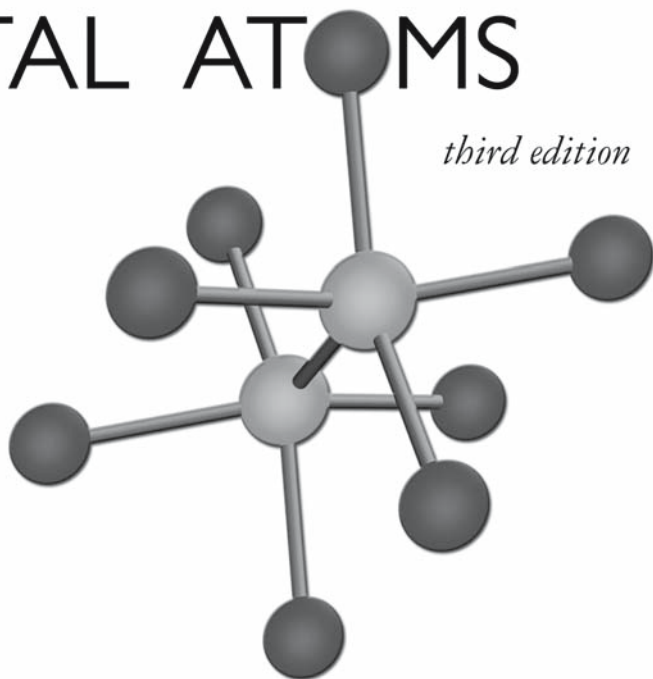


Multiple Bonds Between Metal Atoms

MULTIPLE BONDS BETWEEN METAL ATOMS

third edition



Edited by

F. Albert Cotton, Carlos A. Murillo and Richard A. Walton

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To all of our past and present coworkers

Preface to the Third Edition

Since the second edition of this book there has been so much published in the field that two points seemed clear. One was a sense that a new, up-to-date monograph was needed. The other was the reluctance of two or even three people to undertake the daunting task of covering all the ground. Our response was to call on others to help and, thus, to produce the present, multiauthored volume. Each of the contributing authors was in a position to write authoritatively, from hands-on research experience. We are confident that this has led to a better book than the three of us would have produced. As always in a book where different chapters are written by different authors, there is some variation in style and we chose not to try to smooth it all out.

In every chapter the objective has been to be comprehensive, if not encyclopedic. Putting it a little differently, we, and the other authors, have aimed to mention all pertinent literature references, although the amount of emphasis accorded each paper necessarily varies.

Since the volume of literature to cover is now so large, a few topics that might have been included (or were in the second edition) have been omitted or are covered only in limited detail. Notable ones are the treatment of metal-metal bonding in edge-sharing and face-sharing biocapped octahedra, and metal cluster compounds of rhenium. Also, the vast field of catalysis by dirhodium compounds has been restricted to only the area of chiral catalysts.

The physical properties and bonding of many compounds are, in general, described in two places, to varying degrees. There are some specific reports regarding properties of compounds of certain metals in the first fifteen chapters. Comprehensive discussions (i. e., not element specific) are provided in Chapter 16.

To assist the user of this book a few comments about how it is organized and indexed are pertinent. Because of the element by element (or group of elements) organization, and the division of each chapter into numerous sections and subsections, as well as the extensive tables of compounds, the table of contents plays the part of an index to a major extent. The index itself is thus limited to general topics and concepts that turn up often throughout the book. Individual compounds are, in most instances, not listed there.

Many other people contributed to the production of this volume in addition to those who wrote chapters that were not written by the editors themselves. We are very grateful to these authors, but we are also much indebted to others. The word indispensable must be reserved for Mrs. Debbie Murillo. She created the book from the scattered and mangled fragments available after the tragic and utterly unexpected illness of Ms. Beverly Moore, who contributed much to preparing early drafts. For Debbie's mastery of computerized book publishing as well as her selfless devotion to the task, we owe her a debt that cannot be fully repaid. We have also had major assistance from Dr. Xiaoping Wang and Mr. Dino Villagrán in preparing many of the illustrations, and we thank Mrs. Julie Zercher for efforts in searching computer files.

F. Albert Cotton
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Carlos A. Murillo
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Richard A. Walton
Purdue University

Forward to the Second Edition

Jack Lewis
Cambridge University

The recognition of the multiple bond in $[\text{Re}_2\text{Cl}_8]^{2-}$ by F. A. Cotton was a clear landmark in the development of inorganic transition metal chemistry. Prior to 1960 the mere existence of metal–metal bonding had been under considerable debate. The determination of the structures of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ by Dahl, Ishishi, and Rundle in 1957 established beyond any doubt that molecules occurred containing bonding between metal centres rather than metal interactions, possibly occurring via the agency of bridging groups as is $\text{Fe}_2(\text{CO})_9$. The presence of multiple bonding between metals was recognized, again by Cotton, in the trimeric ion $[\text{Re}_3\text{Cl}_{12}]^{3-}$. However, as with the iron carbonyl $\text{Fe}_2(\text{CO})_9$, the presence of bridging between the metals, in this instance by chloride atoms, left the alternative interpretation of the cause of diamagnetism in this molecule as arising via the bridging groups. The determination of the structure of the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion established both the presence of an unsupported metal–metal bond and a high multiple (quadruple) bond between the metal centres. The trauma in the chemical community of exceeding a bond order of three, the limit of the bonding modes observed in the *p* block, and the unequivocal establishing of a multiple bond between transition metals, was great. It was however considered by many to be an ‘anomaly’, a rare bonding mode. The subsequent work of Cotton and co-workers has established that this molecule is in fact the progenitor of a vast new area of chemistry. This book documents how progress was made in this field. The synthetic methods were developed in a logical manner and the whole force of both structural methods and theoretical interpretation of the bonding was applied to the problems in a masterly way. It provides a prime example of the present day application of chemical methods in mapping this field of chemistry that has now been uncovered, and in particular the importance of X-ray crystallography as a structural tool.

The appearance of the first edition of this book in 1981 was heralded as the authoritative exposition of this area of chemistry and illustrated the vast amount of work and interest that had been generated during the initial twenty years of study. The second edition, a decade later shows how the interest in this field has been maintained and in certain aspects increased to incorporate the majority of the *d*-block elements. The utility of multiple metal bonded

molecules in general synthetic chemistry is well illustrated and what had certainly appeared as an interesting but possibly unique molecule proved to be the genesis of a wide and fundamental area of chemistry. Metal–metal bonding is now accepted as a major pattern in the transition metal complexes, particularly in low oxidation states. The vast range of molecules containing multiple bonding between the metal centres is a reflection of the significant contribution to chemistry made by Cotton and his co-workers.

The authors are to be complimented on maintaining the standard they set in that first edition, their insight into the fascinating study, and their lucid presentation.

Preface to the Second Edition

By mid-1981, with the manuscript for the first edition in the hands of the publishers, we had little inkling that the field of multiple metal–metal bond chemistry would continue to grow at the same explosive rate as it had through much of the 1970s. However, in the intervening 10 years, far more work has been published in the area than in all the period prior to 1981. This spectacular growth of new advances in the field, which continues to this day, along with the favorable response that the first edition received, prompted us to embark on the preparation of a second edition of *Multiple Bonds between Metal Atoms*. The present text is the result.

We have endeavored to include not only those topics that appeared in the first edition, but all significant advances that have been published since. The coverage of the literature in the field is complete up to December 1990, with most of the literature that appeared throughout 1991, during the final stages of manuscript preparation, also being cited. Any omissions of work prior to the end of 1990 are inadvertent. To bring the coverage, at least of the most important topics, as nearly up to date as possible, we have added a short additional chapter (Chapter 11) which includes literature from late 1991 and early 1992.

The dramatic increase in the literature in this field has necessitated some compromise in the depth of coverage of certain topics in order to keep the text size within reasonable bounds. Also, certain topics have grown much more rapidly than others and are therefore afforded more detailed coverage than in the first edition. While there has been some significant reshuffling in the organization, the text is generally along similar lines to those employed previously. Chapters 1–4 cover the same topics as those in the first edition, although Chapter 2 now includes all types of multiply bonded dirhenium and ditchnetium compounds, instead of just those that contain quadruple bonds. Triply-bonded dimolybdenum(III) and ditungsten(III) compounds of the type L_3MML_3 constitute such an important and extensive area of chemistry that they are now afforded coverage in a separate chapter (Chapter 5). There has also been such a dramatic growth in the chemistry of multiply bonded dimetal compounds of the platinum metals, and many of their closely allied singly-bonded analogs, that separate chapters are now devoted to the chemistry of diruthenium and diosmium compounds (Chapter 6), singly-bonded dirhodium (II)

compounds (Chapter 7), and compounds of the other platinum metals, especially those of diplatinum(III) (Chapter 8). There are many other classes of multiply bonded compounds that bear an important and, in some cases, close relationship to those of the types L_3MML_3 , L_4MML_4 , and L_5MML_5 which are the principal focus of this text. These comprise the following: higher nuclearity clusters (trinuclear, tetranuclear, hexanuclear, and octanuclear); various organometallics, such as the mixed cyclopentadienylcarbonyl compounds ($\eta^5-C_5R_5)_2M_2(CO)_n$ (e.g., $(\eta^5-C_5Me_5)_2Mo_2(CO)_4$); edge-sharing and face-sharing bioctahedra; simple diatomic molecules. All are discussed together in Chapter 9. Finally, Chapter 10, which contains the most important physical, spectroscopic, and theoretical results that have been obtained on compounds discussed in earlier chapters, follows closely the format of Chapter 8 in the first edition, except for the omission of diatomic molecules now covered in Chapter 9.

As before, we appreciate the invaluable assistance of our many friends and colleagues who have continued to ply us with preprints and other interesting tidbits of information on unpublished results. These insights have helped us greatly throughout the preparation of this manuscript. In this regard, a particular word of thanks is due to our good friend Professor Malcolm H. Chisholm. One of us (R. A. W.) is most grateful to Keng-Yu (Ivan) Shih for his critical reading of several chapters. Once again, we are particularly grateful for the wonderful secretarial assistance of Mrs Rita Biederstedt and Mrs Irene Casimiro who have patiently helped us overcome many obstacles in the preparation of both editions of this text. This edition is dedicated to both of them, with our profound thanks for their help in this and many other of our scientific endeavours.

F. Albert Cotton,
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March 1992

Forward to the First Edition

Roald Hoffmann
Cornell University

Our central science progresses, but often by uncoordinated steps. Experiments are done here, perceived as important there, fruitfully extended elsewhere. There are satisfactions, to be sure, in the interactive, perforce international nature of modern chemistry. Yet most advances at the frontiers of our lively discipline seem small in scope, chaotic.

Occasionally does one encounter a large chunk of chemistry that is the coherent outcome of the work of one group. Initial observations evolve into an idea. This idea leads to the synthesis of novel molecules or new measurements and to the recognition of an entirely new structural type or a different mechanism. The new field expands, seemingly without limit. All this takes time, for the minds and hands of men and women must be engaged in the effort. The careful observer of the chemical scene seeks out such rare achievements. For when the tangled web of our experience is so transformed, by one person, into symmetries of pristine order and the chemical equivalent of the rich diversity of pattern of an oriental carpet—it is then that one encounters a moment of intellectual pleasure that really makes one feel good about being a chemist.

Such a story is that of metal–metal multiple bonding. A recognition of the structural and theoretical significance of the Re–Re quadruple bond by F. A. Cotton in 1964 was followed by a systemic and rational exploration of metal–metal bonding across the transition series. Cotton and his able co-workers have made most such complexes. The consistent and proficient use of X-ray crystallography results in their studies, not only for structure determination but as an inspiration to further synthetic chemistry, has served as a model for modern inorganic research. Much of the chemistry of metal–metal multiple-bonded species—and interesting chemistry it is indeed—is due to F. A. Cotton and his students. Throughout this intellectual journey into fresh chemistry they have been guided by a lucid theoretical framework. Their bounteous achievement is detailed in this book. I want to record here my personal thanks to them for providing us with the psychological satisfaction of viewing a scientific masterpiece.

Preface to the First Edition

The renaissance of inorganic chemistry that began in the 1950s has been propelled by the discovery of new and important classes of inorganic molecules, many of which do not conform to classical bonding theories. Among these landmark discoveries has been the isolation and structural characterization of transition metal compounds that possess multiple metal-metal bonds. From the seminal discoveries in this area in the early 1960s has developed a complex and fascinating chemistry. This chemistry is simultaneously different from but very relevant to the classical chemistry of the majority of the transition elements. Since the synthetic methodologies, reaction chemistries, and bonding theories are now remarkably well understood, we felt the topic had reached a level of maturity sufficient to justify a comprehensive treatise.

The content of this book encompasses all the classes of compounds currently known to possess, or suspected of possessing, metal-metal bonds of order two or greater, as well as some compounds with single bonds that have a close formal relationship to the multiple bonds. Synthetic procedures, reaction chemistries, spectroscopic properties, and bonding theories are discussed in detail for these molecules, and, in addition, we have attempted to place in historical perspective the most important discoveries in this field. Since both of us have worked in this field for many years, much of our discussion inevitably takes on a rather personal flavor, particularly in our treatment of the circumstances surrounding many of the major advances. We have endeavored to cover all the pertinent literature that was in our hands by the end of December 1980. When possible, we have also referred to those key developments that may have emerged during the early part of 1981, while the manuscript was in press.

Throughout the preparation of the manuscript we were fortunate to have the assistance of many friends and colleagues who not only provided us with valuable information on unpublished results, but on occasion critically read various sections of the text and otherwise helped us surmount minor hurdles. We especially appreciate the assistance of Professors M. H. Chisholm, D. A. Davenport, F. G. A. Stone, O. Glemser, and B. E. Bursten. We also thank the various authors and editors who kindly gave us permission to reproduce diagrams from their papers; the appropriate numbered reference is given in the captions to those figures that were reproduced

directly from the literature or were modified so slightly as to retain an essential similarity to those in the original publications. Finally, we appreciate the expert patient secretarial assistance of Mrs Rita Biederstedt and Mrs Irene Casimiro in the preparation of the manuscript.

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June 1981

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Introduction and Survey

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1.1 Prolog

1.1.1 From Werner to the new transition metal chemistry

From the time of Alfred Werner (*c.* 1900) until the early 1960s, the chemistry of the transition metals was based entirely on the conceptual framework established by Alfred Werner.¹ This Wernerian scheme has as its essential feature the concept of a single metal ion surrounded by a set of ligands. It focuses attention on the characteristics of the individual metal ion, the interaction of the metal ion with the ligand set, and the geometrical and chemical characteristics of this ligand set. It is true that following Werner there was an enormous development and refinement of his central concept. Progress occurred notably in the following areas: metal carbonyls and other compounds where the metal 'ion' is formally not an ion; sophisticated analysis of the electronic structures of complexes; understanding of the thermodynamics and kinetics pertaining to the stabilities and transformations of complexes; structural studies that vastly increase the range of geometries now deemed important (*i.e.* coordination numbers of five and those greater than six); an appreciation of the role of metal ions in biological systems; recognition that ligands, especially organic ones, are not passive but that their behavior is often greatly modified by being attached to a metal atom, in some cases allowing metal atoms to act catalytically.

However, all of these advances constitute *continuous* (evolutionary) progress. They expand upon, augment, 'orchestrate' so to speak, Werner's theme, and that theme is, in essence, *one-center coordination chemistry*.

But the transition metals have another chemistry: *multicenter chemistry*, or the chemistry of compounds with direct metal-to-metal bonds. The recognition and rapid development of this second kind of transition metal chemistry, *non-Wernerian transition metal chemistry*, began in the period 1963-65, and constitutes a *discontinuous* (revolutionary) step in the progress of chemistry. We see in it the creation and elaboration of a new conceptual scheme, one which is becoming as important an intellectual innovation in chemistry as was the Wernerian idea in its time, or the ideas of Kekulé, and of van't Hoff and Le Bel in their time. The recognition of the existence of a wholly new and previously entirely unrecognized chemistry of the transition metals, which constitute more than half of the periodic table, is certainly an important fundamental step in the progress of chemistry.

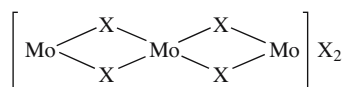
One of the aspects of this overall development of multicenter transition metal chemistry obviously constitutes an innovation with respect to the entire science of chemistry, namely, the recognition that there exist chemical bonds of an order higher than triple. The existence of quadruple bonds was first recognized in 1964, and since then more than a thousand compounds containing them have been prepared and characterized with unprecedented thoroughness by virtually every known physical and theoretical method, as well as by a wide-ranging investigation of their chemistry.

It is especially to be noted that compounds containing quadruple bonds are in most cases not at all exotic, unstable, or difficult to obtain. On the contrary, many of them can be (and are) easily prepared by undergraduate chemistry students and they 'live out in the air with us'. Perhaps the most astonishing thing about this chemistry is that it was discovered so late.

1.1.2 Prior to about 1963

It is well to begin with the following observation. Werner, of course, recognized the existence of polynuclear complexes and, indeed, he wrote quite a number of papers on that subject.² However, the compounds he dealt with were regarded (and correctly so) as simply the result of conjoining two or more mononuclear complexes through shared ligand atoms. The properties of these complexes were accounted for entirely in terms of the various *individual* metal atoms and the local sets of metal-ligand bonds. No direct M–M interactions of any type were considered and the concept of a metal-metal bond remained wholly outside the scope of Wernerian chemistry, even in polynuclear complexes.

Before Werner's time, however, there were a few compounds in the literature that could not be accommodated correctly by the coordination theory. The earliest was chromous acetate, to which we shall return later (p. 10). In the period 1857–61, the Swedish chemist Christian Wilhelm Blomstrand³ and co-workers investigated the dichloride and dibromide of molybdenum and found them to have some surprising properties. For example, only one third of the halide ions could be precipitated with Ag^+ , thus indicating that the smallest possible molecular formula is Mo_3X_6 . Werner himself in the several editions of his *Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie* proposed the following formulation:



Towards the middle and end of Werner's life, further discoveries inconsistent with his theory were made. From 1905 to 1910 Blondel and others⁴ reported dinuclear Pt^{III} compounds, which we now know to contain Pt–Pt bonded $[\text{Pt}_2(\text{SO}_4)_4]^{2-}$ ions. In 1907, 'TaCl₂·2H₂O' (which, as shown below, was later correctly formulated as Ta₆Cl₁₄·7H₂O) was reported.⁵ During the 1920s Lindner⁶ and others attempted to account for the composition of these and other compounds by imaginative (but chimerical) polynuclear structures in which *metal-metal bonds were not included*.

It was only with the advent of X-ray crystallography and its evolution into a tool capable of handling reasonably large structures that the existence of non-Wernerian transition metal chemistry could be recognized with certainty and the character of the compounds exemplifying it disclosed in detail. The first such experimental results were provided by C. Brosset,⁷ who showed that the lower chlorides of molybdenum contain octahedral groups of metal atoms with Mo–Mo distances even shorter (~2.6 Å) than those in metallic molybdenum (2.725 Å). Brosset's publications did not, apparently, stimulate any further research activity.

It was also Brosset⁸ who showed that $\text{K}_3\text{W}_2\text{Cl}_9$ contained a binuclear anion, $[\text{W}_2\text{Cl}_9]^{3-}$, with the tungsten atoms so close together that "[t]hey are, apparently, within these pairs, in

some way bound together.” This promising insight was not pursued.

In 1950, an X-ray diffraction experiment, albeit of an unconventional type carried out on aqueous solutions, showed that $\text{Ta}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$ and its bromide analog, as well as the corresponding niobium compounds, also contain octahedral groups of metal atoms⁹ with rather short M–M distances ($\sim 2.8 \text{ \AA}$). As before, these remarkable observations did not lead to any further exploration of such chemistry.

It was not until 1963, in fact, that attention was effectively focused on non-Wernerian coordination compounds. It was observed at about the same time in two different laboratories^{10,11} that ‘ ReCl_4^- ’ actually contains triangular Re_3 groups in which the Re–Re distances (2.47 \AA) are very much shorter than those (2.75 \AA) in metallic rhenium. In one report¹⁰ not only was the molecular structure described very precisely, the electronic structure was discussed in detail, leading to the explicit conclusion¹⁰ that the rhenium atoms are united by a set of three Re–Re double bonds. This work was important because it was the basis for:

1. the first explicit recognition that direct metal–metal bonds can be very strong and can play a crucial role in transition metal chemistry, and
2. the first formal recognition that there is an entire class of such compounds to which the name *metal atom cluster compounds* was then applied.^{12,13}

In $[\text{Re}_3\text{Cl}_{12}]^{3-}$ it was first shown that metal–metal bonds may be multiple, since the MO analysis^{10(a),12} of this cluster clearly shows that there are six doubly occupied bonding MOs covering the three Re–Re edges of the triangle, thus giving the MO equivalent of double bonds.

It should be noted that during the period of time just considered there were developments in the field of metal carbonyl chemistry that also led to the consideration of direct metal–metal bonds as stereoelectronic elements of molecular structure. In 1938 the first evidence for the structure of a polynuclear metal carbonyl compound, $\text{Fe}_2(\text{CO})_9$, was obtained by X-ray crystallography. To account for the diamagnetism of the compound, it was considered necessary to postulate a pairing of two electron spins, each of which formally originated from a different metal atom. For many years it was taken as obvious that there exists an Fe–Fe bond. The structural integrity does not require such an assumption because there are three bridging carbonyl groups. Today there are convincing (though not entirely conclusive) theoretical arguments in favor of spin coupling via the carbonyl bridges without direct Fe–Fe bonding. It was not until 1957, with the determination of the $\text{Mn}_2(\text{CO})_{10}$ structure,¹⁴ that unequivocal evidence for metal–metal bond formation in metal carbonyls was obtained.

1.2 How It All Began

1.2.1 Rhenium chemistry from 1963 to 1965

By mid-1963, further studies of the chemistry of the trinuclear cluster anion $[\text{Re}_3\text{Cl}_{12}]^{3-}$ had led to the recognition that the trinuclear Re_3 cluster with Re–Re double bonds was the essential stereoelectronic feature of much of the chemistry of rhenium(III), particularly that which used the so-called trihalides as the starting materials. Both the chloride and bromide of Re^{III} had been shown to contain these Re_3 clusters.¹⁵

However, it was precisely the use of these Re^{III} halides as starting materials that posed a practical problem, since their preparation is tedious and time consuming. The idea of obtaining the trinuclear complexes by reduction in aqueous solution of the readily available $[\text{ReO}_4]^-$ ion to give, for example, $[\text{Re}_3\text{Cl}_{12}]^{3-}$ was very attractive. The devising of such an aqueous route into trinuclear Re^{III} chemistry was regarded at MIT as perhaps the one remaining task to be carried out before leaving the field of Re^{III} chemistry. During the autumn of 1963, Dr. Neil Curtis (later Professor of Chemistry at Victoria University in Wellington, New

Zealand) was a visiting research associate at MIT, and he set about trying this, with the added objective of obtaining mixed clusters, such as $[\text{Re}_2\text{OsCl}_{12}]^{2-}$, by using a mixture of $[\text{ReO}_4]^-$ and an osmium compound.

Neither of the original goals has ever been attained because, after a few exploratory experiments, a far more interesting result was obtained by Curtis. He found that by using concentrated aqueous hydrochloric acid as the reaction medium and hypophosphorous acid as the reducing agent (with or without the presence of any osmium compound), the product was an intense blue solution from which materials such as a beautiful royal-blue solid of composition CsReCl_4 could be isolated. Since this substance had the same empirical formula as the red $\text{Cs}_3\text{Re}_3\text{Cl}_{12}$ we were keenly interested in learning its true nature.

By a coincidence, of a sort that seems to occur rather often in research, there was another visiting research associate in the group at the same time, namely, Dr Brian Johnson (today Professor of Chemistry, Cambridge University), who had been checking a rather puzzling report from the USSR¹⁶ to the effect that reduction of $[\text{ReO}_4]^-$ in hydrochloric acid by hydrogen gas under pressure gave $[\text{ReCl}_6]^{3-}$. This was obviously relevant to Curtis's work, since it suggested that aqueous reduction of $[\text{ReO}_4]^-$ might give (previously unknown) mononuclear Re^{III} chloro complexes. An even more remarkable feature of this curious report was that the precipitated ' $\text{M}^I_3\text{ReCl}_6$ ' compounds displayed a variety of colors, depending on the counterion, M^I . Johnson showed quickly that the claim of $[\text{ReCl}_6]^{3-}$ salts was erroneous¹⁷ and that the compounds were in fact the rather uninteresting, very familiar, $\text{M}^I_2\text{ReCl}_6$ salts. The variety of colors displayed is not easy to explain with certainty, but probably arose from incorporation of impurities. The reaction conditions cause serious corrosion of the steel bomb in which the reaction is conducted.

However, it had also been claimed¹⁶ that there was a dark-blue/green product, to which the formula K_2ReCl_4 was assigned. Johnson found that there was indeed such a product and, in view of its apparent similarity to Curtis's new blue ' CsReCl_4 ,' we immediately wondered if the Soviet chemists had simply got their formula wrong and that they really had ' KReCl_4 .' It did not take long to show that this was precisely the case and that the substance had the empirical formula $\text{KReCl}_4 \cdot \text{H}_2\text{O}$. Since it formed better-looking crystals than did the cesium compound (which, incidentally, is actually $\text{CsReCl}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ¹⁸ before drying), and these had a small triclinic unit cell, we considered $\text{KReCl}_4 \cdot \text{H}_2\text{O}$ to be the preferred subject for an X-ray crystallographic study. Mr C. B. Harris (now Professor of Chemistry, University of California, Berkeley), who was just beginning his doctoral research and had never previously done a crystal structure, began a study of these crystals.

The Soviet chemical literature was also examined more carefully to see if there were any further reports of interest on the chemistry of lower-valent rhenium. It was found that between 1952 and 1958 V. G. Tronev and co-workers had published three papers^{16,19,20} that described an assortment of low-oxidation state rhenium halide complexes in which the metal oxidation state was proposed to be +2. Much of the impetus for their investigations was a search for analogies between the chemistry of rhenium and platinum, an approach which no doubt prejudiced them in favor of the Re^{II} oxidation state. The existence of most of the compounds described in their 1952¹⁹ and 1954¹⁶ reports has never been substantiated, for example, products such as ' $\text{Re}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$,' ' $\text{Re}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$,' and ' $\text{Re}(\text{thiourea})_4\text{Cl}_2$.' Two compounds—namely, the ' K_2ReCl_4 ' already mentioned and blue-green ' $(\text{NH}_4)_2\text{ReCl}_4$,' which was also obtained by the action of hydrogen under pressure upon solutions of NH_4ReO_4 in concentrated hydrochloric acid at 300 °C—were further discussed in 1958 when Kotel'nikova and Tronev²⁰ published a more substantial contribution, entitled 'Study of the Complex Compounds of Divalent Rhenium.' Additional details were reported for the various materials emanating from a work-up of the blue solutions produced by these hydrogen reductions of perrhenate (KReO_4) in concen-