Metal–Metal Bonds **Hot Paper**

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A Mixed-Valence Tri-Zinc Complex, [LZnZnZnL] (L = Bulky Amide), Bearing a Linear Chain of Two-Coordinate Zinc Atoms**

Jamie Hicks, Emma J. Underhill, Christos E. Kefalidis, Laurent Maron, and Cameron Jones**

Abstract: *Reduction of a variety of extremely bulky amido Group 12 metal halide complexes, $[LMX(THF)_{0,1}]$ (L = amide; M = Zn, Cd, or Hg; X = halide) with a magnesium(I) dimer gave a homologous series of two-coordinate metal(I) dimers, $[L'MML']$ ($L' = N(Ar^{\dagger})(SiMe_3)$, $Ar^{\dagger} = C_6H_2\{C(H)Ph_2\}_2Pr^i$-2,6,4); and the formally zinc(0) complex, $[L^*ZnMg(^{Mes}Nacnac)]$ ($L^* = N(Ar^*)(SiPr^i_3)$; $Ar^* = C_6H_2\{C(H)Ph_2\}_2Me$-2,6,4; $^{Mes}Nacnac = [(MesNCMe)_2CH]^-$, Mes = mesityl), which contains the first unsupported Zn−Mg bond. Two equivalents of $[L^*ZnMg(^{Mes}Nacnac)]$ react with $ZnBr_2$ or $ZnBr_2(tmeda)$ to give the mixed valence, two-coordinate, linear tri-zinc complex, $[L^*Zn^IZn^0Zn^IL^*]$, and the first zinc(I) halide complex, $[L^*ZnZnBr(tmeda)]$, respectively. The analogues $[L^*ZnMZnL^*]$ (M = Cd or Hg), were also prepared, the Cd species contains the first Zn−Cd bond in a molecular compound. Metal–metal bonding was studied by DFT calculations.*

Although molecular compounds bearing homonuclear metal–metal bonds have been intensively studied for more than 50 years, the boundaries of what is synthetically achievable within this realm have been rapidly pushed back since the turn of the millennium.[1] In this respect, one of the most important advances in the area has been Carmona's stabilization of the zinc(I) dimer, $[Cp^*ZnZnCp^*]$ ($Cp^* = \eta^5\text{-}C_5Me_5^-$), in 2004.[2] Since that time, more than thirty examples of compounds incorporating unsupported zinc–zinc bonds have been reported, and applications of such systems in synthesis, materials chemistry, and catalysis have emerged.[3] All but one of these zinc–zinc bonded species exhibit metal coordination numbers of three or greater, and the majority are kinetically stabilized by sterically bulky bi- or higher dentate ligands. The exception is Power's two-coordinate dimer, $[Ar'ZnZnAr']$ ($Ar' = C_6H_3(C_6H_3Pr^i_2\text{-}2,6)_2\text{-}2,6$), which is stabilized by sterically imposing monodentate terphenyl ligands.[4]

Given these successes, it might be expected that low-oxidation-state zinc chemistry could be extended to mixed-valence "clusters" of the type $[L_mZn_n]$ (L = anionic ligand, $m < n$), which bear "naked" zinc(0), centers, bonded only to other zinc atoms. Nevertheless, although similar homometallic complexes are now well established for the Group 13[5] and 14[6] metals, they remain elusive for the Group 12 metals. A reason for this can perhaps be gleaned from the results of computational studies on mixed-valence zinc "clusters", $[Cp_2Zn_n]$ ($n = 3$–5; $Cp = \eta^5\text{-}C_5H_5^-$),[7] which predict that their structures encompass linear chains of zinc atoms capped by η^5-ligating cyclopentadienyl ligands. They are, however, thermodynamically unstable with respect to the loss of zinc metal, and as a result, it has been suggested that they are unlikely to be experimentally observed. With that said, two low-valent ionic zinc cluster compounds, without "naked" zinc centers, have been described recently. The first of these, $[(\eta^5\text{-}Cp^*Zn)_3]^+$, contains an equilateral triangle of Zn atoms, the Zn−Zn bonding in which was described as σ-aromatic, in that two bonding electrons are delocalized over the three metal centers.[8] That is, two of the zinc atoms are formally in the +1 oxidation state, while the other is in the +2 oxidation state. The second is the anionic cluster, $[Zn_8(Tz)_8(TzH)_4]^{12-}$ (Tz = tetraazole dianion, CN_4^{2-}), which contains a cubic core of eight Zn atoms, formally in the +1 oxidation state.[9] Calculations imply that the metal–metal bonding within the cluster displays "cubic aromaticity", as eight metal-based bonding electrons are delocalized over the cluster core.

Our interest in metal–metal bonded compounds attracted us to the possibility of kinetically stabilizing mixed-valence zinc clusters, containing naked zinc atoms. In addition to being of considerable fundamental appeal, these have the potential to find applications in areas related to those that currently exploit zinc(I) dimers. We believed that an extremely bulky monodentate amide class of ligands developed in our laboratories, for example, $N(Ar)(SiR_3)$ (R = Me or Pr^i; $Ar = C_6H_2\{C(H)Ph_2\}_2R'\text{-}2,6,4$, R′ = Me (Ar*) or Pr^i ($Ar^{\dagger}$),[10] might be suitable for this purpose, especially considering that we have already employed these amides for the stabilization of a variety of low-oxidation-state p- and d-block metal–metal bonded complexes.[11] Herein, we confirm this proposal with the synthesis and characterization of the first mixed-valence neutral tri-zinc complex, [LZnZnZnL] (L = bulky amide). In addition, we report the first example of a compound with an unsupported Zn−Mg bond, [LZnMg-

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Supporting information (full synthetic, spectroscopic and crystallographic details for new compounds; and full details and references for the DFT calculations) for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201504818.

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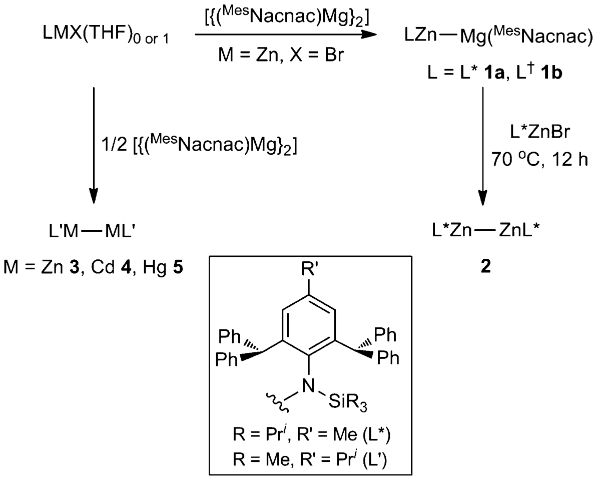
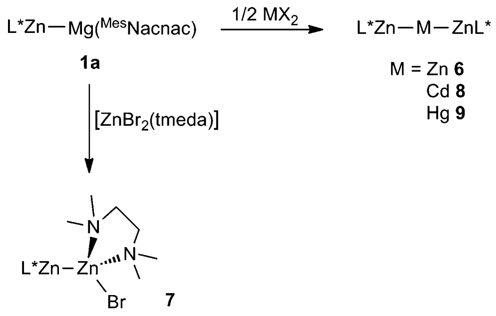
(Nacnac)] (Nacnac = β-diketiminate), the first zinc(I) halide complex, the first zinc–cadmium bonded compound, and a homologous series of two-coordinate Group 12 metal(I) dimers ([LMML], M = Zn, Cd or Hg).

In 2014, we utilized a very bulky amide ligand to stabilize an unprecedented Mg–Mn bonded complex, [LMnMg-(Nacnac)], which we subsequently showed could act as a reagent for the transfer of the "LMn" fragment in the formation of other metal–metal bonded species, for example, [LMnMnL].[11a] A similar strategy was employed herein to access the target tri-zinc complexes. That is, the bulky monomeric amido zinc(II) bromide complexes, [LZnBr] (L = -N(Ar)(SiPr$^i_3$); Ar = Ar* (L*) or Ar† (L†), see Supporting Information for further details), were treated with one equivalent of the magnesium(I) dimer, [{(^{Mes}Nacnac)Mg}$_2$] (^{Mes}Nacnac = [(MesNCMe)$_2$CH]$^-$, Mes = mesityl)[12] to give good yields of the isolated Zn–Mg bonded complexes, [LZnMg(^{Mes}Nacnac)] **1**, as colorless crystalline solids (Scheme 1). The mechanisms of these reactions likely involve the magnesium(I) dimer acting as a two-electron reductant towards the zinc precursor. It is noteworthy that when the reactions were repeated in 2:1 stoichiometries, they returned only **1** and residual [LZnBr] in approximately 1:1 ratios, while none of the expected zinc(I) products, [LZnZnL] was formed. This result can be explained by the extreme bulk of the amide ligand, which hinders the dimerization of the "LZn" fragment at ambient temperature. However, when a 1:1 mixture of **1a** and [L*ZnBr] was heated at 70 °C for 12 h, a reaction slowly proceeded, and the zinc(I) dimer [L*ZnZnL*] **2** was formed and isolated in a good yield.



Scheme 1. Synthesis of compounds **1**–**5** (by-products omitted).

Consistent with the above observations are the results of both the 1:1 and 2:1 reactions of the less-bulky amido zinc bromide precursor, [L′ZnBr(THF)] (L′ = N(Ar†)(SiMe$_3$)), with [{(^{Mes}Nacnac)Mg}$_2$]. These yielded only the zinc(I) dimer, [L′ZnZnL′] **3**, and in the case of the 1:1 reaction, residual [{(^{Mes}Nacnac)Mg}$_2$]. The reactions seemingly proceed via the intermediate, [L′ZnMg(^{Mes}Nacnac)], which is much more reactive than bulkier **1**, and reacts rapidly with [L′ZnBr(THF)], even at low temperatures, to give **3** cleanly. Given the facility of these reactions, the related reductions of both [{L′CdI}$_2$] and [L′HgI] with [{(^{Mes}Nacnac)Mg}$_2$], were carried out, and these afforded good yields of the two-coordinate cadmium(I) and mercury(I) dimers, [L′MML′] (M = Cd **4**, Hg **5**).[13] Compounds **3**–**5** form only the second homologous series of Group 12 metal(I) dimers, the other being Power's terphenyl-coordinated compounds, [Ar′MMAr′] (M = Zn,[4] Cd[14], or Hg[15]). It is of note that a similar reduction of the bulkier amido mercury iodide precursor, [L*HgI], led directly to the mercury(I) dimer, [L*HgHgL*] (see Supporting Information for further details), with no evidence for the formation of the presumed Mg–Hg bonded intermediate, [L*HgMg(^{Mes}Nacnac)]. This situation is in contrast to the stability of the Zn–Mg bonded analogue, **1a**, presumably because the larger covalent radius of Hg (1.32 Å) versus Zn (1.22 Å)[16] allows the reaction of [L*HgMg(^{Mes}Nacnac)] with [L*HgI] to occur rapidly at, or below, room temperature.



Scheme 2. Synthesis of compounds **6**–**9** (by-products omitted).

With **1a** in hand, its reaction with half an equivalent of ZnBr$_2$ was carried out, and this led to the target Zn$_3$ complex, [L*ZnZnZnL*] **6** (Scheme 2) isolated in a moderate yield. In this reaction, **1a** acts as a reagent for the transfer of two "L*Zn" fragments to the zinc bromide precursor. Although the likely intermediate in this process, [L*ZnZnBr], could not be isolated when the reaction was repeated in a 1:1 stoichiometry, the high yield formation of [L*ZnZnBr(tmeda)] **7** (tmeda = tetramethylethylenediamine) from the closely related 1:1 or 2:1 reactions of **1a** and [ZnBr$_2$(tmeda)] gives good evidence for the proposed transient formation of [L*ZnZnBr]. Note that **7** is the first example of a structurally characterized zinc(I) halide complex (see Supporting Information for further details).[17] The utility of **1a** as a transfer reagent in the formation of trinuclear complexes was further tested in its reactions with half an equivalent of either CdI$_2$ or HgCl$_2$. These afforded the two-coordinate heterotrinuclear complexes, [L*ZnMZnL*] (M = Cd **8**, Hg **9**) which were isolated in good yields. Compound **8** exhibits the first examples of Zn–Cd bonds in a molecular complex, while only one example of a Zn–Hg bonded complex, [(^{Dip}Nacnac)ZnHgZn(^{Dip}Nacnac)] (^{Dip}Nacnac = [(DipNC-Me)$_2$CH]$^-$, Dip = C$_6$H$_3$Pr$^i_2$-2,6),[18] has been reported. Note that an attempt to prepare the linear tetranuclear complex, [L*ZnHgHgZnL*], by treating Hg$_2$Cl$_2$ with **1a**, instead led to a mixture of products, including [L*ZnHgZnL*], and the mercury(I) dimer, [L*HgHgL*].

The Zn−Mg bonded complexes, **1**, and all of the metal(I) dimers, **2**–**5** and **7**, are thermally very stable solids, while the trimetallic systems, **6**, **8**, and **9**, slowly decompose in the solid state at ambient temperature, and in solution, to deposit Zn, Cd, or Hg metal, respectively. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra for the bi- and trinuclear compounds, although consistent with their proposed structures, are not overly informative, as they display spectral patterns similar to those of the Group 12 metal(II) halide precursors. More information can be gained from the ^{113}Cd or ^{199}Hg NMR spectra of compounds containing those metals. The ^{113}Cd spectra of **4** and **8** exhibit resonances at $\delta = 270.6$ ppm and $\delta = 688.6$ ppm respectively (cf. $\delta = 110.2$ ppm for [L†CdI]), while the signal for the dimer is flanked by ^{111}Cd satellites with a $^{1}J_{\mathrm{CdCd}}$ coupling of 18 900 Hz. This value is more than double that observed for [Ar′CdCdAr′] ($\delta = 540.3$ ppm, $^{1}J_{\mathrm{CdCd}} = 8650$ Hz),[14] which suggests a stronger and/or higher s-character Cd−Cd bond in **4** (see below). The signal in the ^{199}Hg NMR spectra of **5** occurs at $\delta = -726.3$ ppm (cf. $\delta = -2002.9$ ppm for [L′HgI]), which is considerably upfield from that for [Ar′HgHgAr′] ($\delta = 150.5$ ppm).[15] No signal was observed in the ^{199}Hg NMR spectrum of trinuclear, **9**.

All the new compounds reported herein were crystallographically characterized (see Supporting Information for full details and CCDC numbers), and the molecular structures of representative complexes, **1a**, **3**, and **6**, are depicted in Figure 1. Compound **1a** contains an unprecedented unsupported Zn−Mg bond, the length of which (2.5775(9) Å) lies within the sum of the covalent radii for Zn and Mg (2.63 Å).[16] Its two-coordinate Zn center is formally in the 0 oxidation state (Pauling electronegativities: Zn 1.65, Mg 1.31), and is near linear (N-Zn-Mg 168.88(6)°), while the Mg$^{\mathrm{II}}$ coordination environment is distorted trigonal planar. The metal(I) dimers, **3**–**5**, are isomorphous and have two-coordinate metal centers with near linear geometries (N-M-M: 174.26(5)° **3**, 172.77(4)° **4**, 176.44(8)° **5**). The metal–metal distances in the compounds (**3** 2.3520(6) Å, **4** 2.5786(6) Å, **5** 2.5394(5) Å) are slightly shorter than those in Power's terphenyl ligated dimers, [Ar′MMAr′], and as was the case in that series, the Hg−Hg bond in **5** is shorter than the Cd−Cd bond in **4**, probably due to relativistic effects.[15]

Similar to the metal(I) dimers, the trimetallic species **6**, **8**, and **9** are isomorphous and contain near linear chains (N-M-M: 170.80(15)° **6**, 172.0(4)° **8**, 171.3(9)° **9**; M-M-M 180.0° for all of **6**, **8**, and **9**) of two-coordinate metal atoms. As far as we are aware, such a bonding arrangement in molecular compounds is unknown for any metal in the periodic table, though the structure of **9** is closely related to that of the three-coordinate zinc complex, [($^{\mathrm{Dip}}$Nacnac)ZnHgZn($^{\mathrm{Dip}}$Nacnac)].[18] The linear Zn$_3$ complex, **6**, can be considered as mixed valence, with the two terminal Zn centers formally in the +1 oxidation state, while the central "naked" Zn atom is in the 0 oxidation state. The Zn−Zn bonds in the compound (2.3840(12) Å) are shorter than those in [L*ZnZnL*] **2** (2.4289(11) Å), probably due to the increased steric strain in the dimer, while the Zn−M bond lengths in the heterotrinuclear compounds (**8** 2.487(2) Å; **9** 2.476(5) Å; cf. 2.4846(3) Å for [($^{\mathrm{Dip}}$Nacnac)ZnHgZn($^{\mathrm{Dip}}$Nacnac)][18]) are the same, within experimental error. It is evident from the structures of **6**, **8**, and **9** that they are kinetically stabilized by the extreme bulk of the amide ligands, four phenyl groups of which, enshroud the M$_3$ chains, without coordinating to them (all the M⋯C$_{\mathrm{Ph}}$ distances > 3.05 Å).

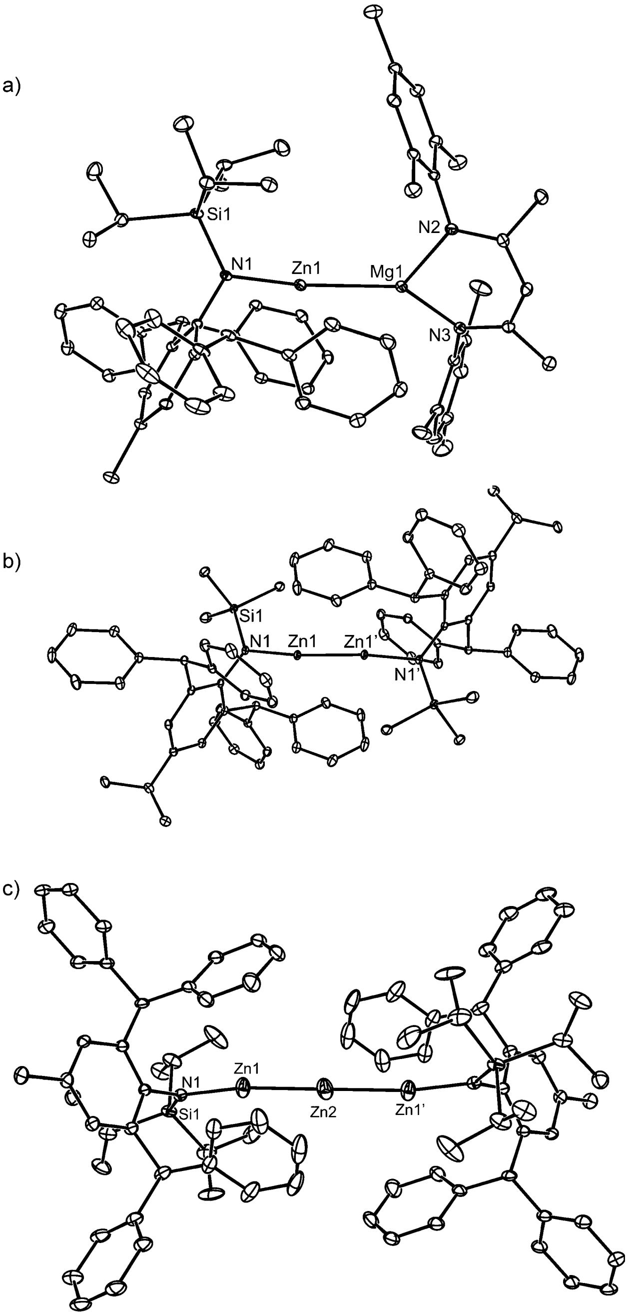


Figure 1. Molecular structures of a) **1a**, b) **3**, and c) **6** (thermal ellipsoids set at 25% probability; hydrogen atoms omitted for clarity). Selected parameters are discussed in the text.

To investigate the nature of the metal–metal bonding in the compounds described above, dispersion-corrected DFT calculations (B3PW91/B3PW91-D3, see Supporting Information for full details) were carried out in the gas phase on the full molecules of the Zn−Mg bonded complex **1a**, the metal(I) dimers **3**–**5**, and the tri-zinc compound **6**. The geometries of all the molecules optimized to be similar to those determined from the crystal structures of the compounds. NBO and NPA analyses of the compounds revealed that their metal–metal bonds have high covalent character, while the N–M interactions in all are largely ionic. The HOMO of **1a**, and of the metal(I) dimers **3**–**5** (Figure 2), exhibit significant metal–metal σ-bonding character, which is largely derived from overlap of valence s orbitals on the metals (over 85% s character in each case). Furthermore, the level of covalency of these bonds is reflected in their Wiberg bond orders (WBOs: **1a** 0.78, **3** 0.87, **4** 0.90, **5** 0.72). With that said, and consistent with the electronegativities of the two metals, the Zn–Mg σ bond of **1a** is partly polarized towards the zinc center in that compound (natural charges: Zn 0.36, Mg 1.07). Also noteworthy is the fact that high metal–metal bond s character, as calculated for the dimers **3**–**5**, has been reported for the majority of Group 12 metal(I) dimers which have been computationally analyzed.[3] The most striking exceptions are the only other two-coordinate systems, [Ar′MMAr′] (M = Zn, Cd or Hg), for which high p character was calculated for their metal–metal bonds.[4,14,15] This difference provides an explanation as to why the $^{1}J_{\text{CdCd}}$ coupling constant for **4** is more than twice that of [Ar′CdCdAr′].

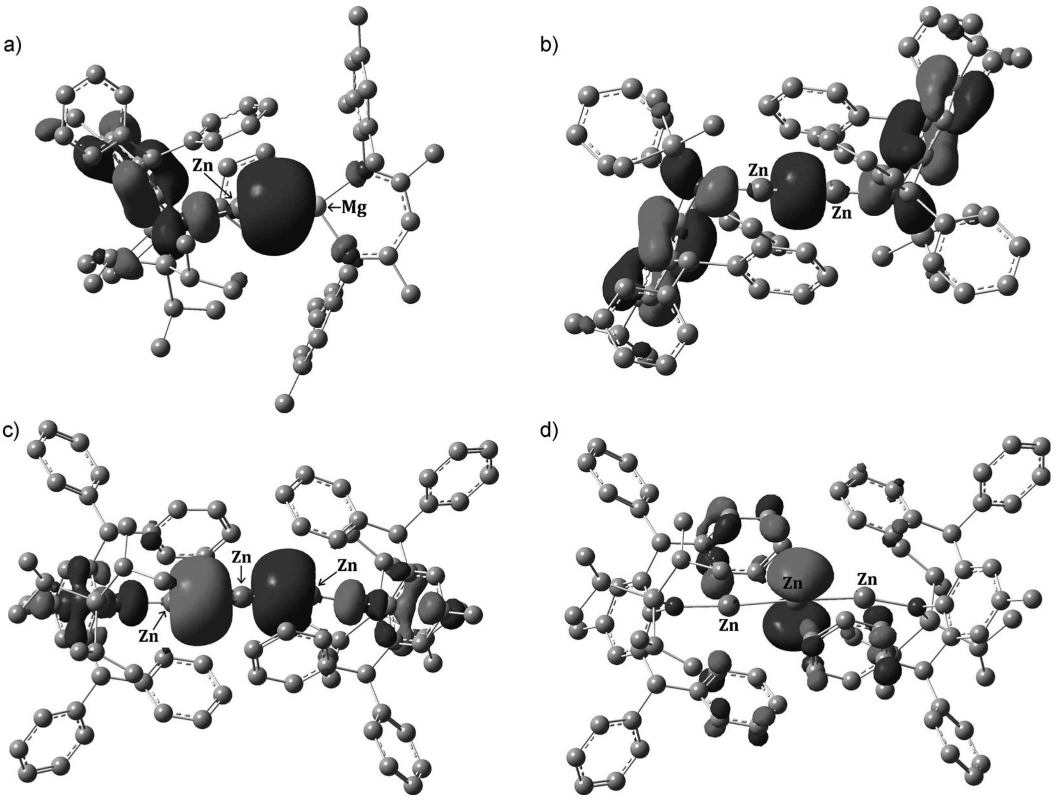


Figure 2. a) HOMO of **1a**, b) HOMO of **3**, c) HOMO of **6**, and d) LUMO of **6**.

The bonding situation in the tri-zinc compound **6** is somewhat different to that in the dimer **3**. While it has what approximates as a linear $[\mathrm{Zn}_3]^{2+}$ core (natural charges: $\mathrm{Zn}_{\text{terminal}}$ 0.50, $\mathrm{Zn}_{\text{central}}$ 0.18) stabilized by two anionic amide ligands (natural charges: N −1.47), the Zn–Zn σ bonding (WBO = 0.68) that is exhibited by the HOMO (Figure 2) is mainly derived from overlap of the valence s orbitals of the terminal zinc centers and a sp orbital on the central zinc atom. Consistent with this view are the LUMO and LUMO + 1 for the compound, each of which encompasses high non-bonding p-orbital character on the central zinc atom. It is also important to note that there are no significant intramolecular Zn···aryl bonding interactions calculated for the compound.

The moderate stability of compound **6** in the solid state at room temperature is intriguing, considering that previous calculations on the related system, [CpZn$_3$Cp], predicted it to be unstable with respect to elimination of Zn metal. So as to explore this further, the Δ*G* for the partial disproportionation of [L*Zn$_3$L*] **6** to give [L*Zn$_2$L*] **2** (B3PW91-D3) and a zinc atom was calculated, and surprisingly found to be endergonic (+12.3 kcal mol^{-1}). However, it must be remembered that this reaction is in the gas phase, and when the enthalpy of vaporization for zinc metal (31.2 kcal mol^{-1}) is taken into account, the reaction yielding bulk zinc would almost certainly be exergonic. Therefore, it seems likely that **6** is kinetically stabilized towards disproportionation by its extremely bulky amide ligands.

In conclusion, examples of a variety of novel compound types containing metal–metal bonds, including at least one Group 12 metal center in the formal 0 or +1 oxidation states, have been prepared and analyzed by spectroscopic, crystallographic, and computational techniques. The stability of all the new compounds can be attributed to the considerable steric protection provided to their metal–metal cores by the extremely bulky amide ligands that coordinate those cores.

Keywords: DFT calculations · magnesium · metal–metal bonding · mixed valence · zinc

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