

Experimental Electron Density Study of the Mg–Mg Bonding Character in a Magnesium(I) Dimer

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With the recent successful reduction of magnesium(II) iodide complexes to unprecedented and surprisingly thermally stable Mg(I) dimer complexes¹ using bulky guanidinate or β -diketiminato ligands, it was shown for the first time that the remarkable discovery of decamethylidizincocene, which possesses a Zn(I)–Zn(I) single bond,² can be successfully extended to the group 2 metal magnesium.

These observations were based on results from conventional single-crystal X-ray diffraction data that tentatively established the presence of metal–metal bonds through evaluation of interatomic distances. In addition, advanced theoretical calculations suggested that the Mg–Mg interactions of the complexes are best denoted as single σ bonds of predominantly *s* type with a Mg–Mg bond dissociation energy (BDE) of ~ 45 kcal mol⁻¹.¹ This is in full accordance with combined spectroscopic and theoretical results on Mg₂Cl₂ and other model compounds (BDE ≈ 47 kcal mol⁻¹).³ Furthermore, the charges of the Mg ions in the bulky complexes were calculated to be roughly +1, and the systems could be described as complexes containing anion-stabilized Mg₂²⁺ entities.

In view of the significant impact of the discovery of these systems, it is imperative to obtain a better understanding of the bonding between the metal atoms. We present here the results of an analysis using the quantum theory of atoms in molecules (QTAIM) developed by Bader,⁴ which was also recently utilized in an experimental charge density study of the dizinc complex Cp*ZnZnCp* (Cp* = C₅Me₅).⁵ This theory entails, within the boundaries of quantum mechanics, a partitioning of space into discrete subunits (atomic basins), each containing one nucleus only, and furthermore provides a vocabulary for describing bond strengths, atomic charges, and higher electric moments, among other fundamental concepts.⁴ Very importantly, this method of analysis is accessible not only to theoreticians but also to experimentalists through multipole modeling of accurate, low-temperature single-crystal X-ray diffraction data. For instance, AIM analyses have recently been used to examine metal–metal bonding⁶ as well as a wealth of other interesting chemical problems.⁷ In the theory, the Laplacian of the electron density [$\nabla^2\rho(r) \equiv -L(r)$] plays a major role. This is a scalar function that by construction clearly identifies regions where charge is accumulated [$L(r) > 0$] or depleted [$L(r) < 0$]. In addition, the interactions between atoms may be characterized by density properties evaluated at the bond critical points (bcp's), which lie at those points on the interfaces of the atomic basins where the gradient of the density is zero, or by assessment of density-derived features along bond paths.

Therefore, to address the nature of the bonding in an Mg^I dimer using an experimental approach, we collected high-resolution single-crystal diffraction data at 89 K on a crystal of [Mg(dippnacac)]₂ (**1**) [dippnacac = (ArNCMe)₂CH, Ar = 2,6-ⁱPr₂C₆H₃; see the

Supporting Information for full experimental details]. As the structure contains a large number of H atoms (17% of the scattering power comes from H atoms), we complemented these data with anisotropic atomic displacement parameters (ADP's) for the H atoms resulting from a rigid-body (TLS) analysis using the SHADE server.⁸ The X-ray diffraction data were used to fit a multipole model based on the Hansen–Coppens formalism as implemented in the XD program package.⁹ The final model consisting of 1407 parameters was refined against 36 113 reflections, yielding a residual of $R(F) = 0.041$ and a goodness of fit of 1.36. Figure 1 shows the molecular structure of **1**.

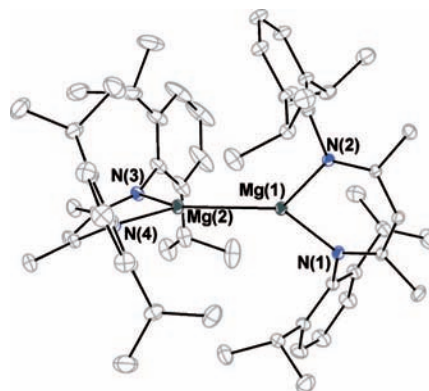


Figure 1. ORTEP-3 plot¹⁰ of **1**, showing thermal ellipsoid surfaces at the 50% probability level. H atoms have been omitted for clarity.

As mentioned above, previous calculations suggested that dimeric systems such as **1** consist of a central Mg₂²⁺ unit having predominantly ionic interactions with the stabilizing anionic ligands. The QTAIM theory provides atomic charges by integration over atomic basins. The results [$q_{\Omega}(\text{Mg}(1)) = +1.18$, $q_{\Omega}(\text{Mg}(2)) = +1.12$] support this description to some extent, as we find monovalent Mg ions (i.e., a Mg₂²⁺ unit) coordinated to negatively charged N atoms [$\langle q_{\Omega}(\text{N}) \rangle = -1.20$].

As the primary focus of this paper is the Mg–Mg interaction, it is interesting to note that the topological analysis of the experimental charge density unambiguously locates a bcp between the atoms, and thus, as expected, a chemical bond exists between the two Mg ions (Table 1). The value of the Laplacian at the bcp is positive and close to zero. Table 1 also gives values for the total energy density, H ,¹¹ which compares the drive to collect electrons between the atoms (given by the potential energy density, V , which is negative everywhere) with the pressure exerted by the electrons on the atomic basins from this interatomic region (given by the kinetic energy density, G , which is positive everywhere).¹² H is small for all of the bonds to Mg, but for the Mg–Mg bond, the constituents of H , V , and G are similarly vanishing because of the

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small values of ρ_c and $\nabla^2\rho_c$. However, H is still negative, suggesting some degree of covalency in this bond. $|W|G$ lies in the transit region with values between 1 and 2, which are difficult to interpret.¹³ Empirical studies of hydrogen-bonded systems have correlated the value of V with the BDE,¹⁴ and this approach was recently applied in a donor–acceptor system containing heavy atoms (a Au–P bond).¹⁵ However, the vanishing density values for the Mg–Mg bond in **1** and the consequently vanishing V render such a correlation meaningless for the diffuse type of bonding that exists between the Mg atoms (i.e., significantly underestimated values result).

Table 1. Topological Properties of **1**^a

bond	ρ_c	$\nabla^2\rho_c$	d	ϵ	H	G/ρ	$ W G$
Mg(1)–Mg(2)	0.10(2)	0.26(1)	2.8456(2)	0.23	−0.01	0.30	1.38
Mg(1)–N(1)	0.40(4)	4.73(7)	2.0693(6)	0.17	−0.06	0.99	1.16
Mg(1)–N(2)	0.29(4)	7.46(7)	2.0577(5)	0.17	0.07	1.54	0.85
Mg(2)–N(3)	0.37(4)	5.93(6)	2.0639(5)	0.30	−0.02	1.16	1.04
Mg(2)–N(4)	0.34(4)	6.48(7)	2.0706(5)	0.27	0.02	1.28	0.96

^a Units: ρ_c , e \AA^{-3} ; $\nabla^2\rho_c$, e \AA^{-5} ; d , \AA ; H , hartree \AA^{-3} ; G/ρ , hartree e^{−1}. The quantities ϵ and $|W|G$ are dimensionless.

Figure 2 shows the behavior of ρ , $\nabla^2\rho$, and H along the Mg–Mg interaction line, providing more information about the bond character. The electron density is low and follows a parabolic curve, while the Laplacian is positive but nearly vanishes in a plateau of 0.25 \AA on either side of the bcp. The total energy density, H , is thus flat and slightly negative over an extended region around the bcp. These are all features that have been identified as fingerprints of covalent interactions between two heavy atoms.⁶ The Mg–Mg bond is similar to the Li–Li bond in Li₂ and the Na–Na bond in Na₂ in the sense that it exhibits a low value of the density at the bcp, but in the latter two cases, the total integrated charge over the entire shared zero-flux surface is significantly larger because of the diffuse nature of the s electrons that participate in the chemical bond.¹⁶ We anticipate similar behavior for **1**, which we are currently studying using theoretical methods.

We also evaluated the properties of the source function, which was recently applied to the study of the bonding character in transition-metal dimers.¹⁷ The integrated source function partitions the density at any given point into separate contributions from atomic basins. For metal–metal bonding in a series of transition-metal dimeric compounds, a trend was observed in which the integral of the source function over the atomic basin of the metal increased with increasing bond strength and eventually changed from negative to positive for the stronger bonds. At the bcp joining Mg(1) and Mg(2) in **1**, the Mg basins give significant contributions of 0.017 e \AA^{-3} (17.4% of ρ_c) and 0.014 e \AA^{-3} (13.7%), respectively, which could indicate a significant covalent interaction. The local source profile along the Mg–Mg interaction line shows an intermediate-sized drop near the bcp (Figure S7 in the Supporting Information). It was noted that this drop disappears with the onset of chemical bonding.¹⁷ Furthermore, the very low positive value of the Laplacian in the interatomic region is also noteworthy, as this was taken as a sign of increased covalency in ref 17). Similarly, the electron density between the Mg atoms is low, despite the short bond length compared with the Mg–Mg separation in Mg metal (3.20 \AA).¹⁸ Notably, the apparently diffuse charge density between the Mg centers of **1** is in line with the shallow potential energy surface calculated for this bond in a model complex. This is experimentally manifested by significant elongation of the Mg–Mg bond in **1** upon coordination by Lewis bases.¹

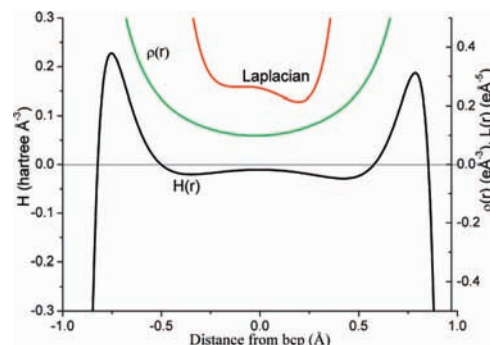


Figure 2. Plots of ρ , $\nabla^2\rho$, and H along the Mg–Mg line, on which the position of the bcp in the Mg–Mg bond is defined as $x = 0$.

To summarize, topological analysis of the experimental density of a magnesium(I) dimer combined with analysis of the energy density and the source function has revealed that the dimer contains two monovalent Mg ions with a significant covalent contribution to their shared chemical bond. We are currently trying to expand the analysis by collecting high-resolution data on a number of related complexes as well as performing additional high-level theoretical calculations.

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Supporting Information Available: Experimental procedures, refinement and model details, and crystallographic data for **1** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>

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