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IN MEMORIAM

The quadruple bond – 60 years – a tribute to F. Albert Cotton and other pioneers

Istvan Hargittai[1]

Abstract
The discovery of the multiple metal-metal bonds had a long history culminating in a 1964 paper by F. Albert Cotton and his associates. The pioneering works of Ida and Walter Noddack, Cyrill Brosset, Linus Pauling, and associates of the Kurnakov Institute in Moscow, are also remembered.

Keywords Multiple metal-metal bonds · F. Albert Cotton · Cyrill Brosset · Kurnakov Institute · Cluster formation

Sixty years ago, in 1964, a historic paper appeared in *Science* that is considered to be the principal report of the discovery of the quadruple metal-metal bond [1]. Its title was "Mononuclear and polynuclear chemistry of rhenium (III): its pronounced homophilicity." Homophilicity refers to bonding between atoms of the same element, in this case rhenium (III). F. Albert Cotton (1930−2007 Fig. 1 [2]) and his associates reported the production and structural elucidation of several series of rhenium-rhenium complexes, among them $Re_2Cl_8^{2-}$, which has become the iconic representative of this new class of compounds.

Cotton was born Frank Abbott Cotton, but he preferred to be called Albert or Al. Frank Abbott was the name of the family doctor who delivered him who was a close friend of his parents. Cotton was an inorganic chemist and one of the shapers of his field in the second half of the twentieth century. He was at home both in experiment and theory.

At his invitation, my wife and I visited him in 1996 at Texas A&M University and I recorded a long conversation with him [2]. Our interactions dated back for years stemming from our overlapping interest in symmetry. He authored an excellent and broadly used text on the chemical applications of group theory [3]. When in a new edition of this book he used some art from our recent book [4] without attribution we had a brief unpleasant exchange of letters. However, our friendship survived this incident unscathed. I used the famous Cotton-Wilkinson *Advanced Inorganic Chemistry* [5] in my graduate studies.

Cotton received his PhD from Harvard University where Geoffrey Wilkinson was his research director. Cotton learned about preparative chemistry from Wilkinson and physical and theoretical chemistry from E. Bright Wilson and William Moffitt. In 1955, Cotton started his career at MIT where he became full professor in 1961. Then, in mid-career, he moved to Texas A&M University. He considered the discovery of multiple metal-metal bonds his most important achievement for their significance in transition metal chemistry [2]. He started thinking about metal-metal bonds in 1958 when the few known examples were thought to be mere anomalies. He read a little book by Leslie Orgel [6] on ligand field theory [7], and the alkali metal-$ReCl_4$ compounds that were diamagnetic caught his attention. In them, rhenium would have four electrons, and this pointed to a low-spin tetrahedral complex.

There were no compounds containing tetrahedral $ReCl_4$ ions known at the time and Cotton decided to prepare them. He failed as, instead, he obtained triangular metal clusters with Re=Re double bonds. They might have been the first metal-metal double bonds ever recognized. He and his colleagues continued their efforts and succeeded in reducing perrhenate to rhenium (III) in the presence of HCl. They produced the $Re_2Cl_8^{2-}$ ion with an extremely short rhenium-rhenium distance of 2.24 Å, corresponding to a quadruple bond. The eclipsed configuration was another peculiarity of the structure. Thinking in terms of the symmetry properties

Contribution to the Column "Foundation of structural science."

✉ Istvan Hargittai
stuceditor@gmail.com

[1] Budapest University of Technology and Economics, PO Box 91, Budapest 1521, Hungary

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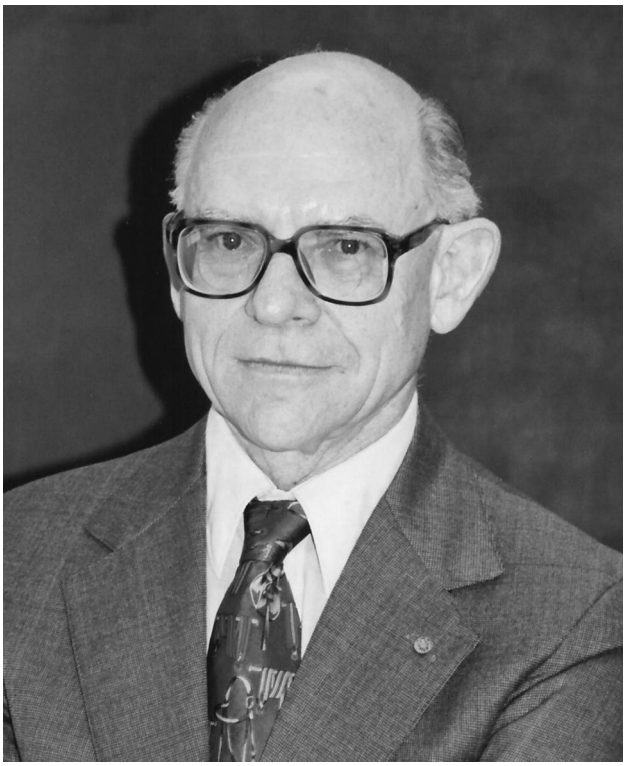

Fig. 1 F. Albert Cotton, 1996 in his office at Texas A&M University, College Station (photograph by Istvan Hargittai)

of the orbitals, Cotton recognized that the quadruple bond would restrict internal rotation. He also realized that this was a new type of bonding and expanded their research to include all transition elements. A new field in structural chemistry was born [8].

The great value in Cotton's discovery was in the *understanding* of the origin of the metal-metal quadruple bonding. Compounds having such bonding had been prepared before without recognizing their bonding peculiarities. Thus, in 1935, Cyrill Brosset in Stockholm observed a dimeric unit $W_2Cl_9^{3-}$ in its potassium salt [9]. Brosset's early contribution was eventually understood by others to have provided the first example of a metal-metal triple bond. As early as 1947, Linus Pauling recognized the importance of metal-metal bonds [10]. This was in an extended treatise entitled "Unsolved problems of structural chemistry," which he produced when he received the 1947 Theodore William Richards Medal (established in 1928) of the Northeastern Section of the American Chemical Society. Pauling presented a panoramic survey of the field with special emphasis of its development during the preceding 25 years. He listed "small" problems and "larger" problems and discussed the metal-metal bonds among the latter. He called attention to Brosset's observation. He assigned a bond number 1.70 in his bond number scheme to the unusually short W−W bond

Fig. 2 Ada S. Kotelnikova (left) and Petr A. Kozmin (right), former associates of the Kurnakov Institute of General and Inorganic Chemistry, Moscow. Both photographs courtesy of Petr A. Kozmin

of 2.46 Å. The crystal structure of $K_3W_2Cl_9$ was verified in Pauling's laboratory by Jürg Waser, then further refined and published in 1958 [11]. Pauling devoted a whole section to molecules and crystals containing metal-metal bonds in the third edition of his classic *The Nature of the Chemical Bond* [12]. He noted ([12], p 437) that in contrast to the diamagnetic $K_3W_2Cl_9$, the similar $Cs_3Cr_2Cl_9$ is paramagnetic with no direct chromium–chromium bond [13].

In the 1950s, extensive research in this area was going on in the N. S. Kurnakov Institute of General and Inorganic Chemistry (KIGICh) of the Soviet Academy of Sciences (today, the Russian Academy of Sciences) in Moscow [14]. They produced low-valent rhenium compounds whose first representative was synthesized as early as 1933 in Germany by Ida Noddack (see, eg, [15]) and Walter Noddack [16]. At the KIGICh, Professor V. G. Tronev and one of his junior associates, Ada S. Kotelnikova (1927−1990, Fig. 2), reported in 1958 that they obtained samples of several low-valent rhenium compounds [17]. It is a safe assumption that Kotelnikova must have done the lion's share of the work. The introductory part of their paper gave an overview of the work preceding their own with references to the Noddacks and other early contributors to rhenium chemistry.

The crystallographers in the same institute determined the structures of some of these compounds and they reported the structure of the $Re_2Cl_8^{2-}$ unit at a crystallography meeting in Kishinev (today, Chișinău, Moldova) in1961 [18]. They found an unusually short Re−Re distance, much shorter than in rhenium metal. In the 1960s, Cotton's laboratory launched an intensive X-ray crystallographic investigation, which included a reinvestigation of the structure of the $Re_2Cl_8^{2-}$ unit. Cotton and his colleagues were doubtful of the correctness of the Moscow group's findings, but their results confirmed them. Cotton then continued the investigation of the multiple metal-metal bonds on a broad scale and their pivotal paper appeared in 1964 [1].

Cotton deserves credit for his profound contribution to this field: for his extended X-ray crystallographic

Fig. 3 Soviet postage stamp, 1968, commemorating the 50th anniversary of the Kurnakov Institute of General and Inorganic Chemistry

investigations and for the theoretical interpretation of the nature of the multiple metal-metal bonds. Credit is also due to the Noddacks, to Brosset, and to the researchers at KIGICh for their pioneering contributions. The achievements of the Moscow group could have been more substantial if they had continued their work on a broader scale and if they had included theoretical studies for the interpretation of their unexpected findings. Eventually, the importance of these studies was recognized and, perhaps, also, what they had missed. In 1968, in celebration the 50th anniversary of the founding of KIGICh, the Soviet Post Office issued a commemorative stamp displaying the square prismatic structure of an Rh_2X_8 unit with the view of the institute in the background (Fig. 3). Looking back at the contribution of the KIGICh scientists to the development of the multiple metal-metal bond studies, Petr A. Kozmin (Fig. 2), a member of the Moscow group, appraised it in 1996 [14]. His evaluation

Fig. 4 Zvi Dori, Avi Bino, and F. Albert Collon, 1980, at Texas A&M University. Courtesy of F. Albert Cotton

and Cotton's account [19] may somewhat differ in emphasis, but they are not that much different if looking at them from today's perspective.

It was an interesting observation to consider the multiple bonds as if a starting point for metal clusters. Cotton moved in this direction in a cooperative effort with Zvi Dori of the TECHNION and Avi Bino of The Hebrew University of Jerusalem (Fig. 4). The two Israeli scientists spent years with him at Texas A&M University and they did also independent work in this area of transition metal chemistry. Their joint efforts showed, for example, that much of molybdenum chemistry in the lower oxidation state of this metal is cluster chemistry (see, eg, [20]).

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