Organometallic Structures

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Main-Group Metal–Alkyls: Simple Formulae but Complex Structural Chemistry

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density functional calculations · solid-state structures · structure elucidation · x-ray crystallography · zinc

Homoleptic main-group metal–alkyl compounds have the deceptively simple general chemical formula R_xM_y, but their structures, especially in the solid state, can be quite complex. Such compounds have a long history in chemical research, being among the first organometallics to be prepared and characterized, and they retain an important place in modern chemistry as key reagents in a variety of organic and inorganic processes. These compounds are also cornerstones in the development of theories of bonding and structure.

The crystallographic characterization of main-group metal–alkyl compounds has been, and to a large extent remains, a major experimental challenge. These compounds are generally very air-sensitive, highly reactive, and often volatile; some are not solid under ambient conditions, particularly those that contain the lightest metals and the smallest alkyl groups. The crystal structures are often disordered or are affected by twinning, and the hydrogen atoms, which are of real interest in these compounds because of their potential interaction with the metal centers, are notoriously difficult to locate precisely by X-ray diffraction.

Many of these obstacles are well illustrated by the pioneering work on lithium alkyls in the years up to 1970.[1] This and subsequent research has demonstrated that lithium alkyls generally form tetrameric or hexameric structures in the solid state, in which the alkyl groups may be terminally bonded, but more often serve as bridging groups in some way.[2] It is noteworthy that no crystal structures of metal–alkyl compounds that contain the heavier alkali metals have been reported to date. Similarly, there is no crystallographic information on alkyls of the alkaline earth metals, except for some dialkylmagnesium compounds.

The degree of aggregation is one fundamental question of interest for these compounds: what is n in $[R_xM_y]_n$? Are there discrete monomers, small oligomers, or polymeric structures in one or more dimensions? The answer is dependent on the choice of metal and alkyl group, but is not always predictable and simple, as shown by the $[RLi]_n$ tetramers and hexamers. Thus, as further examples, Me_3Al actually exists as the dimer Me_6Al_2 in the solid state, but the heavier congeners Me_3Ga, Me_3In, Me_3Tl, and tBu_3Al are all monomers. As an added complication, many alkyls of the heavier main-group metals, such as Sb and Sn, contain direct metal–metal bonds that are not supported by any bridging alkyl ligands. These questions of aggregation and bonding are of interest when the "simple" alkyl compounds are compared with, and potentially used to provide starting models for, more complex materials, in which other ligands are present. These concepts are also important when the metal alkyls are used as reagents in solution, wherein solvent molecules interact with the metal centers and/or the alkyl groups and influence their chemical behavior.

In this difficult field, a notable landmark has been achieved recently by Steiner and co-workers[3] in establishing definitive crystal structures for Me_2Zn and Et_2Zn,[4] the smallest of the zinc alkyls. Two polymorphs of Me_2Zn are reported and the experimental crystallography is complemented by DFT calculations and other computational interpretations of the raw structural results. Previously reported zinc alkyls that contain larger alkyl groups are essentially linear molecules of the form R–Zn–R, although two dialkenylzinc compounds exist as chain polymers, in which unsaturated carbon atoms serve as bridges between the Zn centers. Do the smaller methyl and ethyl groups in Me_2Zn and Et_2Zn, respectively, allow oligomerisation, as in Me_3Al?

The basic answer is no: Me_2Zn and Et_2Zn are also discrete linear molecules, at least from a straightforward inspection of the crystal structures and their intermolecular contacts (Figure 1).

What is particularly impressive about this report is the way in which several relatively new developments in crystallographic techniques have come together and played an

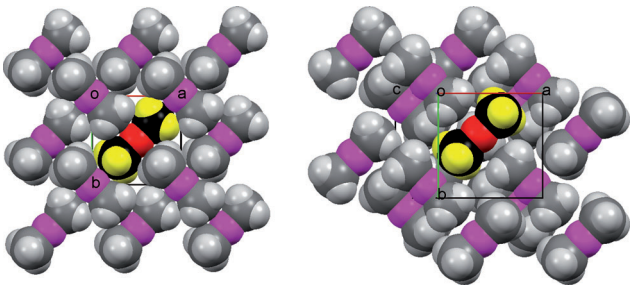

Figure 1. The crystal structures (space-filling models) of α-Me_2Zn (left) and β-Me_2Zn (right). One molecule is colored differently from the others in each structure for clarity. a, b, c, o mark the unit cell axes and origin.

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important role in making the experiment work. Both compounds are volatile, reactive materials with melting points that are well below room temperature, so crystals had to be grown in situ at low temperature, with annealing, and the resultant solid samples displayed various problems with twinning, disorder, and multiple crystal domains. The resolution of these issues took advantage of area-detector technology and powerful modern structure refinement software.

Given the basic structural results from these experiments, some important questions still remain. In particular, how do the two polymorphs of Me_2Zn differ, and how confident can we be about the positions of the hydrogen atoms of the methyl groups? These parameters are essential for a full characterization but are the least precisely determined in all of these structures, and are especially difficult to determine in the low-temperature β-Me_2Zn phase, which gives diffraction data of relatively low quality. The authors provide satisfactory answers by applying two quite different computational approaches. One is an enhanced DFT calculation of possible crystal structures for comparison with the experimental results, while the other is an extensive analysis of intermolecular distances and interactions through Hirshfeld surfaces,[5] which indicates the most probable orientations of the methyl groups. The combination of these calculations with the crystallographic results provides the basis for assessing the relative stabilities of the Me_2Zn polymorphs, as well as the structural relationship and the extent to which the crystal structures are stabilized by small covalent contributions to the intermolecular van der Waals interactions.

From a molecular point of view, the main difference between the two polymorphs of Me_2Zn is that one polymorph has the two methyl groups staggered, and the other polymorph has the two methyl groups eclipsed, as can be seen in the highlighted molecules in Figure 1. Although the two packing arrangements are different, they are related. In addition to the change in molecular conformation from staggered to eclipsed, the transition from the α to the β polymorph on cooling below 180 K involves an approximate doubling of one unit-cell axis, and the reorientation of molecules relative to one another. The high-symmetry and, in some respects, the rather simpler solid-state structure of Et_2Zn has the two ethyl groups arranged mutually *cis* (Figure 2).

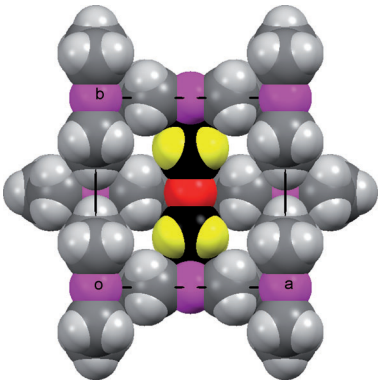

Figure 2. The crystal structure (space-filling model) of Et_2Zn. One molecule is colored differently from the others for clarity.

Apart from the importance of these results for metal–alkyl and more general organometallic structural chemistry, they also contribute to the study of polymorphism, in which there is currently strong interest, and to the enormously challenging pursuit of reliable crystal structure prediction.

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[1] a) H. Dietrich, *Acta Crystallogr.* **1963**, *16*, 681–689; b) E. Weiss, G. Hencken, *J. Organomet. Chem.* **1970**, *21*, 265–268.
[2] Within the space confines of a Highlight, references are not given for all individual crystal structures in the scope of this article. Relevant structures were identified by searches of the Cambridge Structural Database (version 5.32, November 2010); see F. H. Allen, *Acta Crystallogr. Sect. A* **2002**, *58*, 380–388.
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[4] While Zn is often considered together with transition metals, its d^{10} "post-transition" configuration resembles main-group metals, and much of its behavior, especially in organometallic chemistry, is similar to that of Mg.
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