科技资料

METAL-METAL BONDS AND CLUSTERS IN CHEMISTRY AND CATALYSIS

METAL–METAL BONDS AND CLUSTERS IN CHEMISTRY AND CATALYSIS

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PREFACE

This book contains a series of papers and abstracts from the 7th Industry-University Cooperative Chemistry Program symposium held in the spring of 1989 at Texas A&M University. The symposium was larger than previous IUCCP symposia since it also celebrated the 25 years that had elapsed since the initial discovery by F.A. Cotton and his co-workers of the existence of metal-metal quadruple bonds. Cotton's discovery demonstrated that multiple bonding in inorganic systems is not governed by the same constraints observed in organic chemistry regarding s and p orbital involvement. The d orbitals are involved in the multiple bonding description. The quadruple bond involves considerable d orbital overlap between adjacent metal centers. Part I of this series of papers focuses upon the impact of this discovery and describes further contributions to the development of the field. Multiple metal-metal bonding now is known to permeate broad areas of transition metal chemistry.

The understanding of metal-metal bonding that developed as a result of the discovery of multiple metal-metal bonding awakened a new chemistry involving metal clusters. Clusters were defined by Cotton to be species containing metal-metal bonding. Clusters in catalysis therefore seemed a logical grouping of papers in this symposium. Clusters play an every increasing role in the control of chemical reactions. Part II of this book describes some of the interesting new developments in this field.

In Part III the papers examine the role clusters play in describing and understanding solid state materials. Clusters exist throughout solid state chemistry. Modern structural tools now enable us to examine the properties of these materials. Part IV presents papers which relate to the procedures we use today to understand the clusters themselves, the bonding theories and spectroscopy.

The Chemistry Department at Texas A&M University is pleased with the support that comes from industrial members of the IUCCP. Without this support, many of the programs in this department would be less healthy. Furthermore, the program reflects the need to maintain the connection between industrial science and the "ivory tower" of academia. With well established relationships between the research university and modern chemical industries, we can expect to continue to compete effectively with the rapidly developing chemical science elsewhere in the world. We must do this with great skill if we are to remain competitive with our chemical products.

Although several persons helped to make this book a reality and to assure the success of the symposium, there are some that were special. First, I want to thank the committee members who helped me choose the topic and the various lectures. They were Arthur E. Martell, Larry M. Cirjak, William J. Kroenke, Brian Kolthammer, Graham Mott, George Vaughn and John Smegal. Professor Arthur Martell was a great help to me on various aspects of the programming and planning. His wife, Mary Martell, also gave special attention to the details. My students also helped with transportation and the audio-visual aids. I am especially grateful to Mrs. Carol Dissen who organized the paperwork associated with the symposium and made sure that the manuscripts were properly treated. Her organizational skills made the whole activity painless for the editor. I am indebted to Mrs. Sherri Sanford for her efforts as the book neared completion.

I also wish to express my appreciation to Lord Lewis of Cambridge University and Dean Abraham Clearfield of Texas A&M. Lord Jack Lewis presented a beautiful lecture on the environment which, unfortunately, is not included in this book. He also kept other speakers in fine tune by sitting in the first row of the lecture hall for each talk. His questions led to important answers which made the symposium exceptionally lively. Abe Clearfield presented a significant story of the development of the materials research trust underway at Texas A&M University. This paper also is not included in the book. Information about both topics is available from the editor, however. I will be pleased to respond to your written request.

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ABSTRACTS

A QUARTER-CENTURY OF METAL-METAL MULTIPLE BONDS

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A lot can happen in twenty five years. Actually, the roots of my work on metal-metal multiple bonds go back even more than twenty five years. As early as the late 1950's I wondered about how many instances of definite, confirmed M-M bonds (even single ones) were to be found in the literature. Very few, I quickly discovered. I then wondered whether it would make sense to seek out more. However, it was not until I had acquired the knowledge and equipment necessary for X-ray crystallography that I could actually embark on such a program. It also happened that chance favored a prepared mind. Although I undertook a structural study of "$CsReCl_4$," without anticipating that it would turn out to be $Cs_3[Re_3Cl_{12}]$, the interpretation of that structure in terms of metal-metal bonds, but particularly double bonds, was almost automatic to me.[1]

Chance, or should one say serendipity, continued to write the scenario for another few months. As recounted in detail elsewhere,[2] we "discovered" compounds containing the quadruply-bonded $Re_2Cl_8^{2-}$ ion while attempting to explore further the chemistry of the $Re_3Cl_{12}^{3-}$ ion. We reported our preparation of $Re_2Cl_8^{2-}$ compounds and the assignment of a bond of order 4 in 1964 and it is on that basis that one can consider 1989 as the twenty fifth anniversary of the discovery of a consistent pattern of multiple bonding between metal atoms.

Reports of compounds that were entirely misformulated at the time reported but can now known to contain quadruple bonds antedate 1964 by various periods. Chromium(II) acetate, $Cr_2(O_2CCH_3)_4$ was described in

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1844.[3] The earliest reports[4,5] of compounds with Mo-Mo quadruple bonds appear to be those of several molybdenum(II) carboxylates (whose structures were all incorrectly formulated) and "$MoBr_2(NMe_2)\cdot NHMe_2$, which we now know to be $Mo_2Br_4(NHMe_2)_4$. We also now recognize that the first compounds containing Pt-Pt single bonds within a square-prismatic arrangement of ligands were reported in 1905.[6] The first compound containing the $Tc_2Cl_8^{3-}$ ion was reported in 1963 but without any suggestion of its true nature.[7] Finally, of course, it is now well known that chemists in the Soviet Union began reporting compounds that were later shown to contain $Re_2Cl_8^{2-}$ or $Re_2Br_8^{2-}$ ions as early as 1952.[8]

The early growth of the field was slow, but soon revealed itself to be exponential, as shown in Fig. 1, for close to two decades. In the past few years activity has leveled off at about 140 publications per year.

It is interesting to see which elements have been most actively studied, once the nature of the bonding was recognized. This is summarized in Fig. 2. Rhenium, of course, had the early lead, but around 1970 it was surpassed by molybenum. Molybdenum is truly extraordinary in its facility for forming metal-metal bonds of many kinds, including a great variety of cluster compounds in which there are bonds of order one, or thereabout. It enjoys its place as front runner in multiple bond formation in part because it has two arenas in which to play: quadruple bonds and triple bonds, of different types structurally. The quadruple bonds are found in compounds that have (at least in a formal sense) a fourfold axis while the triply bonded compounds are characteristically based on threefold symmetry. Tungsten has potentially the same advantage, but does not compete with molybdenum because of the relative instability and reactivity of its quadruple bonds. Rhenium, incidently, also forms extensive series of both quadruple and triple bonds, but both in the compass of fourfold symmetry.

Turning to other features of Fig. 2, we note that rhodium is the other member of the top four, and has been for over a decade. A pedant could argue that the Rh_2^{4+} species do not merit mention here at all because they do not contain metal-metal multiple bonds. Another pedant might try to justify their inclusion because some are (and others probably could be) the parents of Rh_2^{5+} species in which there is a bond order of 1.5 based on the loss of an antibonding electron on going from

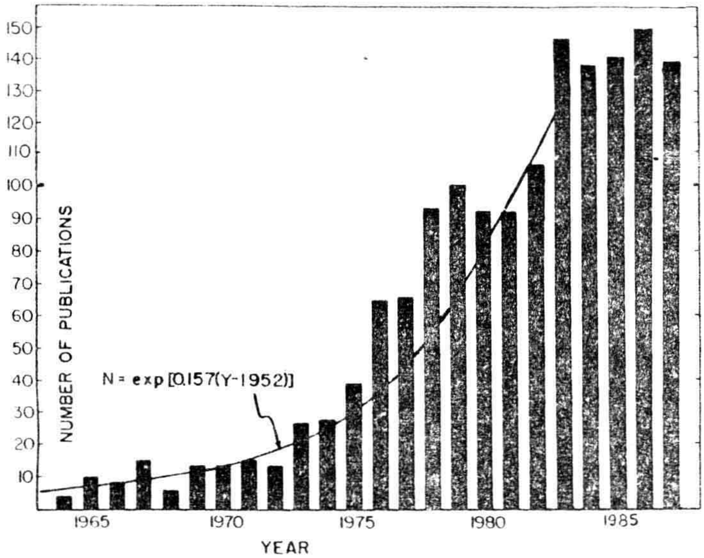

Fig. 1. The approximate number of publications on all types of M-M multiple bonds each year, 1964-1988.

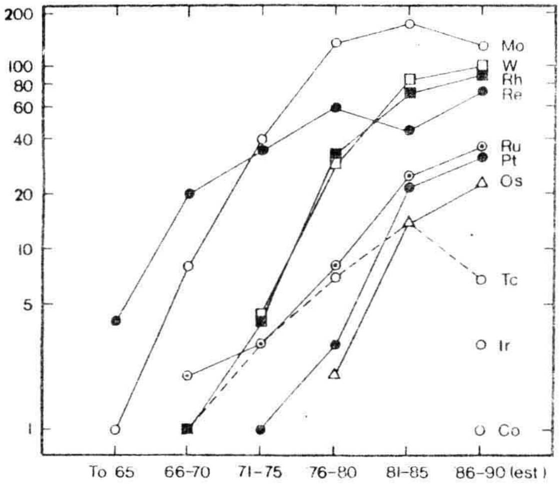

Fig. 2. The approximate number of publications dealing with different M-M bonds. Note logarithmic scale.

Rh_2^{4+} to Rh_2^{5+}. As a real-world, practical chemist, I justify their inclusion because their electronic structures (and molecular structures) are simply logical extensions of those in which the M-M bond orders are higher, as shown by the following progression:

$Mo_2(O_2CR)_4$	$\sigma^2\pi^4\delta^2$	bond order = 4
$Ru_2(O_2CR)_4$	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$	bond order = 2
$Rh_2(O_2CR)_2$	$\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$	bond order = 1

As Fig. 2 shows, work on ruthenium, osmium and platinum species has been growing steadily. Technetium has a somewhat restricted role because of the nuisance factor (i.e., its low-level radioactivity) involved in working with it. Western chemists have almost completely avoided it and the small literature that exists is largely produced by Soviet chemists.

The element chromium has not been included in Fig. 2, partly because it is hard to determine a temporal point of departure. Prior to the present era a number of papers dealt with $Cr_2(O_2CR)_4L_2$ compounds. However, it was with the discovery of the supershort Cr-Cr bonds (<2.0 Å) in 1977,[9] that the study of Cr-Cr multiple bonds acquired an enormously greater interest. These super-short bonds are fully comparable in electron density with their Mo and W cogeners, and, indeed, surpass them in this respect. This extraordinarily high bond electron density has lead to very formidable problems in calculating their electronic structures.[10] Of course, there are even greater problems for the "simple" diatomic Cr_2 itself, and for neighboring ones such as V_2, Nb_2, Mo_2 and Ru_2, where electron correlation problems are what Texans call humongous.

Until very recently, chromium was the only element in the first transition series to form M-M bonds analogous to those of its heavier congeners. In general terms, we can understand the reluctance of the other first series elements to do so. Their d orbitals are small and thus <u>inter</u>atomic overlaps are relatively poor while <u>intra</u>atomic d-d interactions are strong, thus making it energetically costly to reach the appropriate valence states. Recently, however, we have obtained a Co_2^{4+} analog[11] to certain Rh_2^{4+} species and it contains the shortest Co-Co bond ever reported, 2.265Å. This encourages us to believe that with judicious choice of ligands we may succeed in forming other M-M bonds in the first series, such as $V{\equiv}V^{4+}$ triple bonds, $Fe{=}Fe^{4+}$ double bonds, and even $Mn{\equiv}Mn^{6+}$ quadruple bonds.

The region of the d-block in which multiple M-M bonds along 3- or 4-fold molecular axes may be formed has also been extended in other directions. The first $Ir-Ir^{4+}$ compound that is isostructural with a rhodium analog has been made[12] and compounds containing $Nb{\equiv}Nb^{4+}$ and $Ta{\equiv}Ta^{4+}$ triple bonds have been synthesized and found to be extremely stable.[13]

To sum up, it is clear that over a quarter of a century an entirely new and increasingly important aspect of transition metal chemistry has been discovered and explored. Moreover, recent work shows that in addition to continued evolution of such chemistry for some 8 to 10 elements about which a great deal is already known, there are quite attractive and realistic possibilities for extending the scope to other elements.

In conclusion, it is fitting for me to thank the National Science Foundation for unfailing support of our work in this field (as well as others) over all of the past quarter of a century. A new grant, recently awarded, will continue that support into the future. Certain phases of the work have also been supported, in the years since 1972, by funds from The Robert A. Welch Foundation. Finally, in recent years Texas A&M University has provided important facilities and services through the Laboratory for Molecular Structure and Bonding.

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THE MULTIPLE METAL-METAL BOND: TWENTY-FIVE YEARS OF SYNTHETIC SERENDIPITY AND STRUCTURAL DISCOVERY

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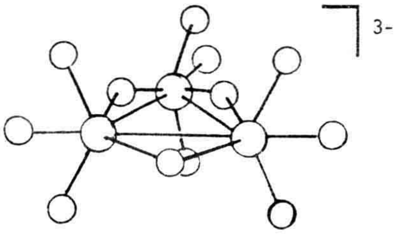
INTRODUCTION

The development of the field of multiple bond chemistry had as its genesis the studies in the early 1960's by Cotton and co-workers that established the existence of salts of the $\{[ReX_4]^-\}_n$ anions (X = Cl or Br) that differed in nuclearity (n = 2 or 3).[1,2] The structural characterization of the $[Re_3X_{12}]^{3-}$ (1) and $[Re_2X_8]^{2-}$ (2) anions, and the recognition that these species (and closely related ones) contain Re-Re bonds of order 2 and 4, respectively, were the seminal discoveries that provided the impetus for the flood of later work which demonstrated that metal-metal multiple bond chemistry is an important feature in the chemistry of many of the transition elements. Multiple bonds between metal atoms are not only of relevance to the field of metal cluster chemistry,[3,4] but they constitute one of the important classes of multiple bonds in general, the others being multiple bonds between the main group elements, and multiple metal-ligand bonds.[5] Multiple metal-metal bonds of orders 4, 3.5, 3, 2.5 and 2 are all well documented. Their place in the scheme of things is represented below.



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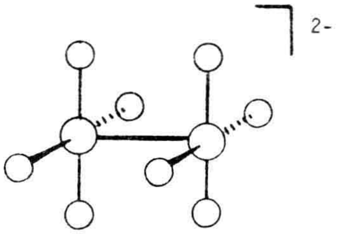

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◯ Re ○ Cl or Br

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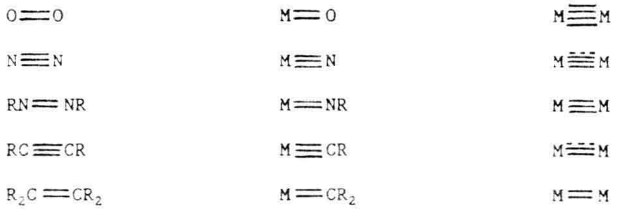

The close relationships that can exist in some instances between these different species is illustrated by the metathesis reaction between W_2(O-*t*-Bu)$_6$, a complex which contains a W≡W bond, and aliphatic acetylenes to give (*t*-BuO)$_3$W≡CR.[7]

As we commemorate the twenty-fifth anniversary of the quadruple bond, as first recognized in $[Re_2Cl_8]^{2-}$,* I am pleased to have this opportunity to reflect upon some of our own contributions in the area of metal-metal multiple bonding. In fact, my own involvement began way back in the fall of 1965 when I arrived fresh off-the-boat (literally!) in Boston Harbor, at the doorstep of M.I.T., to begin a 12-month post-doctoral stint with Professor F. A. Cotton. At the time, I never dreamed that this would lead to the stimulating collaboration and friendship that has lasted for almost twenty-five years.

THE FIRST METAL-METAL TRIPLE BOND: $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$.

In hindsight, my involvement in this area of research was also something of an accident. I had decided to avoid working on any problem relating to the recently discovered quadruple bond since a large proportion of Al's group was already gainfully employed in this area and I judged the opportunities for quick and useful new results to be somewhat limited (some misjudgement!). Apparently, my "escape" was to be in carbonyl chemistry, but after several dismal and abortive attempts to do something useful, and fearing Al's displeasure (post-docs were of course expected to be productive very quickly!) I thought I had better find something to do that worked. Accordingly, I decided to try to clarify some of the rather messy chemistry that had been reported on the reactions of the trinuclear halide Re_3Cl_9 with bidentate ligands. While a certain amount of headway was made in this project,[8] the most useful development from my point of view was discovering the effectiveness of 2,5-dithiahexane ($CH_3SCH_2CH_2SCH_3$, dth) as a ligand, in spite of its rather objectionable odor. As a consequence, I began to look at the reactions of dth with the salt (n-$Bu_4N)_2Re_2Cl_8$ very early in 1966, and discovered that the course of the reaction depended, to a large extent, upon the reaction conditions. Mild conditions with methanol/conc. HCl as solvent afforded $Re_2Cl_6(dth)_2$,[9] whereas prolonged reflux in this solvent, or preferably in acetonitrile, gave red-black dichroic crystals of $Re_2Cl_5(dth)_2$,[9-11] a formally mixed-valent complex whose structure is represented in Fig. 1.

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*It's also the twenty-sixth anniversary of the metal-metal multiple bond, since the Re=Re bond in $[Re_3Cl_{12}]^{3-}$ was the first such bond to be explicitly recognized (J. A. Bertrand, F. A. Cotton and W. A. Dollase, *J. Am. Chem. Soc.*, 1963, *85*, 1349); although many years before, Linus Pauling had speculated on the existence of metal-metal bonds of order greater than unity (L. Pauling, *Chemical & Engineering News*, 25:2970 (1947)).