

Forward to the Second Edition

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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.

Multiple Bonds between Metal Atoms

Cotton, F.A.; Murillo, C.A.; Walton, R.A. (Eds.)

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