METAL–METAL BONDED COMPOUNDS AND METAL CLUSTERS

Larry R. Falvello

Carlos A. Murillo

This special issue of *Inorganica Chimica Acta* on metal–metal bonded compounds and metal clusters commemorates the 50th anniversary of the publication on September 18, 1964, of the seminal paper describing how interactions between d-orbitals lead to a quadruple and a delta bond in species with idealized D_{4h} symmetry, in particular the $\text{Re}_2\text{Cl}_8^{2-}$ anion (F.A. Cotton, N.F. Curtis, C.B. Harris, B.F.G. Johnson, S.J. Lippard, J.T. Mague, W.R. Robinson and J.S. Wood, *Science* 145 (1964) 1305). In this type of species, each of the metal atoms is surrounded by a square or square pyramidal MX₄ arrangement, and the two metal atoms approach each other at a distance significantly shorter than that in the metal. Importantly the two MX₄ units are eclipsed as seen in the hand-drawn figure reproduced from a follow-up paper published the following year describing the structure of $\text{K}_2[\text{Re}_2\text{Cl}_8] \cdot 2\text{H}_2\text{O}$ (F.A. Cotton and C.B. Harris, *Inorg. Chem.* 4 (1965) 330) (see Fig. 1). It is important to note that other compounds now known to contain quadruple bonds between metal atoms were known at the time. Perhaps one of the earliest examples is that of chromium acetate first made by Eugène-Melchor Peligot as early as 1844 but whose correct molecular formula and structure were not known until much later. It is relevant that in the *Science* paper Al Cotton had the vision to describe and explain the eclipsed configuration in the $\text{Re}_2\text{Cl}_8^{2-}$ anion as the result of a quadruple bond derived from a sigma, two pi and a delta bond resulting from overlap of four of the d-orbitals. Because the fifth d orbital, d_{xy}, in these D_{4h} species is used in metal-to-ligand bonding the maximum number of bonds is attained when there are eight metal-based orbitals. Thus the quadruple bond formed. Now, modifications in the geometry allow the formation of an even larger number of bonds, and quintuple bonds are also common. Today, understanding of these D_{4h} species is aided by fitting together the pieces of the puzzle consisting of data from the structural effects of torsional changes, crystallographic studies, EPR and NMR spectroscopies, visible/NIR and photoelectron spectra, circular dichroism, magnetism, electrochemistry as well as theoretical computations. Some details of how this puzzle has been put together are provided in a Viewpoint article (L.R. Falvello, B.M. Foxman and C.A. Murillo, *Inorg. Chem.* 53 (2014) 9441). The articles that comprise this special issue of *Inorganica Chimica Acta* accredit the continuing vibrancy of research into metal–metal bonds and clusters. These fields continue to attract leading-edge work involving synthesis, structural and spectroscopic characterization and theoretical modelling. As the contents of this issue attest, the fields of metal–metal bonds and clusters are as rich as chemistry itself. We are pleased to offer here articles from leading chemists involving the preparation and characterization of new compounds to which a veritable cornucopia of preparative, analytical and theoretical techniques have been brought to bear. Besides synthesis and structure determination, the articles herein report the application of leading-edge techniques such as ultrafast spectroscopy, luminescence, microwave and solvothermal synthesis, and DFT analysis.

We are also pleased to have among the contributions to this issue several reflections on various aspects of metal-metal bonds and clusters, and their characterization. We want to thank our colleagues and friends who have contributed to the celebration of the 50th anniversary of this important breakthrough in metal-metal bonding and who have joined in keeping alive the memory of F. Albert Cotton, Al for those of us who had the privilege of knowing him. This special issue provides an overview of where this field currently stands. We reserve special acknowledgment for those contributors to this special issue who were members of the group that discovered the quadruple bond and co-authors, with Al Cotton, of the seminal report whose fiftieth anniversary we celebrate with this publication.