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Citation: [AIP Conference Proceedings](#) **1642**, 563 (2015); doi: 10.1063/1.4906743

View online: <http://dx.doi.org/10.1063/1.4906743>

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A Comparative Topological Study of Different Metal-Metal and Metal-Ligand Interactions in Polynuclear Organometallic Clusters

Juan F. Van der Maelen and Santiago García-Granda

Dept. Physical and Analytical Chemistry, University of Oviedo, Avda. Julián Clavería 8, E-33006 Oviedo (Asturias), Spain

Abstract. The existence and characterization of a bond between the Zn atoms in the recently synthesized complex $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (I), as well as between two of the three Ru atoms in $[\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-MeImCH})(\text{CO})_9]$ ($\text{Me}_2\text{Im}=1,3\text{-dimethylimidazolin-2-ylidene}$) (II), are firmly based on low temperature X-ray synchrotron diffraction experiments. The multipolar refinement of the experimental electron densities and their topological analyses by means of the Atoms in Molecules (AIM) theory reveal the details of the Zn-Zn and Ru-Ru bonds, such as their open-shell intermediate character. The results are consistent with a typical metal-metal single σ bond for the former, whereas a delocalized kind of bond involving 5c-6e is present in the latter. In addition, experimental results are compared with theoretical *ab initio* calculations of the DFT (density functional theory) and MP2 (Møller-Plesset perturbation theory) electron densities, giving a coherent view of the bonding in both complexes. Many other topological properties of both compounds are also studied, in particular the different metal-ligand interactions.

Keywords: AIM calculations, Metal-Metal Bonding, X-ray Synchrotron Diffraction, Multipolar Analysis.

PACS: 31.15.ae, 31.15.es, 33.15.Dj, 61.05.cp, 61.05.fm.

INTRODUCTION

Since the seminal paper published a few years ago by E. Carmona and his co-workers [1] on the synthesis and X-ray characterization of the first ever compound exhibiting a Zn-Zn bond, namely complex (I), some other examples have appeared in the literature also having this unusual feature [2-4]. In parallel to the experimental work, some groups have performed theoretical calculations as well in order firstly to explain the stability observed in these compounds and secondly to characterize their bonding [5-7]. The experimental Zn-Zn distance found from these earlier studies for (I) was quite short and comparable to other typical metal-metal bond distances in similar organometallic compounds. On the other hand, theoretical calculations, made all of them within the framework of the Molecular Orbital (MO) theory, led to several stable optimized geometries within a wide range of metal-metal distances, depending on the theoretical model used. The most important conclusions from the theoretical calculations were, firstly, that the Zn-Zn bond is a typical σ bond formed mainly by the 4s atomic orbitals of the Zn atoms, and, secondly, that the metal-ligand bonds are basically electrostatic interactions between Zn(I) and Cp^* . However, there are some well known examples in the literature of structures firstly published as having a metal-metal bond, but, in fact, being a hydride [8]. In order to eliminate the remote possibility of having missed any bridging hydrogen atom between the Zn atoms in the standard X-ray experiment, a neutron diffraction experiment was carried out. Additionally, in order to get a complete picture for the bonding, not only from the theoretical but also from the experimental point of view, a multipolar analysis of the experimental electron density was performed over the data obtained from a synchrotron radiation experiment [9]. Finally, a comparison of the theoretical and experimental points of view for the bonding by the light of the Atoms In Molecules (AIM) approach is made for this compound (Fig. 1a).

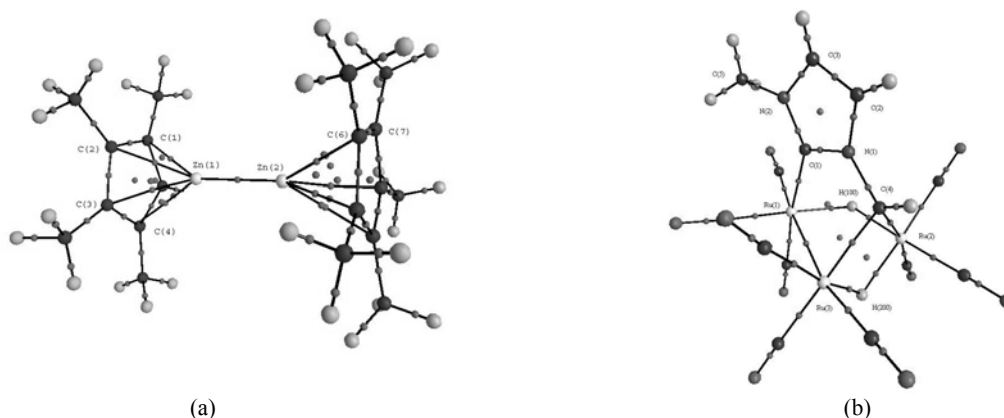


FIGURE 1. (a) Bond critical points, ring critical points, cage critical points, and bond paths for complex (I). (b) Bond critical points, ring critical points, and bond paths for complex (II).

On the other hand, the triruthenium cluster selected for the current study, namely complex (II), was firstly synthesized and characterized by X-ray diffraction by the group of Prof. Cabeza [10], and its molecular geometry was further confirmed by theoretical calculations made within the framework of the MO theory [11]. Although many studies have been made to date on compounds similar to this one, from the perspective of the AIM theory, only a few instances involving Ru-Ru bonds have been previously explored, either from the experimental or theoretical point of view [12-14]. The three experimental Ru-Ru distances found for (II) from these earlier studies were not very different from each other, but quite surprisingly the unabridged Ru-Ru distance is neither the longest nor the shortest of the three distances, but the one in the middle. Theoretical calculations on the molecular geometry confirmed this interesting result. Other interatomic distances found from the conventional X-ray data were not completely satisfactory; for instance, while distances from one of the bridging hydrogen atoms to both Ru atoms are rather similar, as may be expected, this is not the case for the two distances involving the other bridging hydrogen atom. In order to better characterize the molecular geometry and also to clarify the nature of the different bonds present in this cluster, a multipolar analysis of the experimental electron density was performed, again over the data obtained from a synchrotron radiation experiment [15]. Additionally, a comparison of the AIM topological calculations for both the theoretical and experimental electron densities is also made for this compound (Fig. 1b).

RESULTS AND DISCUSSION

Topological properties for the Zn-Zn bond of compound (I) are summarized in Table 1, where the following magnitudes are included: the bond path length, the electron density at the bond critical point (*bcp*), the Laplacian of the electron density at the *bcp*, and finally the so-called delocalization index for this bond (a non-local but integral property not available from the experimental electron density). First of all, it may be seen that there is a reasonable agreement between the values obtained from experimental and theoretical electron densities. Secondly, by comparing the bond path lengths with the experimental interatomic distances (2.292(1) Å from the neutron diffraction experiment, and 2.3186(3) Å from the X-ray synchrotron diffraction experiment), it may also be seen that this is a nearly straight bond path, with hardly bending. Thirdly, from the delocalization index, it could be said that there is just one electron pair shared by the two atoms. And finally, from the other values included in the table, it must be concluded that this is a rather strong bond, not so strong as a typical covalent bond between non-metal atoms, like a C-C bond, for instance, but comparable in magnitude to other single metal-metal bonds found in similar organometallic compounds [9]. The analogous table for the Zn-C bonds, Table 2, shows, conversely, that these are donor-acceptor bonds with a moderate charge transfer of about one electron from each metal to its ligand. From the figures included in the table, and also from the calculated (4.20) and experimental (3.21) ellipticities at the *bcp*, and from the integrated electron densities along the bond paths (0.254 e Å⁻¹, on average) as well, it should be concluded that these bonds have a definite π character, as expected. Further studies on this compound based on maps of the Laplacian of the electron density, including the topological analysis of the ligands themselves, will be published elsewhere.

TABLE 1. Selected topological properties of the Zn-Zn bond in (I).^a

Electron density	$d_{\text{Zn-Zn}}$ (Å)	ρ_b (e Å ⁻³)	$\nabla^2\rho_b$ (e Å ⁻⁵)	$\delta_{\text{Zn-Zn}}$
Theoretical	2.1657	0.426	1.622	0.919
Experimental	2.3206(3)	0.348(3)	1.824(17)	

^aData taken from Ref. [9].TABLE 2. Selected topological properties of the Zn-C bonds in (I).^a

Electron density	$d_{\text{Zn-C}}$ (Å)	ρ_b (e Å ⁻³)	$\nabla^2\rho_b$ (e Å ⁻⁵)	$\delta_{\text{Zn-C}}$
Theoretical	2.1699	0.332	3.922	0.225
Experimental	2.2642(12)	0.398(8)	1.952(20)	

^aData taken from Ref. [9].

Topological calculations for the Ru-Ru and Ru-H bonds of cluster (II) are summarized in Table 3. From the delocalization indexes for these bonding interactions it could be said in principle that there is about half an electron pair shared by each pair of bonded atoms. However, calculations of the delocalization indexes also for the *non-bonding* interactions involving the three Ru atoms (0.415) and the two bridging hydrogen atoms show that there are almost exactly three electron pairs shared by the five atoms in this fragment, just the same as if three Ru-Ru single bonds were present in the cluster. The analogous table for the Ru-C bonds that link the previous fragment to the heterocyclic carbene ligand (Table 4) shows that these three bonds are indeed very similar to each other. By adding this data to the calculated (0.067, on average) and experimental (0.078, respectively) ellipticities at each *bcp* and also to the integrated electron densities over each interatomic surface (1.798 e Å⁻¹, on average), whose values are not shown in this table, it can be concluded that these three bonds are almost pure σ bonds, with no evidence of π -bonding in the Ru-C_{carbene} bond. Further analysis on this cluster based on topological calculations over the experimental electron density will be published elsewhere.

By comparing data of Tables 1 and 3, it is readily seen that the Zn-Zn bond in (I) and the Ru-Ru bond in (II) are very different. While results for (I) are consistent with a well-localized kind of bond, the values for (II) suggest a moderate degree of delocalization. Results for (II) are much in line with those found from an experimental electron density study for Ru₃(CO)₁₂ [12] and differ significantly from those found from a theoretical electron density study for Ru₂(formamidinate)₄ [13], the latter showing a highly localized single Ru-Ru bond. On the other hand, topological properties for the Zn-Zn bond in (I) are not far from those found in saturated carbonyl complexes with metal-metal interactions unsupported by bridging ligands, and involving Co-Co, Mn-Mn or Fe-Fe bonds [13,16-18].

TABLE 3. Selected topological properties of the Ru-Ru and Ru-H bonds in (II).

Electron density	$d_{\text{A-B}}$ (Å)	ρ_b (e Å ⁻³)	$\nabla^2\rho_b$ (e Å ⁻⁵)	$\delta_{\text{A-B}}$
Ru-Ru				
Theoretical ^a	2.838	0.292	0.823	0.458
Experimental ^b	2.838(5)	0.210(5)	2.266(19)	
Ru-H (on average)				
Theoretical ^a	1.790	0.564	4.556	0.474
Experimental ^b	1.963(8)	0.699(7)	3.138(20)	

^aData taken from Ref. [15]. ^bThis work.

TABLE 4. Selected topological properties of several Ru-C bonds in (II).

Electron density	$d_{\text{Ru-C}}$ (Å)	ρ_b (e Å ⁻³)	$\nabla^2\rho_b$ (e Å ⁻⁵)	$\delta_{\text{Ru-C}}$
Ru(1)-C(1)				
Theoretical ^a	2.084	0.745	7.145	0.764
Experimental ^b	2.225(5)	0.655(3)	3.413(21)	
Ru-C(4) (on average)				
Theoretical ^a	2.126	0.719	4.952	0.759
Experimental ^b	2.308(6)	0.651(7)	6.284(22)	

^aData taken from Ref. [15]. ^bThis work.

CONCLUSIONS

The first conclusion of this work is that Zn-Zn bond in complex (I) is not a typical covalent bond but an open-shell metal-metal interaction of intermediate character with a bond order of about unity. Secondly, Zn-C bonds in (I) are not purely ionic but donor-acceptor bonds, with a moderate charge transfer from the metal atoms to their ligands, but also including a small amount of transfer from the ligands themselves. Thirdly, in complex (II) there is not just one bond between two of the Ru atoms but a delocalized multicenter interaction involving the three Ru atoms and the two bridging hydrogen atoms of the molecule. Fourthly, there is no trace of π -bonding between Ru atoms and the heterocyclic carbene ligand. And finally, inside the five-membered ring of this ligand, evidences for a slightly hindered π -electron delocalization have been found.

ACKNOWLEDGMENTS

This work has been supported by the Spanish MCINN (projects MAT2006-01997 and CSD2006-00015). We also thank P. Pattison and H.-P. Weber, from the ESRF (Grenoble, France) for their help with the synchrotron diffraction experiments, and last, but by no means least, E. Gutiérrez-Puebla and A. Monge (ICMM-CSIC, Madrid, Spain) for many helpful discussions.

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