in the formation of three consecutive *2*c-*2*e Re-Re π-bonds of ON = 1.99 |e| (Figure 2c), as predicted by Cotton and co-workers.[6,8,9] In the neutral Re_3Cl_9 a pair of doubly degenerate LUMO + 2 of e'' symmetry is not occupied. These orbitals lie higher in energy than the totally antibonding tangential π-CMO of a_1'' symmetry due to the contribution of electron density from the six apical chlorine atoms, which increases the antibonding nature of these doubly degenerate π-CMOs compared to that of LUMO ($2a_1''$).

Addition of two excess electrons to the totally antibonding π-tangential $2a_1''$ lowest unoccupied MO (LUMO) of Re_3Cl_9 to produce doubly charged $Re_3Cl_9^{2-}$ changes the chemical bonding picture distinctly (Figure 3).

The totally bonding $5a_2''$ MO is the major contributor to the bonding between rhenium atoms. If only this orbital were occupied out of the whole set of π-canonical molecular orbitals with the main electron density contribution coming from d-AOs of rhenium atoms ($5a_2''$, $6e''$, $7e''$, and $2a_1''$ π-CMOs), the system would be π-aromatic (a model $Re_3Cl_9^{4+}$

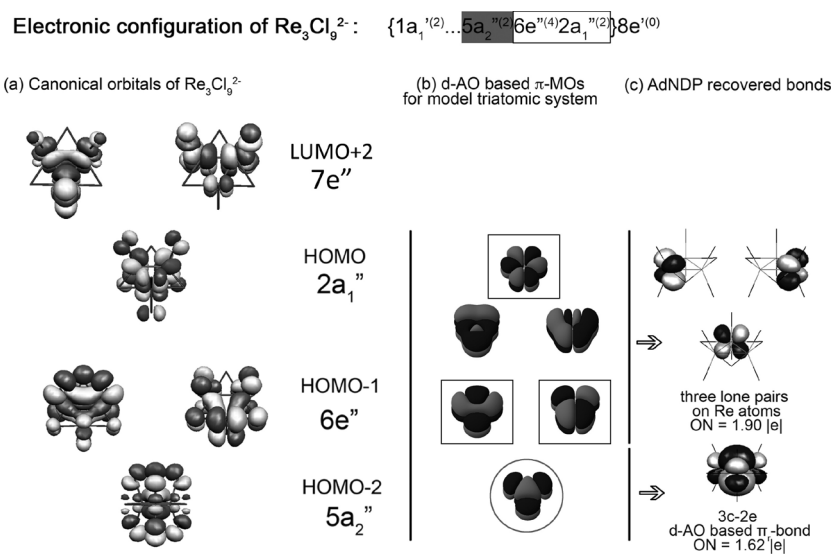

Figure 3. (a) CMOs of $Re_3Cl_9^{2-}$; (b) d-AO based π-molecular orbitals for model triatomic system; and (c) three lone pairs on rhenium atoms formed out of three CMOs (HOMO and doubly degenerate HOMO-1), and totally delocalized d-AO based radial π-bond recovered by the AdNDP analysis.

system). The occupation of a pair of doubly degenerate 6e″ MOs by four electrons brings antibonding character to the bonding between rhenium atoms and results in the formation of three *2*c-*2*e Re-Re π-bonds (as revealed by the AdNDP method for neutral Re_3Cl_9). The subsequent occupation of the antibonding π-tangential $2a_1''$ MO by two electrons to yield the $Re_3Cl_9^{2-}$ cluster brings even more antibonding character to the Re-Re bonding and increases electron "crowding" in the Re_3 triangle. The AdNDP method showed that in the case of the $Re_3Cl_9^{2-}$ cluster, the density associated with these four CMOs can be considered as three lone pairs (ON = 1.90 |e|) on rhenium atoms and a totally bonding π-radial (π_r) *3*c-*2*e bond of ON = 1.62 |e|. The loss of three double *2*c-*2*e Re-Re π-bonds is now partially compensated by the formation of a totally bonding π-radial (π_r) *3*c-*2*e bond, and formation of three lone pairs allows the electron "crowding" in Re_3 triangle to diminish. The $Re_3Cl_9^{2-}$ cluster is, thus, π-aromatic with the two electrons of the *3*c-*2*e π_r-bond satisfying the $4n + 2$ rule for aromaticity ($n = 0$). The low value of the ON for the d-AO based π_r-bond means that this bond is

delocalized over more than just three rhenium atoms. If we allow the AdNDP method to increase the number of atoms on which the π_r-bond can be delocalized, this bond can be found as a *9*c-*2*e π_r-bond with ON = 2.00, now also involving electron density coming from apical chlorine atoms (Figure 4).

The major contribution of 81% of the electron density of the *9*c-*2*e π_r-bond still comes from rhenium atoms. Again, in the doubly charged $Re_3Cl_9^{2-}$ a pair of doubly degenerate LUMO + 2 of e″ symmetry is not occupied. These two orbitals lie higher in energy than the totally antibonding tangential π-CMO of a_1'' symmetry due to the contribution of electron density coming from the six apical chlorine atoms, which increases the antibonding nature of these doubly degenerate π-CMOs compared to that of HOMO ($2a_1''$).

To summarize, in the neutral Re_3Cl_9 cluster each rhenium atom is bound by double (*2*c-*2*e σ- and π-) bonds to the two neighboring rhenium atoms, exactly as Cotton and co-workers predicted 45 years ago, while in the doubly charged $Re_3Cl_9^{2-}$ cluster rhenium atoms are bound together by three single d-AO based *2*c-*2*e σ-bonds and a completely delocalized *9*c-*2*e (which can be reduced to a *3*c-*2*e) π_r-bond responsible for the aromaticity in the $Re_3Cl_9^{2-}$ cluster.

The erroneous proposition of aromatic nature of neutral Re_3Cl_9 has been deduced on the basis of negative NICS values only. It should be kept in mind that NICS does not always give a correct evaluation of aromaticity. The most spectacular failure is assigning cyclopropane (C_3H_6)

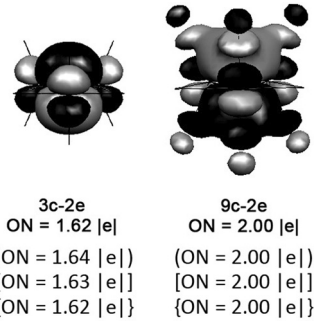

Figure 4. Variation of the occupation number of the d-AO based π_r-bond of $Re_3Cl_9^{2-}$ upon changing the number of centers (atoms) on which it is allowed to be delocalized. Occupation numbers (ON) are given at B3LYP/LANL2DZ, HF/LANL2DZ (in parenthesis), BPW91/LANL2DZ (in square brackets), PBE1PBE/LANL2DZ (in squiggle brackets).

to the family of aromatic species on the basis of negative NICS values. Indeed, $NICS_{zz}$ values for C_3H_6(-29.82 ppm (0.0 Å), -30.87 ppm (0.4 Å), and -24.15 ppm (1.0 Å)) are comparable to those of benzene, a prototypical aromatic hydrocarbon (-14.49 ppm (0.0 Å), -20.57 ppm (0.4 Å), and -29.25 ppm (1.0 Å)), all calculated at the B3LYP/6-311++G** level of theory. Though there has been a long discussion on whether cyclopropane is σ-aromatic or not, Schleyer and co-workers, who developed the NICS criteria, have concluded:[30] "there is no need to invoke σ-aromaticity in cyclopropane energetically" because "the extra σ-stabilization energy (at most 3.5 kcal mol^{-1}) is far too small to explain the small difference in strain energy between cyclopropane (27.5 kcal mol^{-1}) and cyclobutane (26.5 kcal mol^{-1}) by σ-aromaticity."

There are various criteria for aromaticity that have been proposed in the literature[31–34] such as enhanced stability, high symmetry, low reactivity, bond length equalization, enhanced anisotropy of diamagnetic susceptibility, diatropic (low-field) ^{1}H NMR shifts, large negative nucleus independent chemical shift (NICS) values, and high electron detachment energies in photoelectron spectra. We propose a new criterion of aromaticity: a chemical molecule should be considered as being aromatic if there is a delocalized bonding encountered in a cyclic system by means of the AdNDP analysis that satisfies the $4n + 2$ rule. The key feature of AdNDP is to recover first all the localized bonding elements, such as lone pairs and *2*c-*2*e bonds, and only then rationalize the residual density in terms of delocalized objects. This procedure assures that the recovered delocalized objects cannot be localized. The AdNDP method has proven itself as the right tool in determining such delocalization in organic molecules,[4] boron clusters,[3] and transition metal compounds, as shown in the current work, as an example of doubly charged rhenium trichloride.

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