Cluster Compounds

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Bridging the Gap between Coordination and Cluster Compounds: Unusual Bonding Modes for Zinc

Deborah L. Kays and Simon Aldridge**

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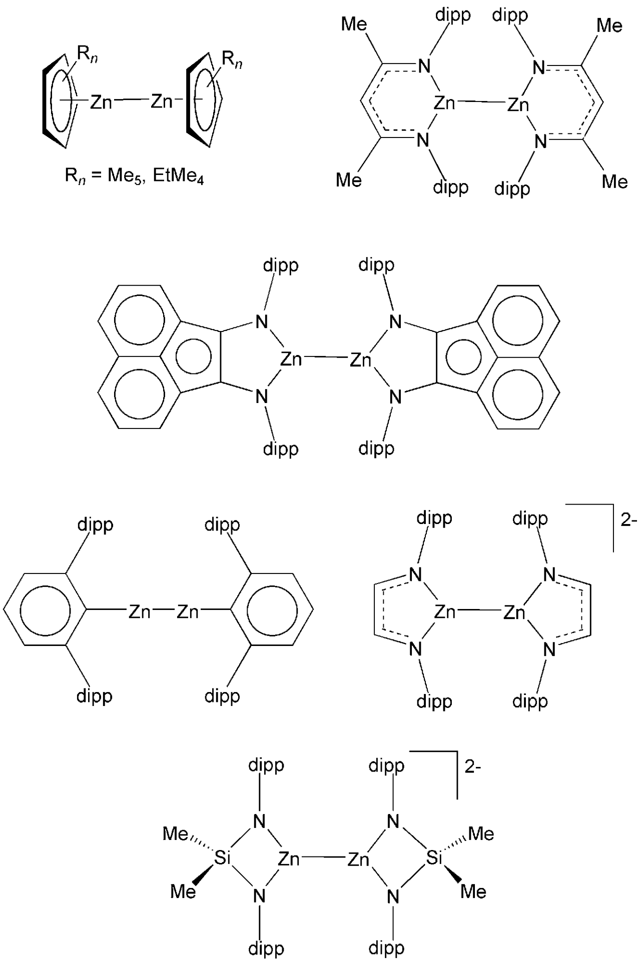
Molecular compounds featuring metal–metal bonds have been the focus of significant recent research interest, leading to advances both in terms of novel bond orders (e.g. Power and co-workers' chromium–chromium quintuple bond) and in linking pairs of atoms with no previous precedent for metal–metal bonding (e.g. Jones and co-workers' magnesium–magnesium bond).[1,2] Complexes featuring metal–metal bonds between Group 12 elements have been attracting renewed interest since reports of the first direct Zn–Zn bond by Carmona and co-workers in 2004.[3] The strength of direct metal–metal bonds decreases significantly on going from mercury to cadmium to zinc, so while Hg–Hg bonds feature in undergraduate textbooks, prior to [Cp*ZnZnCp*] (Cp* = η^5-C_5Me_5), compounds containing Zn–Zn bonds had been trapped only at low temperatures in matrix-isolation experiments.[4] The chemistry of direct Zn–Zn bonds has subsequently been expanded by other recent reports and now encompasses both charge-neutral and anionic species (Scheme 1).[3,5] However, although zinc is prevalent in alloys and in intermetallic and solid-state phases,[6] its incorporation into discrete molecular clusters is somewhat rare.[7,8]

Recently, Fischer and co-workers reported novel metal-rich compounds containing zinc, which appear to offer a bridge between classical coordination and cluster chemistries.[9,10] Given the Carmona group's synthesis of [Cp*ZnZnCp*] from [Cp^*_2Zn] and $ZnEt_2$[3] and the comparable covalent radii (ca. 1.22 Å)[11] and electronegativities of zinc and gallium (1.7 and 1.8, respectively, on the Allred–Rochow scale),[12] the reactivities of GaCp*-containing systems towards ZnR_2 (R = Me, Et, Cp*) were investigated.[9,10] In particular, the reactions of the molybdenum(0) complexes [$Mo(GaCp^*)_2L_4$] (L = CO (**1**), GaCp* (**2**)) with $ZnMe_2$ (Scheme 2) have been shown to provide access to novel multinuclear zinc systems that superficially resemble classical Wade–Mingos clusters, but which in reality feature little direct Zn–Zn bonding.



Scheme 1. Structurally characterized compounds containing discrete Zn–Zn bonds (dipp = 2,6-$iPr_2C_6H_3$).

Reaction of **1** with four equivalents of $ZnMe_2$ gives [$\{Mo(CO)_4\}_4(Zn)_6(\mu$-$ZnCp^*)_4$] (**3**), a multinuclear, bimetallic framework compound which features a tetrahedral array of molybdenum centers, each edge of which is bridged by a naked zinc atom. Further substitution at each molybdenum

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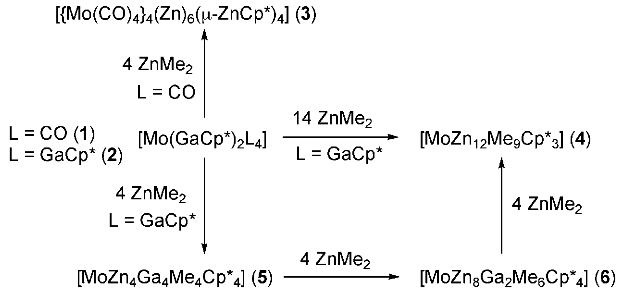
[*] Dr. D. L. Kays
School of Chemistry, University of Nottingham
University Park, Nottingham, NG7 2RD (UK)
Fax: (+44) 115-9513-555
E-mail: deborah.kays@nottingham.ac.uk
Homepage: http://www.nottingham.ac.uk/chemistry/staff/staffrole.php?id=ODA4NDQz&page_var=personal
Dr. S. Aldridge
Inorganic Chemistry Laboratory, University of Oxford
South Parks Road, Oxford, OX1 3QR (UK)
Fax: (+44) 1865-272-690
E-mail: simon.aldridge@chem.ox.ac.uk
Homepage: http://users.ox.ac.uk/~quee1989/



Scheme 2. Syntheses of compounds **3**–**6** from **1** and **2**.

center (such as would be required for the construction of further Mo–Zn bonds) is presumably inhibited by the strong coordination of the four ancillary carbonyl ligands. Thus, the reactivity of the homoleptic Cp*Ga-ligated molybdenum(0) complex **2** was targeted, given the weaker coordination of Cp*Ga (vs. CO) at Mo^0. Accordingly, the reaction of **2** with fourteen equivalents $ZnMe_2$ gives rise to the unprecedented icosahedral species $[MoZn_{12}Me_9Cp^*_3]$ (**4**), which features a central molybdenum atom coordinated only by zinc-donor ligands. Moreover, some idea of the mechanism for the formation of **4** can be gained through the isolation of two intermediate compounds featuring both zinc and gallium donors. $[MoZn_4Ga_4Me_4Cp^*_4]$ (**5**) and $[MoZn_8Ga_2Me_6Cp^*_4]$ (**6**) were obtained from the reactions of **2** with four and eight equivalents of $ZnMe_2$, respectively. In more general terms, both **3** and **4** appear to be formed by radical mechanisms, the reduction of Zn^{II} to Zn^{I} (and Zn^0 in the case of **3**) being concomitant with the oxidation of Ga^{I} to Ga^{III}. In a similar vein, the formation of the Zn^{I} complex [Cp*ZnZnCp*] from $[Cp^*_2Zn]$ and $ZnEt_2$ has also been shown to proceed by a radical mechanism.[5e]

The unusual structure of compound **3** (Figure 1) is based around a super-tetrahedron defined by the four $\{Mo(CO)_4\}$ units, together with ten zinc centers: a Zn_6 distorted octahedron defined by the "naked" Zn^0 centers which bridge each of the Mo···Mo supertetrahedral edges and four $\{Cp^*Zn^I\}$ moieties which bridge four of the twelve Mo–Zn bonds. It has been proposed that **3** provides a molecular mimic of components of the Mo/Zn Hume–Rothery phases, in particular of the intermetallic phase $MoZn_{20.44}$.[6a] Although the bonding situation in **4** has been probed in depth by computational means (see below), **3** has not yet been investigated to the same extent. Summation of the formal electron counts of the carbonyl, Cp*Zn, and "naked" zinc ligands at each molybdenum center is consistent with a straightforward 18-electron configuration, and on this (albeit simplistic) basis, the interactions between the zinc centers are likely to be primarily weak closed-shell dispersion forces. The relatively long Zn···Zn separations in **3** (2.6428(7)–3.0259(7) Å between the "naked" Zn atoms and 2.5861(7)–2.6261(7) Å between the "naked" Zn centers and the bridging ZnCp* ligands; cf. 2.305(3) Å for the formal Zn–Zn single bond in [Cp*ZnZnCp*]), are at first glance consistent with such relatively weak interactions. However, an in-depth quantum chemical study of the bonding interactions in this molecule is needed before such arguments can be placed on a firmer footing.

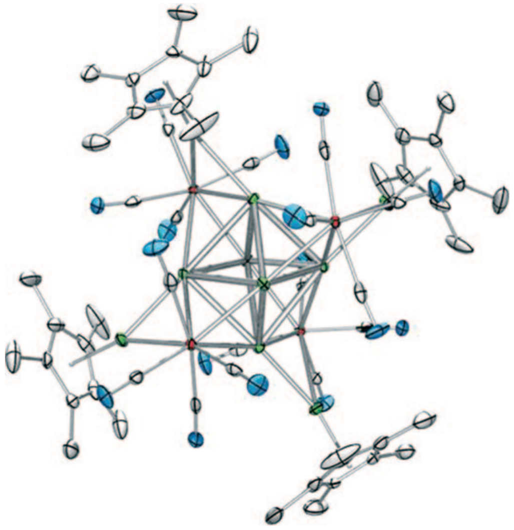


Figure 1. Crystal structure of **3**. Mo red, Zn green, O blue, C gray.

With its molybdenum atom encapsulated by an icosahedral arrangement of zinc atoms, compound **4** (Figure 2) offers a unique parallel between molecular chemistry and zinc-rich intermetallic phases. Such geometric similarities are reminiscent of those identified, for example, in the pioneering work of Schnöckel and co-workers, as linking subvalent gallium clusters and various phases of the elemental metal.[13] Quantum chemical calculations carried out on simplified models of **4** allow for interesting insight into the prevailing bonding situation. Crucially, while the geometric structure of the $MoZn_{12}$ core in **4** may resemble endohedral Zintl anions such as $[Pt@Pb_{12}]^{2-}$[14] or hypoelectronic species such as Al_{13}^-,[15] its electronic structure is markedly different from these interstitial cluster systems. The bonding in the model system $[Mo(ZnH)_{12}]$ (of I_h symmetry) is thought to be best described in terms of an sd^5-hybridized molybdenum atom engaging in six Mo–Zn three-center, two-electron bonds with

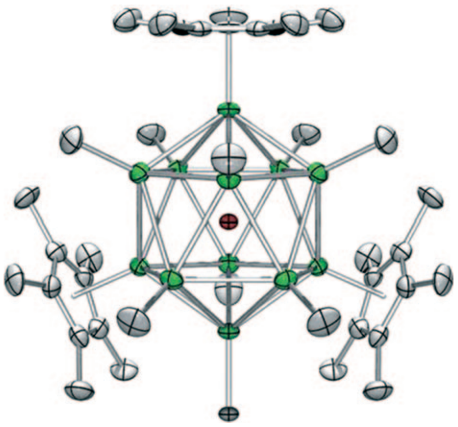


Figure 2. Crystal structure of **4**. Mo red, Zn green, C gray.

the twelve peripheral {ZnH} fragments. Each three-center, two-electron bond stretches across one of the body diagonals of the idealized icosahedron, resulting in six high-lying molecular orbitals (of h_g and a_g symmetries) contributing to Mo–Zn bonding. By contrast, the Zn–Zn interactions are found to be very weak, resulting from the delocalization of the remaining six valence electrons over the Zn cage (to give the HOMOs of t_{1u} symmetry). Since a total of thirty Zn–Zn edges are implied by an icosahedral geometry, the formal bond order for each would be a mere 0.1. Consistent with this model, 1) analysis by Bader's "Atoms in Molecules" (AIM) approach yields no Zn–Zn bond paths; and 2) the Zn–Zn separations for **4** (2.724(2)–2.853(2) Å), while similar to those found in $MoZn_{20.44}$ (2.748(3)–2.790(3) Å),[6a] are relatively long (cf. Cp*ZnZnCp*: 2.305(3) Å).[3] Thus, while classical cluster systems are characterized by the existence of significant bonding between the cage vertices, the lack of such interactions in **4** highlights its alternative description as a transition-metal complex featuring an unusually high coordination number.

Further applicability of this synthetic methodology has also been demonstrated and hints at exciting future developments. While the reaction of **2** with $ZnEt_2$ yields the related system $[MoZn_{12}Et_{10}Cp^*_2]$ (**7**),[10] which is tantalizingly close to a truly homoleptic species, precursors featuring other transition metals have also been shown to display similar reactivity. The reaction of $[Pt(GaCp^*)_4]$ with $CdMe_2$ gives rise to an unusual example of an octacoordinated platinum complex, $[PtCd_8Me_4Cp^*_4]$ (**8**).[10] Such results highlight the possibilities for further advances in this area, thereby bridging the gap between molecular species and solid-state materials, both in terms of synthetic chemistry and in terms of the insight offered into electronic structure.

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