



Research Article

Quantum theory of atoms-in-molecules (QTAIM): Study of the bonding in di-ruthenium di-chloro cluster

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Abstract

Theoretical investigations were conducted to explore the nature of interactions between ruthenium (Ru) atoms and chlorine (Cl) ligands in the di-bridged diruthenium carbonyl cluster $[\text{Cp}^{\ddagger}\text{Ru}(\mu\text{-Cl})_2]$, employing the Quantum Theory of Atoms-in-Molecules (QTAIM) approach. The study involved an analysis of the topological properties of electron density within both the metal-metal and metal-ligand bonds, along with the computation of bond delocalization indices $\delta(A, B)$. These findings were then compared with data from prior research on organometallic systems. Notably, the presence of bridging chlorine atoms was found to influence the electron density distribution in Ru-Ru interactions. Interestingly, no direct bonding, as indicated by the absence of bond critical points or bond paths, was observed between the transition metal atoms. It was proposed that a multicenter $4c-4e$ interaction exists within the bridged regions, Ru_2Cl_2 , of the cluster. Moreover, the Ru-Cl bonds within the cluster exhibited small positive values for electron density $\rho(b)$, small positive values for Laplacian $\nabla^2\rho(b)$, and small negative values for total energy density $H(b)$, all characteristic of an open-shell interaction.

Keywords: AIM approach, Bonding analysis for the dinuclear cluster, DFT calculation, Topological properties, and Di-Ruthenium Di-Chloro Cluster.

Introduction

In modern quantum chemistry, the atoms-in-molecules (AIM) theory (Bader, 1990a; Kumar et al., 2016), is a good and complementary tool to characterize the nature of chemical bonds and predict the properties of the molecular structure (Nakanishi et al., 2008; Gatti, 2005). Useful parameters, such as electronic density ($\rho(b)$), Laplacian ($\nabla^2\rho(b)$) and the ellipticity, ϵ , which are computed at bond critical points are used to concept structure and interaction in organometallic compounds through valence bonds(VS) and non-valence interactions (Van Der Maelen & Cabeza, 2012; Niskanen et al., 2009; Maelen et al., 2011). The aim of this paper is thus to explore the nature of their bonding and analysis the electron density distributions via topological parameters associated with Ru-Ru, Ru-Cl bonds in di nuclear clusters:- $[\text{Cp}^{\ddagger}\text{Ru}(\mu\text{-Cl})_2]$ (Shimogawa et al., 2013).

Computational Methods

The X-ray diffraction data of the systems under study were used as starting points to calculate the optimized geometries. These systems were optimized at the PBE1PBE (Adamo & Barone, 1999). level theory in conjunction with the SDD (Fuentelba et al., 1982) basis set for Ru atoms and the 6-31G (d,p) (Hehre et al., 1972) basis set for remaining atoms using the Gaussian 09 program packages(Gaussian, 2009). The geometry of the complex is confirmed to be a local minimum by the absence of imaginary vibrational frequencies. QTAIM approach has been performed with the AIM2000 program packages (Bader et al., 2002). The large all-electron “well-tempered basis set” WTBS (Sakai et al., 1997) was used for the Ru atoms while the 6-31G (d,P) basis set was used for Cl, O, C and H atoms.

Results and Discussion

Topological Properties of the Electron Density

The QTAIM method, employed using the AIM2000 program, plays a pivotal role in elucidating molecular and nanocluster structures and their bonding characteristics. One of its central features is the determination of the metal-metal bond critical point (BCP) through calculations (Jabłoński & Palusiak, 2010; Mosapour Kotena et al., 2014). These critical points carry crucial information regarding the nature of bonding, distinguishing between open and closed-shell interactions. A specific class of critical points, known as bond critical points (BCPs) and labeled as (3,-1), is indicative of the presence of bonding (Grimme, 1996; Bader, 1998). BCPs are characterized by a decrease in electron density along two directions and concentration in the third direction. Conversely, ring critical points (RCPs), labeled as (3,+1), are characterized by a decrease in electron density in one direction and an increase in two directions. Some structures exhibit cage critical points (CCPs), labeled as (3,+3), which lead to an increase in charge density in all three directions. In the context of chemical bonding within a compound, a bond is characterized by a bond path that connects two nuclei while passing through their respective bond critical point (Biegler-könig et al., 1982; Aray et al., 2000; Richard, 2009). The chemical structure of the system can be represented as a topological graph generated from the network of bond paths and the maxima of charge densities (Gatti, 2005; Richard, 2002). In the cluster graph (Fig. 1), various critical points, including bond critical points and ring critical points, are connected by bond paths, illustrating the bonding between

nuclei. Of particular significance is the absence of direct bonding between the transition metal nuclei in the cluster. Notably, no bond critical point or bond path was found between these transition metal atoms. Additionally, several ring critical points were identified.

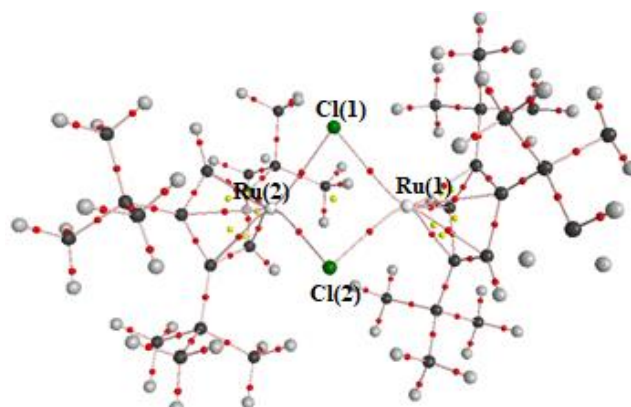


Fig. 1 Molecular graphs of complex, illustrating the presence bond paths (solid line) and bond and ring critical points with red and yellow dots, respectively.

Fig. 2 a gradient trajectory map in chosen core plane of all clusters is shown, where all BPs and BCPs with the atomic basins in the selected planes are clearly seen. Furthermore, for cluster, the electron density allocation is very similar around Ru atoms, but no BPs and BCPs between in most Ru-Ru metallic atom which bonding to Cl bridge. The bps and bcps found between Ru-Cl are also shown.

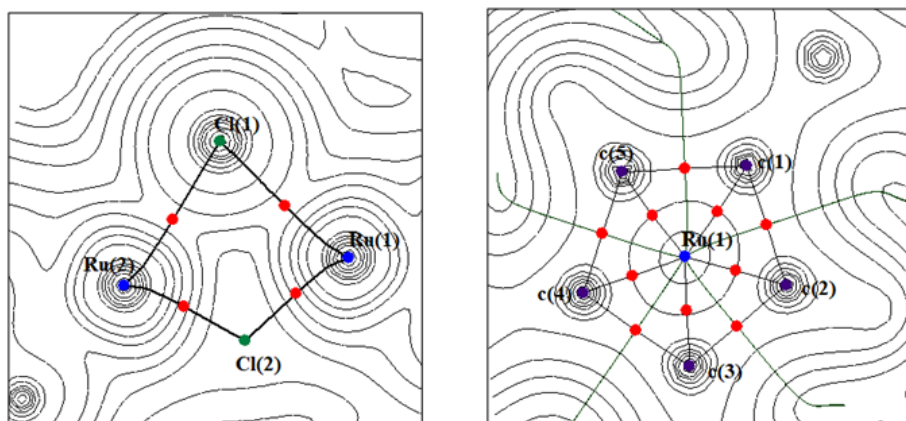


Fig. 2 Gradient trajectories map on a total electron density plot through the core plane of clusters. The atomic basins, bp's and bcp's are also shown.

M-M interactions in cluster

The quantum theory of atoms in molecules is a very popular tool for evaluation properties of atoms and nature of the chemical bonding (Coppens et al., 1999). Based on AIM theory (Bader, 1990a), the characterization and understanding of topology of the electron density ρ_b , the Laplacian of

electron density $\nabla^2\rho_b$, and the total energy density H_b at the bond critical point (BCP) are useful tools for the concept of chemical bonds (Bader, 1990b; Cremer & Kraka, 1984).

The large values of electron density and negative values of the Laplacian and the total energy density are denoted as the open shell or shared (covalent) interactions. On the other hand, small values of electron density, positive values of Laplacian

and total energy density the interactions are closed shells. An additional total energy density $H_b(r)$ is defined as

$$H_b(r) = G_b(r) + V_b(r),$$

where $G_b(r)$ and $V_b(r)$ indicate, respectively, the kinetic and potential energy density, and have been identified as a more

appropriate index than Laplacian to characterize an interaction (Rozas et al., 2000).

In Table 1, The results of the above-mentioned topological properties for the selected bonds of the cluster are included.

Table 1. Selected topological parameters at the bond critical points for the cluster 1-4. ρ_b : electron density, $\nabla^2\rho_b$: Laplacian of the electron density, G_b : kinetic energy density ratio, V_b : potential energy density ratio, H_b : total energy density ratio, ϵ_b : ellipticity

Bond	$\rho_b(\text{e}\text{\AA}^{-3})$	$\nabla^2\rho_b(\text{e}\text{\AA}^{-5})$	$G_b(\text{he}^{-1})$	$H_b(\text{he}^{-1})$	$V_b(\text{he}^{-1})$	ϵ_b
Ru(1)-Cl(1)	0.054	0.236	0.063	-0.003	-0.066	0.644
Ru(1)-Cl(2)	0.053	0.232	0.061	-0.003	-0.064	0.6707
Ru(2)-Cl(1)	0.054	0.232	0.061	-0.003	-0.064	0.670
Ru(2)-Cl(2)	0.054	0.236	0.063	-0.003	-0.066	0.644
Ru-C (ave)	0.297	0.668	0.1144	-0.2816	-0.3956	0.216

An intriguing observation, as previously mentioned, is the complete absence of any bond critical points (BCPs) of type (3,-1) between the Ru atoms at the core, which are interconnected by Cl groups. This discovery underscores the complete lack of localized electron density between the Ru atoms, compelling us to assert that there is no direct chemical bonding between any pair of Ru atoms at the core (Bader, 1998). The robust bridging interaction provided by the Cl groups disrupts the topological Ru-Ru connectivity. However, bond critical points with their associated bond paths have been identified in interactions involving both supported and unsupported metal-metal atoms (Racioppi et al., 2018). Regarding the Ru-Cl bonds, the topological properties were computed and are presented in Table 1. The calculated

electron density values are notably higher than zero (0.054 $\text{e}\text{\AA}^{-3}$), the Laplacian values are positive (0.236 $\text{e}\text{\AA}^{-5}$), and the $H(b)$ values exhibit negativity (-0.003 he^{-1}). Based on this data and in line with arguments in the literature, Ru-Cl interactions are categorized as open-shell interactions (Macchi & Sironi, 2003). Additionally, the computed AIM ellipticities for Ru-Cl bonds are greater than zero, suggesting that these interactions tend to be approximately linear in nature.

The plot of Laplacian map for the cluster core shows the polarization of the VSCCs of bridging chloro toward the midpoint of Ru-Ru interactions (Fig. 3) and the valence shell charge concentration (VSCC) the carbonyl C atoms toward the Ru atoms.

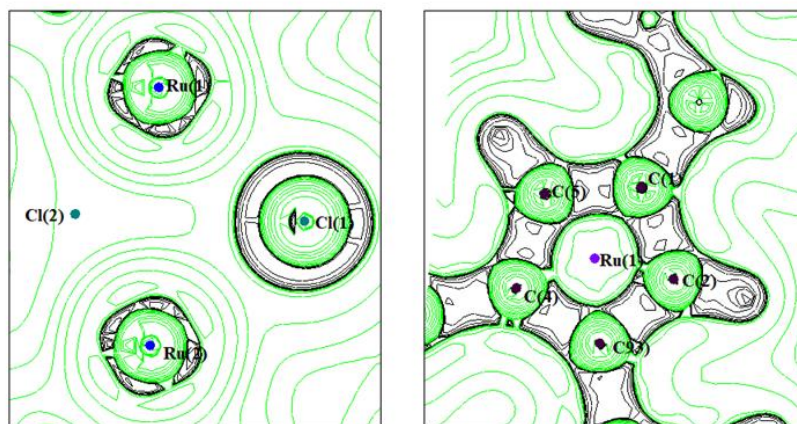


Fig. 3 Laplacian distribution $\nabla^2\rho(b)$ plot of the di-bridged diruthenium carbonyl cluster

The delocalization index, denoted as $d(A, B)$ (Van der Maelen et al., 2020), serves as a quantification of the shared electrons between two atoms. It is a pertinent AIM indicator used to characterize chemical bonding between atoms, and notably, it doesn't rely on the presence of a bond critical point. In Table 2, you can find the computed values of the delocalization index $\delta(A-B)$ for the Ru cluster. The magnitude of $d(\text{Ru}, \text{Ru})$

falls within the range of 0.113, closely resembling values previously computed by the Cabeza group (Maelen et al., 2011). Furthermore, these computed data are akin to, or even exceed, values calculated for various bridged M-M interactions (Macchi & Sironi, 2003; Cabeza et al., 2009; Bo et al., 1993). To summarize the data, which involves the summation of delocalization index values for the nonbonding

Ru-Ru interactions and the four Ru-Cl bonding interactions, it can be concluded that the total $\delta(A-B)$ for the core amounts to 2.069 electron pairs within the Ru_2Cl_2 core. Consequently, the

interaction within this core can be described as a 4c-4e interaction.

Table 2. The delocalization indices for specific atomic $\delta(A, B)$ interactions

atom pairs (A, B)	Ru(1) -Ru(2)	Ru(1)-Cl(1)	Ru(1)-Cl(2)	Ru(2)-Cl(1)	Ru(2)-Cl(2)
$\delta(A, B)$	0.1134	0.486	0.492	0.486	0.492

Conclusion

In summary, the application of Quantum Theory of Atoms in Molecules (QTAIM) to analyze $[(Cp^*_2Ru(\mu-Cl))_2]$ cluster has provided valuable insights into the electron density topological parameters and bonding characteristics within this cluster. A particularly noteworthy finding is the identification of a bond critical point and its associated bond path within the Ru-H bond in the core part Ru_2Cl_2 . Interestingly, while no bond critical points or bond paths were detected between any pair of Ru metal atoms, a significant delocalization index was computed. This complex bonding situation in the Ru_2Cl_2 core can be aptly described as a series of multiple 4c-4e interactions within the cluster. Additionally, the topological properties determined for the Ru-Cl bonds strongly indicate that all these bonds exhibit characteristics typical of open-shell interactions.

Conflict of Interest

The author hereby declares no conflict of interest.

Consent for publication

The author declares that the work has consent for publication.

References

- Adamo, C., & Barone, V. (1999). Toward reliable density functional methods without adjustable parameters: The PBE0 model. *Journal of Chemical Physics*, 110(13), 6158–6170. <https://doi.org/10.1063/1.478522>
- Aray, Y., Rodriguez, J., & Vega, D. (2000). Topology of the Electron Density and Cohesive Energy of the Face-Centered Cubic Transition Metals. *Journal of Physical Chemistry B*, 104(19), 4608–4612. <https://doi.org/10.1021/jp993976a>
- Bader, R.F.W. (1998). A Bond Path: A Universal Indicator of Bonded Interactions. *Journal of Physical Chemistry A*, 102, 7314–7323. <https://doi.org/10.1021/jp981794v>
- Biegler-König, F., & Schönbohm, J. (2002). Update of the AIM2000-Program for atoms in molecules. *Journal of Computational Chemistry*, 23(15), 1489–1494. <https://doi.org/10.1002/jcc.10085>
- Bader, Richard F. W. (2002). Atoms in Molecules. In *Encyclopedia of Computational Chemistry* (pp. 9–15). <https://doi.org/10.1002/0470845015.caa012>
- Bader, Richard F.W. (2009). Bond paths are not chemical bonds. *Journal of Physical Chemistry A*, 113(38), 10391–10396. <https://doi.org/10.1021/jp906341r>
- Biegler-könig, F. W., Bader, R. F. W., & Tang, T. -H. (1982). Calculation of the average properties of atoms in molecules. II. *Journal of Computational Chemistry*, 3(3), 317–328.

- <https://doi.org/10.1002/jcc.540030306>
- Bo, C., Sarasa, J. P., & Poblet, J. M. (1993, June). Laplacian of charge density for binuclear complexes: terminal vs bridging carbonyls. *The Journal of Physical Chemistry*, 97(24), 6362–6366. <https://doi.org/10.1021/j100126a009>
- Cabeza, J. A., Van Der Maelen, J. F., & Garcia-Granda, S. (2009). Topological analysis of the electron density in the N-heterocyclic carbene triruthenium cluster $[Ru_3(\mu-H)_2(\mu_3-MelmCH)(CO)_9]$ (Me2im = 1,3-dimethylimidazol-2-ylidene). *Organometallics*, 28(13), 3666–3672. <https://doi.org/10.1021/om9000617>
- Coppens, P., Abramov, Y., Carducci, M., Korjov, B., Novozhilova, I., Alhambra, C., & Pressprich, M. R. (1999). Experimental Charge Densities and Intermolecular Interactions: Electrostatic and Topological Analysis of dl-Histidine. *Journal of the American Chemical Society*, 121(11), 2585–2593. <https://doi.org/10.1021/ja983320f>
- Cremer, D., & Kraka, E. (1984). Chemical Bonds without Bonding Electron Density — Does the Difference Electron-Density Analysis Suffice for a Description of the Chemical Bond? *Angewandte Chemie International Edition in English*, 23(8), 627–628. <https://doi.org/10.1002/anie.198406271>
- Fuentealba, P., Preuss, H., Stoll, H., & Von Szentpály, L. (1982). A proper account of core-polarization with pseudopotentials: single valence-electron alkali compounds. *Chemical Physics Letters*, 89(5), 418–422. [https://doi.org/10.1016/0009-2614\(82\)80012-2](https://doi.org/10.1016/0009-2614(82)80012-2)
- Gatti, C. (2005). Chemical bonding in crystals: new directions. *Zeitschrift Für Kristallographie - Crystalline Materials*, 220(5–6), 399–457. <https://doi.org/10.1524/zkri.220.5.399.65073>
- Grimme, S. (1996). Theoretical bond and strain energies of molecules derived from properties of the charge density at bond critical points. *Journal of the American Chemical Society*, 118(6), 1529–1534. <https://doi.org/10.1021/ja9532751>
- Hehre, W. J., Ditchfield, K., & Pople, J. A. (1972). Self-consistent molecular orbital methods. XII. Further extensions of gaussian-type basis sets for use in molecular orbital studies of organic molecules. *The Journal of Chemical Physics*, 56(5), 2257–2261. <https://doi.org/10.1063/1.1677527>
- Jabłoński, M., & Palusiak, M. (2010). Basis set and method dependence in quantum theory of atoms in molecules calculations for covalent bonds. *Journal of Physical Chemistry A*, 114(47), 12498–12505. <https://doi.org/10.1021/jp106740e>
- Kumar, P. S. V., Raghavendra, V., & Subramanian, V. (2016). Bader's Theory of Atoms in Molecules (AIM) and its Applications to Chemical Bonding. *Journal of Chemical Sciences*, 128(10), 1527–1536. <https://doi.org/10.1007/s12039-016-1172-3>
- Macchi, P., & Sironi, A. (2003). Chemical bonding in transition metal carbonyl clusters: Complementary analysis of theoretical and experimental electron densities. In *Coordination Chemistry Reviews* (Vols. 238–239, pp. 383–412). Elsevier. [https://doi.org/10.1016/S0010-8545\(02\)00252-7](https://doi.org/10.1016/S0010-8545(02)00252-7)
- Maelen, J. F. Van Der, Garcia-granda, S., & Cabeza, J. A. (2011). Theoretical topological analysis of the electron density in a series of trisium carbonyl clusters: $[Os_3(CO)_{12}]$, $[Os_3(\mu-H)_2(CO)_{10}]$, $[Os_3(\mu-H)(\mu-OH)(CO)_{10}]$ and $[Os_3(\mu-H)(\mu-Cl)(CO)_{10}]$. *Computational and Theoretical Chemistry*, 968(1–3), 55–63. <https://doi.org/10.1016/j.comptc.2011.05.003>
- Mosapour Kotena, Z., Behjatmanesh-Ardakani, R., & Hashim, R. (2014). AIM and NBO analyses on hydrogen bonds formation in sugar-based surfactants (α/β -d-mannose and n-octyl- α/β -d-mannopyranoside): a

- density functional theory study. *Liquid Crystals*, 41(6), 784–792. <https://doi.org/10.1080/02678292.2014.886731>
- Nakanishi, W., Hayashi, S., & Narahara, K. (2008). Atoms-in-molecules dual parameter analysis of weak to strong interactions: Behaviors of electronic energy densities versus Laplacian of electron densities at bond critical points. *Journal of Physical Chemistry A*, 112(51), 13593–13599. <https://doi.org/10.1021/jp8054763>
- Niskanen, M., Hirva, P., & Haukka, M. (2009). Computational DFT Study of Ruthenium Tetracarbonyl Polymer. *Journal of Chemical Theory and Computation*, 5(4), 1084–1090. <https://doi.org/10.1021/ct800407h>
- Racioppi, S., Della Pergola, R., Colombo, V., Sironi, A., & Macchi, P. (2018). Electron Density Analysis of Metal Clusters with Semi-Interstitial Main Group Atoms. Chemical Bonding in [Co₆X(CO)₁₆]- Species. *Journal of Physical Chemistry A*, 122(22), 5004–5015. <https://doi.org/10.1021/acs.jpca.8b02690>
- Rozas, I., Alkorta, I., & Elguero, J. (2000). Behavior of ylides containing N, O, and C atoms as hydrogen bond acceptors. *Journal of the American Chemical Society*, 122(45), 11154–11161. <https://doi.org/10.1021/ja0017864>
- Sakai, Y., Miyoshi, E., Klobukowski, M., & Huzinaga, S. (1997). Model potentials for main group elements Li through Rn. *Journal of Chemical Physics*, 106(19), 8084–8092. <https://doi.org/10.1063/1.473816>
- Shimogawa, R., Takao, T., & Suzuki, H. (2013). Synthesis, Characterization, and Reactions of Ruthenium(II), -(III), and -(IV) Complexes with Sterically Demanding 1,2,4-Tri-tert-butylcyclopentadienyl Ligands. *Organometallics*, 33(1), 289–301. <https://doi.org/10.1021/om401035y>
- Van der Maelen, J. F., Brugos, J., García-Álvarez, P., & Cabeza, J. A. (2020). Two octahedral σ -borane metal (MnI and RuII) complexes containing a tripod $\kappa^3\text{N,H,H}$ -ligand: Synthesis, structural characterization, and theoretical topological study of the charge density. *Journal of Molecular Structure*, 1201, 127217. <https://doi.org/10.1016/j.molstruc.2019.127217>
- Van der Maelen, J. F., & Cabeza, J. A. (2012). QTAIM Analysis of the Bonding in Mo–Mo Bonded Dimolybdenum Complexes. *Inorganic Chemistry*, 51(13), 7384–7391. <https://doi.org/10.1021/ic300845g>

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