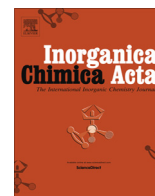




Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: [www.elsevier.com/locate/ica](http://www.elsevier.com/locate/ica)

Research Paper

# The dizinc bond as a ligand: A computational study of elongated dizinc bonds

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## ARTICLE INFO

## Article history:

Received 6 March 2017

Received in revised form 31 May 2017

Accepted 3 June 2017

Available online xxx

Dedicated to our colleague and friend Professor Carlo Mealli, who introduced to some of us to the “*busilis* of theoretical chemistry.

## Keywords:

Zinc

DFT

QTAIM

Dizinc

Organometallic complexes

Cyclopentadienyl

## ABSTRACT

Following the synthesis of  $[\text{Zn}_2(\eta^2\text{-C}_5\text{Me}_5)_2]$  (in short  $[\text{Zn}_2\text{Cp}_2^*]$ ) many complexes of the directly bonded Zn–Zn unit were prepared and characterized, leading to the recognition of an isolobal analogy between the Zn–Zn bond and the molecule of dihydrogen. Prompted by these results, we have investigated  $\eta^2\text{-Zn}_2$ -coordination of  $[\text{Zn}_2\text{Cp}_2]$  and  $[\text{Zn}_2\text{Ph}_2]$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ,  $\text{Ph} = \text{C}_6\text{H}_5$ ) to several selected transition metal fragments and report herein the results of a QTAIM study of complexes  $[(\text{ZnR})_2\text{Fe}(\text{CO})_4]$ ,  $[(\eta^2\text{-Zn}_2\text{R}_2)\text{M}(\text{CO})_5]$  and  $[(\eta^2\text{-Zn}_2\text{R}_2)\text{Pd}(\text{PR}'_3)_2]$  (for  $\text{R} = \text{Cp}$ ,  $\text{Ph}$ ;  $\text{M} = \text{Cr}$ ,  $\text{Mo}$ ,  $\text{W}$ ; and  $\text{R}' = \text{F}$ ,  $\text{H}$ ,  $\text{Me}$ ). A decrease of  $\rho_{\text{BCP}}$ ,  $\nabla^2\rho_{\text{BCP}}$  and delocalization indexes  $\delta(\text{Zn},\text{Zn})$ , relative to corresponding values in the parent molecules of  $[\text{Zn}_2\text{Cp}_2]$  and  $[\text{Zn}_2\text{Ph}_2]$ , accompanied dizinc coordination. In most cases the computed  $\delta(\text{Zn},\text{Zn})$  parameters were indicative of significant electron density sharing between the two Zn atoms. Nevertheless, the interaction with  $[\text{Fe}(\text{CO})_4]$  resulted in oxidative cleavage of the coordinated Zn–Zn bond, due to high  $\pi$  backdonation to the  $\sigma^*\text{Zn}_2$  MO as deduced from the  $\delta(\text{M},\text{O}_{\text{CO}})$  index. The Zn–Zn bond critical points identified in our study are discussed. The computed Zn–Zn contacts concentrate in the range 2.44–2.58 Å, and we propose that this interval corresponds to *elongated dizinc bonds*.

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## 1. Introduction

The isolation and characterization of complex  $[\text{Zn}_2\text{Cp}_2^*]$  **1** ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) [1,2] displaying a directly bonded dizinc Zn(I)–Zn(I) unit, opened a new chapter in the chemistry of this element [3,4]. A good number of theoretical and experimental studies followed the synthesis of this compound [5–7], providing a clear picture of the, until then, unknown Zn–Zn bond [8], and expanding significantly the number of well-defined complexes of this sort [9–11]. In general, the Zn(I)–Zn(I) moiety of these molecules is kinetically stabilized toward disproportionation to Zn(0) and Zn(II) by the presence of substituted cyclopentadienyl rings [2], bulky terphenyl groups [9], or a variety of chelating N-donor ligands [12]. A notable exception is the isolation of the dication  $[\text{Zn}_2]^{2+}$  containing only substituted pyridines as ligands [13] or  $\text{GaCp}^*$  fragments [14]. Comparatively less attention has been paid to disclose the chemical reactivity of these molecules, though complex **1** has been used as a

precursor for other Zn–Zn bonded compounds [15], in catalytic hydroamination reactions [16], as well as for the synthesis of metal-rich compounds and clusters [17,18]. Fischer, Frenking and coworkers have identified a variety of  $\text{M-ZnCp}^*$  and  $\text{M-Zn-ZnCp}^*$  fragments and have highlighted the isolobal analogy of  $\text{ZnCp}^*$  and  $\text{ZnR}$  with the H atom. The use of  $\text{ZnCp}^*$  and other organozinc ligands in transition metal chemistry has also been reviewed [19].

In accordance with the quantum theory of atoms in molecules (QTAIM) [20], the topological analysis of the electron density ( $\rho$ ) estimated at the bond critical point (BCP) provides fingerprints revealing the nature of the atomic interactions. Bonds between atoms may be divided into two categories on the basis of the sign of laplacian  $\nabla^2\rho_{\text{BCP}}$ : shared and closed shell interactions have negative and positive  $\nabla^2\rho_{\text{BCP}}$ , respectively. In shared interactions the bond electronic charge concentrates in the internuclear region and  $\rho_{\text{BCP}}$  has a high value, whereas closed shells are characterized by low  $\rho_{\text{BCP}}$  values in the interatomic surfaces. On the basis of this simple classification, the first type refers to covalent or covalent polar bonds, while the second is associated with ionic bonds, hydrogen bonds and van der Waals interactions. In addition, it has been proposed [21] that local energetic parameters like the kinetic energy density  $G(r)$ , the potential energy density  $V(r)$  and

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the total energy density  $H(r) = G(r) + V(r)$ , also play an important role in the characterization of atomic interactions. In this way, when comparing closed shells and shared interactions, it is advisable to use the kinetic energy per electron  $G_{BCP}/\rho_{BCP}$ . Closed shells interactions generally exhibit  $G_{BCP}/\rho_{BCP} > 1$ , while shared interactions have  $G_{BCP}/\rho_{BCP} < 1$ .

As already pointed out [22], interpretation of bonds when heavy atoms (those with more than three atomic shells) are involved is not straightforward. Heavy atoms are characterized by diffuse electron densities, giving rise to low electron densities and concentrations in the bonding region. This usually complies with very low  $\rho_{BCP}$  and  $\nabla^2\rho_{BCP}$  values which rules out the use of  $\nabla^2\rho_{BCP}$  for a bonding classification. Espinosa et al. [23] proposed a classification based on the adimensional  $|V_{BCP}|/G_{BCP}$  ratio, introducing the concept of bond degree (BD) as  $BD = H_{BCP}/\rho_{BCP}$ , for the characterization of bond types. They divided atomic interactions into three categories. Region I corresponds to pure closed shells, where  $|V_{BCP}|/G_{BCP} < 1$ , implying that  $\nabla^2\rho_{BCP} > 0$  and  $H_{BCP} > 0$ . Region III refers to pure shared shells, with  $|V_{BCP}|/G_{BCP} > 2$  and therefore  $\nabla^2\rho_{BCP} < 0$  and  $H_{BCP} > 0$ . Region II is then a transit region, with  $1 < |V_{BCP}|/G_{BCP} < 2$  and  $\nabla^2\rho_{BCP} > 0$  and  $H_{BCP} < 0$ . In region I, the BD parameter is positive and gives an idea of the non-covalent interaction, such that the larger its value, the more closed and weaker in nature is the interaction. Conversely, in regions II and III the BD parameter is negative and measures covalency. Hence, the greater its magnitude, the more covalent and stronger the bond is. This classification was followed by Gervasio et al. to describe metal-metal bonding in polynuclear complexes [24]. The bond ellipticity ( $\varepsilon_{BCP}$ ) is another interesting parameter to be analyzed. The ellipticity measures the extent to which electron density is preferentially accumulated in a given plane containing the bond path. It is calculated as suggested by Bader et al. [25] for the quantitative description of the electron density deviation from the cylindrical symmetry in the BCP. In fact, the value of  $\varepsilon_{BCP}$  is a measure of the  $\pi$ -component of the bonding [25].

Macchi et al. [22a,26] proposed to consider in addition the integrated properties within atomic basins. The most interesting clues are the delocalization index for a pair of atoms,  $\delta(A,B)$ , and the electronic density integrated over the whole interatomic surface,  $\int_{A-B}\rho$ . The former hints the number of electron pairs that are exchanged or shared between two atomic basins and can be interpreted as the covalent bond order if identical atoms are considered. These basins need not have a common interaction surface, so that the index may be computed for any pair of atoms, regardless of whether or not they are formally bonded. Delocalization indexes are typically related to bonding mechanism and only indirectly to the interaction strength, which is revealed by the value of  $\int_{A-B}\rho$ . Bonds between heavy atoms are now classified in: (i) open (or shared) shells, when  $\rho_{BCP}$  is small,  $\nabla^2\rho_{BCP} \sim 0$ ,  $G_{BCP}/\rho_{BCP} < 1$ ,  $H_{BCP}/\rho_{BCP} < 0$  and  $\delta(A,B)$  is the formal bond order (unless bond delocalization occurs); (ii) donor-acceptor, if  $\rho_{BCP}$  is small,  $\nabla^2\rho_{BCP} > 0$ ,  $G_{BCP}/\rho_{BCP} \sim 1$ ,  $H_{BCP}/\rho_{BCP} < 0$  and  $\delta(A,B) < \text{formal bond order}$ . In both cases  $\int_{A-B}\rho$  has a medium/large value, despite  $\rho$  being one order of magnitude lower than for covalent interactions between light atoms. When heavy atoms are involved the distinction between shared and donor-acceptor bonds is subtler than between corresponding light atom interactions [27].

On the basis of these considerations, to gain theoretical information on the bonding capabilities of compounds  $[Zn_2Cp_2]$  (as model for  $[Zn_2Cp_2^*]$  [1]) and  $[Zn_2Ph_2]$  (as model for  $Zn_2Ar'_2$  with  $Ar' = C_6H_3-2,6-(C_6H_3-2,6-iPr_2)_2$  [9]) towards several  $ML_n$  metal fragments, a QTAIM study was undertaken. An analysis of the preservation of the Zn-Zn interaction after coordination of the dizinc compound as a ligand was carried out. While our work was in pro-

gress, an experimental and theoretical study of the Zn-Zn interactions in nickel and palladium complexes in which the dizinc unit act as a ligand was published [23c].

## 2. Computational details

Quantum chemical optimizations on the basis of the density functional theory (DFT) at the BP86 [28]/Def2TZVPP [29] level of theory together with the D3(BJ) [30] correction by Grimme were carried out. Mo, W and Pd atoms were described with the LANL2DZ pseudopotential basis set [31]. The need for dispersion corrections has already been demonstrated by previous results on similar compounds [14]. The optimized geometries of all the compounds were characterized as energy minima either by non-existent imaginary frequencies ( $N_{\text{Imag}} = 0$ ), or by very low vibrational frequencies ( $< 20 \text{ cm}^{-1}$ ) in the diagonalization of the analytically computed Hessian (vibrational frequencies calculations). These very low vibrational frequencies that do not lead to energy minimum optimization have been reported in other cases, and seem to be associated to numerical errors in the DFT integration grid. They could be eliminated by much more expensive calculations with a better grid [32]. Electronic calculations were performed using Gaussian09 rev. D01 program [33] and topology parameters were studied within the framework QTAIM method as implemented in AIMALL program [34]. Cartesian coordinates of all optimized compounds are collected in the Supplementary Material (Table S1).

## 3. Results and discussion

### 3.1. Some qualitative considerations on the Zn-Zn bond

From an experimental point of view, the existence of a zinc-zinc bond is deduced from the Zn-Zn distance obtained by X-ray crystallography. For this reason, a CSD search [35] of X-ray characterized complexes containing Zn-Zn bonds was carried out. Fig. 1 shows the resulting histogram, in which Zn-Zn bond distances span the range 2.29–2.48 Å, with a mean value of 2.38 Å. It can, therefore, be anticipated that Zn-Zn lengths higher than 2.48 Å would correspond to weak interactions. Additionally, with a zinc metallic radius of 1.34 Å, Zn-Zn distances larger than 2.68 Å should denote very weak or negligible interactions. Besides these experimental considerations, the available theoretical tools will doubtless aid to define the features of weak Zn-Zn interactions.

The existing knowledge on the nature of the Zn-Zn bond [5–7] in these  $d^{10}s^1$  complexes allows the comparison of  $CpZn$  and  $RZn$  fragments with the H atom by means of the isolobal analogy [17]. Therefore, dizinc compounds would be isolobally related to the  $H_2$  molecule (Scheme 1) [23]. As dihydrogen can act as a  $\sigma$ -ligand in transition metal chemistry, we decided to explore theoretically the behaviour of  $[Zn_2Cp_2]$  and  $[Zn_2Ph_2]$  model compounds as  $\eta^2-Zn_2$  ligands against some representative metal fragments,  $ML_n$ , and to analyze whether or not the Zn-Zn interaction would be preserved on coordination (Scheme 2).

The bonding scheme for the electronic interaction between a  $\eta^2-Zn_2$  ligand and a transition metal (I in Scheme 2) is analogous to that well known for the dihydrogen ligand. For  $\sigma$  bonding electron density would be transferred from the filled  $\sigma$  molecular orbital (MO) of the dizinc compound (for instance, the HOMO-4 for  $[Zn_2Cp_2]$ ), that features large contribution of the Zn  $s$  orbitals [5], to the metal (donation). A second interaction could involve the empty  $\sigma^*$  MO of the dizinc compound (the LUMO for  $[Zn_2Cp_2]$ ), again with major contribution of  $s$  orbitals), accepting by  $\pi$  back-bonding electron density from filled M  $d\pi$  orbitals. To accomplish this classical donation-backdonation scheme, the metal fragment must possess two electrons in MOs ( $\sigma$  and  $\pi$  hybrid orbitals) topo-

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