CENTENARY LECTURE*

Quadruple Bonds and other Multiple Metal to Metal Bonds

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1 Introduction

Almost exactly 120 years elapsed between the first discovery[1] (1844) of a compound which contains a quadruple bond, namely, $Cr_2(O_2CCH_3)_4(H_2O)_2$, and the recognition (1964) that quadruple bonds exist.[2,3]† However, following this improbably long hiatus, the field has enjoyed a decade of explosive efflorescence and now stands poised for further broad growth. The purposes of this review are to trace the developments over the past ten years, to summarize our present knowledge, and to point out the areas where further work is most needed and further progress is most likely.

The planned and deliberate investigation of quadruple bonds, and other highly multiple bonds, between metal atoms began in the only way that it could – with the first conscious and explicit recognition of a multiple, specifically quadruple, bond between two transition-metal atoms. This occurred only in 1964 in my laboratory in a way that I shall now briefly describe.

Our studies[4–6] of rhenium(III) chloride and its derivatives, which showed that the characteristic structural unit in the chloride itself is an Re_3 triangular cluster, and that this cluster persist in all complexes obtained under mild conditions, *e.g.* $Re_3Cl_{12}^{3-}$ and $Re_3Cl_9(PR_3)_3$, had been essentially concluded. Dr. Neil Curtis was then a guest in the laboratory and I suggested that he examine the aqueous chemistry of rhenium with a view to finding ways of preparing Re^{III} compounds by reduction of ReO_4^- and also with the idea of preparing, if possible, some mixed clusters (an $Re_2OsCl_{12}^{2-}$ cluster was a possibility we specifically discussed). After a short period of exploratory work, trying different reductants and various

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†I am reminded in this connection of the similar history of transition-metal π-complexes. The first one was discovered in 1829 (W. C. Zeise, *Pogg. Ann.*, 1831, **21**, 497), but here also, almost exactly 120 years elapsed until the true nature of such complexes was recognized (M. J. S. Dewar, *Bull. Soc. chim. France*, 1951, C71; J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2979).

[1] E. Peligot, *Compt. rend.*, 1844, **19**, 609.

[2] F. A. Cotton, *et al.*, *Science*, 1964, **145**, 1305.

[3] F. A. Cotton, *Inorg. Chem.*, 1965, **4**, 334.

[4] J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Amer. Chem. Soc.*, 1963, **85**, 1349; *Inorg. Chem.*, 1963, **2**, 1106.

[5] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 1094.

[6] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 1402.

reaction conditions, Curtis presented me one day with a sample of a royal blue compound which had an analytical composition of $CsReCl_4$. Since the '$CsReCl_4$' which had already been shown to be $Cs_3Re_3Cl_{12}$ was dark red, we were naturally very intrigued, and immediately began work to discover the true molecular formula and structure of this substance.

Simultaneously, Dr. Brian Johnson, another guest in the laboratory, had been checking a report[7] in the Russian literature in which it was claimed that $ReCl_6^{3-}$ species could be isolated by reduction of ReO_4^- in aqueous hydrochloric acid with hydrogen gas. These claims proved erroneous, all of the alleged $M^I_3ReCl_6$ compounds being, in fact, $M^I_2ReCl_6$ compounds.[8] However, the Russian authors mentioned that a blue-green product, to which they assigned the formula K_2ReCl_4, was also obtained. We also observed this product. In view of its colour, we wondered if this too could have been incorrectly formulated; we wondered if it might be '$KReCl_4$' and thus related to Curtis' '$CsReCl_4$'. It was soon shown that indeed the stoicheiometry had been reported incorrectly and that the substance isolated by hydrogen reduction of ReO_4^- is $KReCl_4,H_2O$. Since the substance crystallized very nicely, an *X*-ray crystallographic study of it was undertaken by Mr. C. B. Harris, then beginning his doctoral research.

A thorough check of the Russian literature, which was impeded by delays in getting papers translated, then revealed that several other blue or green compounds alleged to be rhenium(II) compounds had also been reported,[9–11] among them $(NH_4)_2ReCl_4$, $KHReCl_4$, and $(pyH)HReCl_4$. With regard to the last two, the proposed presence of H appeared to lack any direct support, but was based, apparently, on the result of a determination of oxidation state by a method devised by the Noddacks in their pioneer studies of rhenium chemistry.[12] According to Tronev and co-workers, the oxidation state was found to be $+2$. Presumably, then, in order to reconcile this result with the analytical data, it was considered necessary to introduce a hydrogen atom, as H^+, into the formula. We repeated this work and found that, in our hands,[13] the Noddacks' procedure led to an oxidation number of 2.9 ± 0.2.

While Harris was proceeding slowly with the crystal structure analysis on $KReCl_4,H_2O$, learning crystallography as he went, we received an issue of the *Zhurnal strukturnoi Khimie* containing an article[14] on the structure of '$(pyH)HReCl_4$'. S. J. Lippard, who had just completed a course in Russian, was pressed into service, and he speedily produced a translation which revealed that this compound had been found to have 'the dimeric group $[Re_2Cl_8]^{4-}$. Eight chlorine atoms constitute a square prism . . . the rhenium atom has for its

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[7] V. G. Tronev and S. M. Bondin, *Khim. Redkikh, Elementov, Akad. Nauk S.S.S.R.*, 1954, **1**, 40.

[8] F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, 1964, **3**, 780.

[9] V. G. Tronev and S. M. Bondin, *Doklady Akad. Nauk, S.S.S.R.*, 1952, **86**, 87.

[10] V. G. Tronev and A. S. Kotel'nikova, *Zhur. neorg. Khim.*, 1958, **3**, 1008.

[11] G. K. Babeshkina and V. G. Tronev, *Zhur. neorg. Khim.*, 1962, **7**, 215.

[12] I. Noddack and W. Noddack, *Z. anorg. Chem.*, 1933, **215**, 182.

[13] F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, 1965, **4**, 326.

[14] B. G. Kuznetzov and P. A. Koz'min, *Zhur. strukt. Khim.*, 1963, **4**, 55.

neighbours one rhenium atom, at a distance of 2.22 Å, and four chlorine atoms at a distance of 2.43 Å. It may be surmised that four hydrogen atoms are situated between Cl atoms on centres of symmetry . . . and serve to bond the $[Re_2Cl_8]^{4-}$ groups . . . to each other.'

We viewed this extraordinary structure with misgivings. The state of refinement was poor and uncertain. The presence of isolated protons 'on centres of symmetry' was unaccountable. The Re–Re distance seemed unbelievably short and the prismatic rather than antiprismatic array of chlorine atoms seemed inexplicable. Finally, it was stated that severe difficulty with twinning had been encountered, and we wondered if the difficulties had in fact all been sorted out. Harris was impressed with the urgency of solving the $KReCl_4,H_2O$ structure, which he did in a very short time.[15] *Mirabile dictu*, $KReCl_4,H_2O$ was found to contain an Re_2Cl_8 entity essentially identical to that described by the Russian workers. Some apparent discrepancies between their dimensions and ours were later resolved, and the best value of the Re–Re distance is 2.24 ± 0.01 Å. The structure is shown in Figure 1.

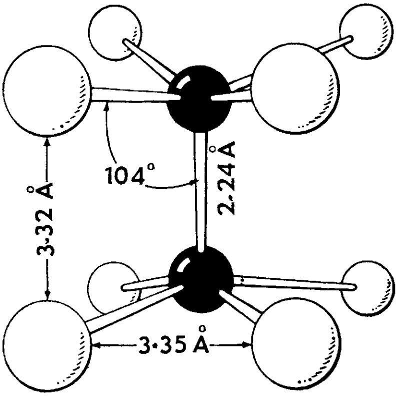

Figure 1 *The structure of the* $Re_2Cl_8^{2-}$ *ion.*

Once assured that the structure was correct, the obvious challenge was to interpret it in terms of bonding and electronic structure. This was soon done and resulted in the proposal[2,3] that a quadruple bond, consisting of one σ-, two π-, and a δ-component, exists between the rhenium atoms. In so doing, the ion was taken to be $Re_2Cl_8^{2-}$, that is, a compound of rhenium(III), and the previously postulated hydrogen ions were dismissed as spurious. There has never, in my opinion, been the slightest reason to believe they exist, but the myth that they are,

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[15] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, **4**, 330.

or at least may be, present seems to persist in the Russian literature,[16–18] with formulas such as $ReCl_2,CH_3COO(H),H_2O$,[16,17] where the significance of (H) is left entirely to the reader's imagination, unless the description[16] of it as 'free hydrogen (H)' is considered enlightening.

The original discussion[3] of the quadruple bond was based on qualitative considerations of orbital symmetries and rough estimates of overlap integrals. The Re–Re axis was defined as the z-axis, and the Re–Cl bonds were assumed to project upon the x- and y-axes. The $d_{x^2-y^2}$ orbital on each metal atom was assumed to be employed mainly in Re–Cl bonding and the remaining four d-orbitals on each metal atom were used to form the Re–Re bond. Overlap of the d_{z^2} orbitals gives rise to a σ-bond; overlap of corresponding pairs of the d_{xz} and d_{yz} orbitals leads to formation of a pair of π-bonds. Finally, overlap of the d_{xy} orbitals gives rise to a δ-bond. The extraordinary shortness of the Re–Re distance is explained by the high multiplicity of the bond. The eclipsed configuration is a consequence of the δ-component of the bond since that is the only component which is angle-dependent. As Figure 2 shows, the δ overlap is maximal in the eclipsed configuration and goes to zero upon rotation by 45° to the staggered configuration.

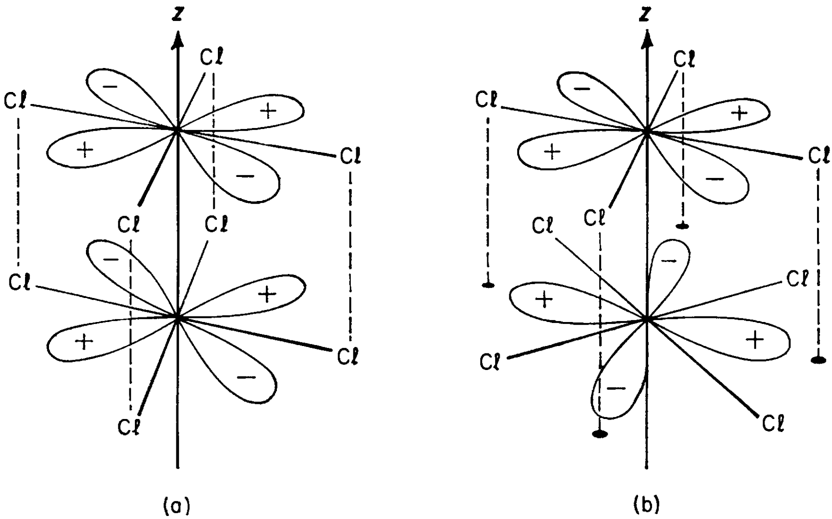

Figure 2 *Sketches showing (a) the maximization of δ overlap in the eclipsed configuration and (b) how it becomes zero for a staggered configuration.*

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[16] P. A. Koz'min, M. D. Surazhkaya, and V. G. Kuznetzov, *Zhur. strukt. Khim.*, 1967, **8,** 1107.
[17] P. A. Koz'min, M. D. Surazhkaya, and V. G. Kuznetzov, *Zhur. strukt. Khim.*, 1970, **11,** 313.
[18] P. A. Koz'min, *Doklady Akad. Nauk S.S.S.R.*, 1972, **206,** 1384.

2 Elaboration of Dirhenium Chemistry

With the existence and structure of $Re_2Cl_8^{2-}$, as well as a working hypothesis as to the bonding, established, attention was next turned to the chemistry of this and related species. An immediate question concerned the ability of the Re_2 unit to persist as the ligands were changed. The existence of the bromo-analogue was already known.[19] It could be prepared directly,[13,19] in the same manner as $Re_2Cl_8^{2-}$ by using HBr in place of HCl, or it could be obtained by treating a salt of $Re_2Cl_8^{2-}$ with an excess of HBr.[13] The ligand exchange was shown to be completely reversible.[13] The existence of the $Re_2Br_8^{2-}$ ion, incorrectly described as $Re_2Br_8^{4-}$ or $H_2Re_2Br_8^{2-}$, was established in a crude crystallographic study in which inaccurate Re–Re distances of 2.21 and 2.27 Å for two crystal forms were given.[20] An accurate study [21] made later gave a metal–metal distance of 2.228(4) Å, in excellent accord with the best value, 2.24 ± 0.01 Å in $Re_2Cl_8^{2-}$. The insensitivity of the Re–Re distance to replacement of Cl by the larger Br is in accord with the expected strength of the metal–metal bond.

The first non-trivial chemistry of the $Re_2X_8^{2-}$ species to be discovered[13,22] was their reversible reaction with carboxylic acids. When RCO_2H is present in excess the reactions proceed quantitatively according to reaction (1); moreover, the reactions are completely reversible.

$$Re_2X_8^{2-} + 4RCO_2H = Re_2(O_2CR)_4X_2 + 4HX + 2X^- \qquad (1)$$

The $Re_2(O_2CR)_4X_2$ compounds had previously been obtained in small yields by reaction of rhenium(V) compounds with carboxylic acids[23] and much earlier, by Russian workers,[24] but the latter formulated them incorrectly as rhenium(I) compounds and their true identity became evident only after they had been rationally synthesized by reaction (1). Their structures[25,26] are as shown in Figure 3(a). The tetracarboxylate is a limiting stoicheiometry, and species with fewer carboxy-groups and correspondingly more halide ions can easily be envisioned. The intermediate case, $Re_2(O_2CR)_2X_4$, is well documented,[28,29] and structures of both the *trans*-type [Figure 3(b)] and the *cis*-type have been reported. The compound $Re_2(O_2CPh)_2I_4$, shown in Figure 4, provides an example of the former[28] while $Re_2(O_2CCH_3)_2Cl_4,H_2O$ affords an example of the latter.[29] Factors affecting the relative stabilities of the *cis* and *trans* structures are not understood.

A considerable number of other ligand-substitution reactions[22,27,30,31] have

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[19] G. K. Babeshkina and B. G. Tronev, *Doklady Akad. Nauk S.S.S.R.*, 1963, **152**, 100.

[20] P. A. Koz'min, V. G. Kuznetzov, and Z. V. Popova, *Zhur. strukt. Khim.*, 1965, **6**, 651.

[21] F. A. Cotton, B. G. DeBoer, and M. Jeremic, *Inorg. Chem.*, 1970, **9**, 2143.

[22] F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, 1966, **5**, 1798.

[23] F. Taha and G. Wilkinson, *J. Chem. Soc.*, 1963, 5406.

[24] A. S. Kotelnikova and V. G. Tronev, *Zhur. neorg. Khim.*, 1958, **3**, 1016.

[25] M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, 1968, **7**, 1570.

[26] C. Calvo, N. C. Jayadevan, C. J. L. Lock, and R. Restivo, *Canad. J. Chem.*, 1970, **48**, 219.

[27] F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, 1967, **6**, 214.

[28] K. W. Bratton and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1299.

[29] P. A. Koz'min, M. D. Surazhskaya, and V. G. Kuznetsov, *Zhur. strukt. Khim.*, 1970, **11**, 313.

[30] F. A. Cotton, N. F. Curtis, and W. R. Robinson, *Inorg. Chem.*, 1965, **4**, 1696.

[31] F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.*, 1967, **6**, 929.

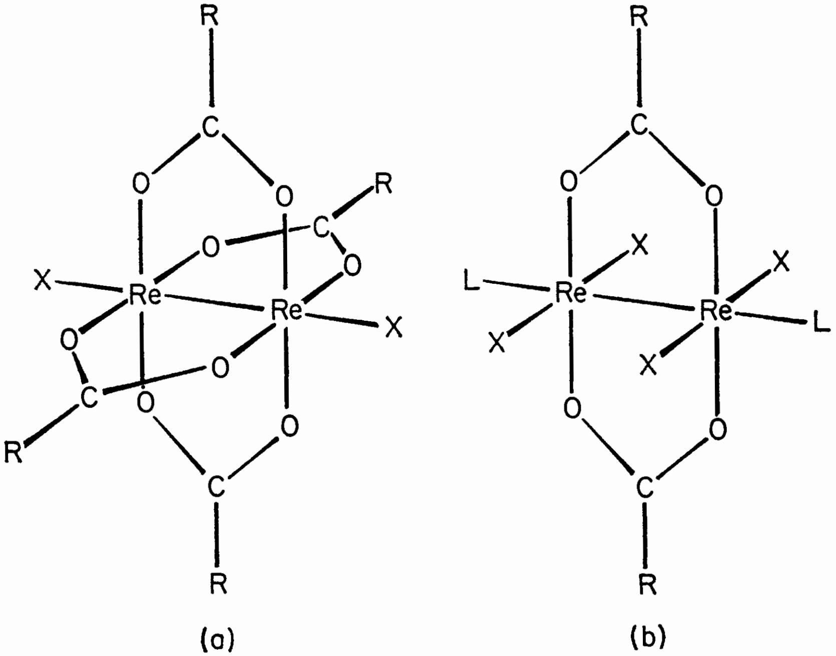

Figure 3 *Two important types of mixed halogeno-carboxylato-dirhenium molecules. In addition to the* trans-*structure* (*b*) *for the stoicheiometry* $Re_2(O_2CR_2X_4)$, *a* cis *one is also known.*

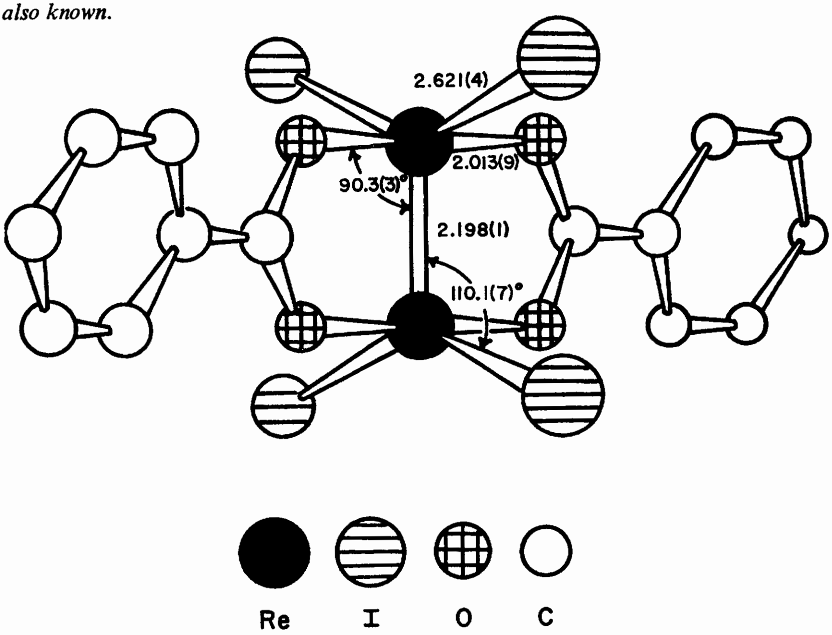

Figure 4 *The structure of* $Re_2(O_2CPh)_2I_4$.

been carried out on the $Re_2Cl_8{}^{2-}$ ion, leading to products such as $Re_2(SCN)_8{}^{2-}$ and $Re_2Cl_6L_2$, where L = tetramethylthiourea or a phosphine. The retention of the Re$\overset{4^{\circ}}{-}$Re bond is shown by i.r.[32] and Raman[33] spectra and *X*-ray crystallographically, as in the case of $Re_2Cl_6(PEt_3)_2$,[34] the structure of which is shown in Figure 5. The $Re_2(SO_4)_4{}^{2-}$ ion, with bridging sulphate ions, has also been prepared.[35] It should be noted that there are also many reactions of $Re_2Cl_8{}^{2-}$, and other quadruply bonded species, in which destruction of the Re$\overset{4^{\circ}}{-}$Re unit occurs.[36] A list of all published structures which contain a quadruple bond between two Re^{III} atoms is given in Table 1.

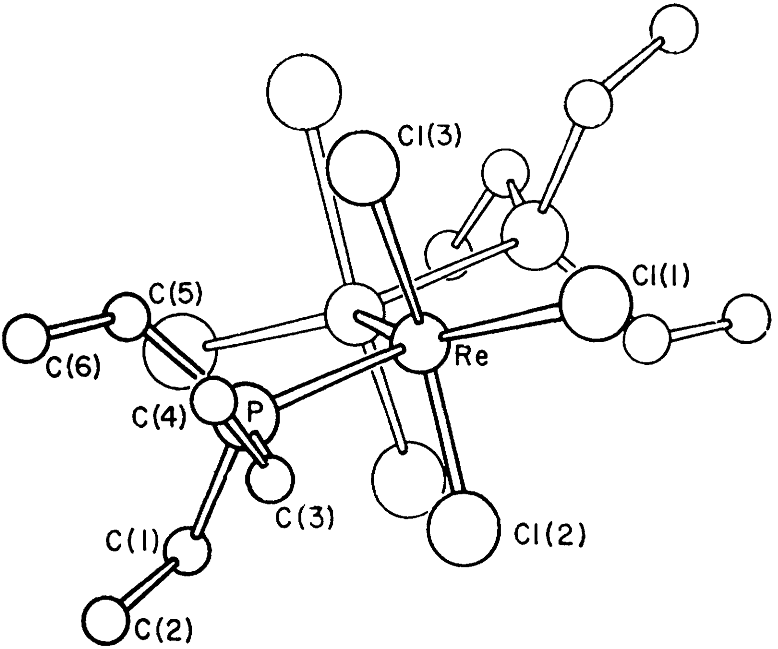

Figure 5 *The molecular structure of* $Re_2Cl_6(PEt_3)_2$.

Oxidation and reduction reactions have not yet been extensively studied, but it appears that they sometimes cause extensive structural change, expecially the oxidations.[38] When Cl_2 and Br_2 were used as oxidants towards $Re_2Cl_8{}^{2-}$ and $Re_2Br_8{}^{2-}$, respectively, the products were $Re_2X_9{}^{1-,2-}$, which appear to have the

[32] C. Oldham and A. P. Ketteringham, *J.C.S. Dalton*, 1973, 2304.
[33] J. San Flippo, jun., and H. J. Sniadoch, *Inorg. Chem.*, 1973, **12**, 2326.
[34] F. A. Cotton and B. M. Foxman, *Inorg. Chem.*, 1968, **7**, 2135.
[35] F. A. Cotton, B. A. Frenz, and L. W. Shive, *Inorg. Chem.*, in the press.
[36] J. A. Jaecker, W. R. Robinson, and R. A. Walton, *J.C.S. Chem. Comm.*, 1974, 306.
[37] P. A. Koz'min, G. N. Novitskaya, V. G. Kuznetsov, and A. S. Kotel'nikova, *Russ. J. Inorg. Chem.*, 1971, **12**, 861.
[38] F. Bonati and F. A, Cotton, *Inorg. Chem.*, 1967, **6**, 1353,

Table 1 Re–Re *Bond lengths in various quadruply bonded dirhenium*(III) *species*

Species	*Compound*	Re–Re *Distance* Å	*Ref.*
$Re_2Cl_8^{2-}$	$Cs_2Re_2Cl_8,2H_2O$	2.235(?)	37
$Re_2Cl_8^{2-}$	$K_2Re_2Cl_8,2H_2O$	2.241(7)	15
$Re_2Cl_8^{2-}$	$(C_5H_6N)_2Re_2Cl_8$	2.244(15)	28
$Re_2Cl_8(H_2O)_2^{2-}$	$Cs_2Re_2Cl_8,2H_2O$	2.213(?)	37
$Re_2Br_8^{2-}$	$Cs_2Re_2Br_8$	2.228(4)	21
$Re_2Cl_4(OAc)_2$	$Re_2Cl_4(O_2CCH_3)_2,2H_2O$	2.224(5)	29
$Re_2(O_2CC_3H_7)_4$	$Re_2(O_2CC_3H_7)_4(ReO_4)_2$	2.251(2)	26
$Re_2(O_2CPh)_4Cl_2$	—	2.235(2)	25
$Re_2(SO_4)_4(H_2O)_2^{2-}$	$Na_2Re_2(SO_4)_4,8H_2O$	2.214(1)	35
$Re_2I_4(O_2CPh)_2$	—	2.198(1)	28
$Re_2Cl_6(PEt_3)_2$	—	2.222(3)	34

well known confacial bioctahedral structure. Reduction of $Re_2Cl_8^{2-}$ to $Re_2Cl_8^{3-}$ can be carried out electrochemically, but the product decomposes with a rate constant of about 0.4 s^{-1} and is thus not likely to be isolable, at least at room temperature.[39] The one-electron reduction[40] of $Re_2(O_2CCH_3)_4Cl_2$ has been observed to give a yellow product, $Re_2(O_2CCH_3)_4^+$ or $Re_2(O_2CCH_3)_4Cl$, which is stable for hours in solution. Its e.s.r. spectrum affords valuable information on its electronic structure, as will be noted later.

3 Extension to Other Metals

However remarkable and interesting the quadruply bonded dirhenium compounds might be, this chemistry could scarcely have been regarded as important if it began and ended with the element rhenium. Therefore one of our earliest goals, to which effort was directed immediately after the main facts about the dirhenium compounds were established, was to see whether similar, multiply-bonded pairs of metal atoms did not also occur in the chemistry of other metals in their lower oxidation states. This work was in fact undertaken with considerable optimism since it did not seem likely that a phenomenon which was so prominent in the chemistry of one element could be entirely lacking in that of others.

The first developments in extending the chemistry to other elements were completely logical ones. The basic concept of the Periodic Table, namely, that elements with analogous chemical properties occur in the same column, naturally led to early consideration of technetium. Also, it was thought probable that elements from neighbouring columns in oxidation states that would make them isoelectronic with Re^{III} might well behave similarly. These ideas furnished guidance but no guarantee of success, since the move from the third to the second transition series is in the direction of decreasing stability of metal-to-metal bonds, and changes in oxidation number necessarily involve differences in charge and orbital size which could oppose the formation of multiple metal-to-metal

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[39] F. A. Cotton and E. Pedersen, *Inorg. Chem.*, in the press.

[40] F. A. Cotton and E. Pedersen, *J. Amer. Chem. Soc.*, in the press.

bonds. Thus the position was precisely that expressed in the well-known maxim: Die Theorie leitet, das Experiment entscheidet.

With respect to technetium, success came very quickly. The literature already recorded a compound with the empirical formula $(NH_4)_3Tc_2Cl_8,2H_2O$,[41] and we were able to show[42] that it contains $Tc_2Cl_8^{3-}$ ions essentially isostructural with $Re_2Cl_8^{2-}$. The difference in charge, implying the presence of one more electron than the eight required for the quadruple bond, was the only surprising feature. It has been shown[39] that $Tc_2Cl_8^{3-}$ can be reduced electrochemically to $Te_2Cl_8^{2-}$, which is diamagnetic and has a lifetime of at least 5 minutes. A more recent claim[43] that compounds of the stoicheiometry $M^I_8[Tc_2Cl_8]_3,4H_2O$ can be prepared is entirely erroneous; the compounds in question are all $M^I_3[Tc_2Cl_8],2H_2O$, with $M^I = NH_4$, K, and Cs.[44]

Simultaneously with our discovery of the $Tc_2Cl_8^{3-}$ ion, it was found by Lawton and Mason[45] that molybdenum(II) acetate, which had been reported earlier by Wilkinson,[46] has a dinuclear structure with four bridging acetate groups, and a very short Mo–Mo distance, reported as 2.11 Å but more recently[47] found to be 2.093(1) Å. The structure is essentially the same as that shown in Figure 3(a) but without the coaxial ligands, X. Since Mo^{II} is isoelectronic with Re^{III}, it was immediately obvious that a quadruple bond exists between the molybdenum atoms.

In view of the close analogy of $Mo_2(OCCH_3)_4$ to $Re_2(O_2CCH_3)_4Cl_2$, it was natural to think in terms of a reversible reaction comparable to reaction (1) above, which would lead to the molybdenum analogue of $Re_2Cl_8^{2-}$, namely $Mo_2Cl_8^{4-}$. Such a reaction can be carried out, although the conditions of temperature and concentration are critical and the $Mo_2Cl_8^{4-}$ ion is readily hydrolysed. A number of salts of the $Mo_2Cl_8^{4-}$ ion were prepared and structurally characterized[48-51] by Mr. J. V. Brencic, a visitor from Jugoslavia, in 1967–1969.

Since that time there has been an enormous output of new compounds[52-72] containing the Mo_2^{4+} unit. Those which have been structurally characterized are listed in Table 2, where their Mo–Mo distances are given. Virtually any carboxylic acid will serve in the $Mo_2(O_2CR)_4$ compounds.[46,52,53] Two of the most stable and easy to handle are the acetate and, particularly, the trifluoroacetate,[51,55] which is soluble and volatile. It has been shown that one factor that can increase the chemical stability of the carboxylates is the ability of large R groups to impede access of attacking groups to the coaxial positions.[56] Amidine anions

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[41] J. D. Eakins, G. D. Humphreys, and C. E. Mellish, *J. Chem. Soc.*, 1963, 6012.

[42] F. A. Cotton and W. K. Bratton, *J. Amer. Chem. Soc.*, 1965, **87**, 921; *Inorg. Chem.*, 1970, **9**, 789.

[43] M. I. Glinkina, A. F. Kuzina, and V. I. Spitsyn, *Zhur. neorg. Khim.*, 1973, **18**, 403.

[44] F. A. Cotton and L, W. Shive, to be published.

[45] D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 1965, **87**, 921.

[46] T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 1964, 2538.

[47] F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Cryst.*, in the press.

[48] J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 7.

[49] J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 2698.

[50] J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 1970, **9**, 346.

[51] J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 1970, **9**, 351.

Table 2 *Dimolybdenum species having multiple bonds with confirmed structures*

Mo_2 *Entity*	*Compound*	Mo–Mo *Distance*/Å	*Ref.*
(*a*) *Bond Order* 4			
$Mo_2Cl_8^{4-}$	$K_4Mo_2Cl_8,2H_2O$	2.139(4)	48
	$(enH_2)_2Mo_2Cl_8,2H_2O$	2.134(1)	49
	$(NH_4)_5Mo_2Cl_9,H_2O$	2.150(5)	50
$Mo_2(CH_3)_8^{4-}$	$Li_4Mo_2(CH_3)_8,4THF$	2.147(3)	72
$Mo_2(O_2CCH_3)_4$	$Mo_2(O_2CCH_3)_4$	2.093(1)	47
$Mo_2(O_2CCF_3)_4$	$Mo_2(O_2CCF_3)_4$	2.090(4)	54
$Mo_2(O_2CCF_3)_4,2py$	$Mo_2(O_2CCF_3)_4,2py$	2.129(2)	55
$Mo_2(N_2CPh_3)_4$	$Mo_2(N_2CPh_3)_4$	2.090(1)	57
$Mo_2(SO_4)_4^{4-}$	$K_4Mo_2(SO_4)_4,2H_2O$	2.110(3)	58, 59
$Mo_2(S_2COC_2H_5)_4$	$Mo_2(S_2COC_2H_5)_4,2THF$	2.125(1)	60
$Mo_2(allyl)_4$	$Mo_2(C_3H_5)_4$	2.183(2)	68
(*b*) *Bond Order* 3.5			
$Mo_2(SO_4)_4^{3-}$	$K_3Mo_2(SO_4)_4,3.5H_2O$	2.164(3)	75, 59
(*c*) *Bond Order* 3			
$Mo_2(CH_2SiMe_3)_6$	$Mo_2(CH_2SiMe_3)_6$	2.167(?)	76
$Mo_2(NMe_2)_6$	$Mo_2(NMe_2)_6$	2.214(2)	78

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[52] A. B. Brignole and F. A. Cotton, *Inorg. Syntheses*, Vol. 13, ed., F. A. Cotton, McGraw-Hill, New York, 1972, p. 87.

[53] S. Dubicki and R. L. Martin, *Austral. J. Chem.*, 1969, **22**, 1571.

[54] F. A. Cotton and J. G. Norman, jun., *J. Coordination Chem.*, 1971, **1**, 161.

[55] F. A. Cotton and J. G. Norman, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 5697.

[56] E. Hochberg, P. Walks, and E. H. Abbott, *Inorg. Chem.*, 1974, **13**, 1824.

[57] F. A. Cotton, T. Inglis, M. Kilner, and T. R. Webb, *Inorg. Chem.*, in the press.

[58] C. L. Angell, F. A. Cotton, B. A. Frenz, and T. R. Webb, *J.C.S. Chem. Comm.*, 1973, 399.

[59] F. A. Cotton, B. A. Frenz, E. Pedersen and T. R. Webb, *Inorg. Chem.*, in the press.

[60] L. Richard, P. Karagiannidis, and R. Weiss, *Inorg. Chem.*, 1973, **12**, 2179.

[61] D. F. Steele and T. A. Stephenson, *Inorg. Nuclear Chem. Letters*, 1973, 9, 777.

[62] E. H. Abbott, F. Schoenewolf, jun., and T. Backstrom, *J. Coordination Chem.*, 1974, **3**, 255.

[63] J. San Filippo, jun., *Inorg. Chem.*, 1972, **11**, 3140.

[64] J. San Filippo, jun., H. J. Sniadoch, and R. L. Grayson, *Inorg. Chem.*, 1974, **13**, 2121.

[65] J. V. Brencic, D. Dobenik, and P. Segedin, *Monatsh.*, 1974, **105**, 142.

[66] G. Wilke, *et al.*, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151.

[67] W. Oberkirch, Dissertation, Technische Hochschule, Aachen, 1963.

[68] F. A. Cotton and J. R. Pipal, *J. Amer. Chem. Soc.*, 1971, 93, 5441.

[69] Imperial Chemical Industries, Ltd., 1967, B.P. 1 091 296.

[70] V. I. Skohlikova, *et al.*, *Vysokomol. Soedineniya*, 1968, **10**, *B*, 590 (*Chem. Abs.*, 1969, **70**, 5060z).

[71] R. P. A. Sneddon and H. H. Zeiss, *J. Organometallic Chem.*, 1971, **28**, 259.

[72] F. A. Cotton, J. M. Troup, T. R. Webb, D. H. Williamson, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1974, **96**, 3824.

[73] B. Heyn and H. Still, *Z. Chem.*, 1973, **13**, 191.

[74] A. R. Bowen and H. Taube, *Inorg. Chem.*, 1974, **13**, 2245.

[75] F. A. Cotton, B. A. Frenz, and T. R. Webb, *J. Amer. Chem. Soc.*, 1973, **95**, 4431.

[76] F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Comm.*, 1971, 1079.

[77] M. H. Chisholm and W. W. Reichert, *J. Amer. Chem. Soc.*, 1974, **96**, 1249.

[78] M. H. Chisholm, W. W. Reichert, F. A. Cotton, B. A. Frenz, and L. Shive, *J.C.S. Chem. Comm.*, 1974, 480, 804.

$R^1NC(R^2)NR^{1-}$, which are isoelectronic with RCO_2^-, can also serve as bridges,[57] as can the sulphate ion,[58,59] the ethylxanthate ion,[60,61] apparently also ethyl acetate,[62] the trifluoromethanesulphonate ion,[62] and the thiobenzoate ion.[61] There is a large derivative chemistry of $Mo_2Cl_8^{4-}$, principally involving molecules of the type $Mo_2Cl_4L_4$, in which there are at least 16 varied types of L group.[63–65] Some $Mo_2Br_4L_4$ analogues were also made.[64]

There are several organo-derivatives of the Mo_2^{4+} unit. The first to be reported,[66,67] $Mo_2(C_3H_5)_4$, has been structurally characterized;[68] it has the structure shown in Figure 6, and has been shown to possess catalytic activity for olefin[69] and stereospecific butadiene[70] polymerization. It appears, however, that it is the allyl groups rather than the Mo_2 unit which are the source of the catalytic function. The analogous $Cr_2(allyl)_4$ has similar activity.[71] The reaction of $Mo_2(O_2CCH_3)_4$ with $LiCH_3$ in ether[72] produces $Li_4[Mo_2(CH_3)_8],2(C_2H_5)_2O$, from which derivatives with other ethers can be obtained. The structure of the THF-containing compound has been determined;[72] it contains the eclipsed octamethyldimolybdenum anion shown in Figure 7. The preparation of a substance with the empirical formula $Li_2Mo(C_6H_5)_2H_2,2THF$ has been reported.[73] It would seem very probable that this compound is similar to the octamethyl one and contains the $Mo_2(C_6H_5)_4H_4^{4-}$ anion.

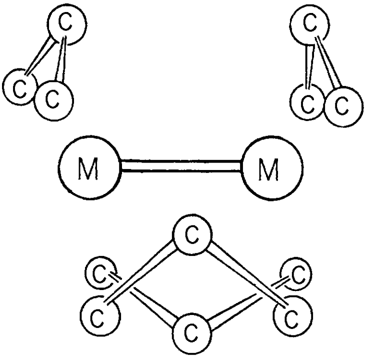

Figure 6 *The structure of* $Mo_2(allyl)_4$ *and* $Cr_2(allyl)_4$. *Hydrogen atoms are omitted.*

A considerable aqueous chemistry of the Mo_2^{4+} ion has already been developed by Bowen and Taube.[74] They found that the $Mo_2Cl_8^{4-}$ ion in 0.1M-HSO_3CF_3 is hydrolysed to $Mo_2Cl_2^{2+}$(aq). The addition of an excess of K_2SO_4 to a solution of $K_4Mo_2Cl_8$ in 0.2M-HSO_3CF_3 causes a pink precipitate of $K_4[Mo_2(SO_4)_4],2H_2O$ to form in >90% yield. This can be dissolved in 0.01M-HSO_3CF_3 and a slight excess of $Ba(SO_3CF_3)_2$ can be added to precipitate all the sulphate and leave what is presumed to be the Mo_2^{4+}(aq) ion in solution. Despite numerous attempts in various laboratories (all unpublished) no one has succeeded in precipitating this ion with a nonco-ordinating anion. The Mo_2^{4+}(aq) has an electronic spectrum not greatly different from that of $Mo_2(O_2CCH_3)_4$.

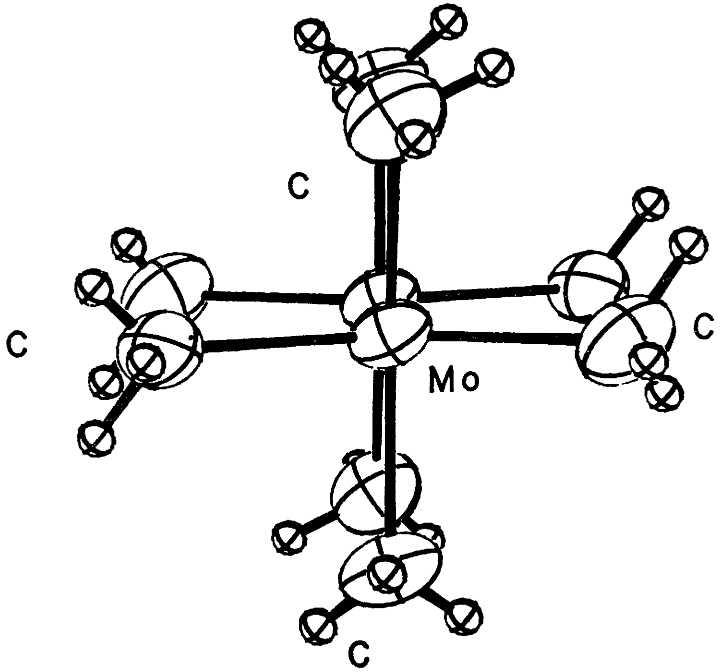

Figure 7 *The structure of the* $Mo_2(CH_3)_8^{4-}$ *ion.*

The compound $Mo_2(en)_4Cl_4$ was prepared by treating $K_4Mo_2Cl_8$ with neat ethylenediamine on the steam bath for 30–60 minutes followed by washing with ethanol and ether. It is the first compound containing a cationic complex of Mo_2^{4+}. It has an electronic spectrum quite similar to that of Mo_2^{4+}(aq). The $[Mo_2(en)_4]^{4+}$ complex undergoes aquation only slowly (*ca.* 30 minutes) and reacts slowly enough with O_2 to permit the solutions to be handled without rigorous exclusion of air.

In the process of crystallizing pink $K_4[Mo_2(SO_4)_4]$,$2H_2O$ slowly so as to obtain crystallographically useful crystals, it was found that lavender crystals also formed.[59,75] *X*-Ray crystallography showed that they have the composition $K_3Mo_2(SO_4)_4$,$3.5H_2O$ and contain the $[Mo_2(SO_4)_4]^{3-}$ ion, which has a structure very similar to that of $[Mo_2(SO_4)_4]^{4-}$ (Figure 8). According to the accepted description of the quadruple bond, the electron lost from the 4– ion to give the 3– ion should come from the δ-bonding orbital, thereby giving the latter species a $^2B_{2g}$ ground state. There is considerable evidence to support this idea and thus, indirectly, to support the general picture of the quadruple bond. Thus, as Table 2 shows, loss of this weakly bonding δ-electron causes a lengthening of the Mo–Mo bond, by about 0.05 Å. The two ions are related by an electrode potential of +0.22 V. The 3– ion is paramagnetic, with μ = 1.65 BM, $g_{\parallel}$ = 1.891, and

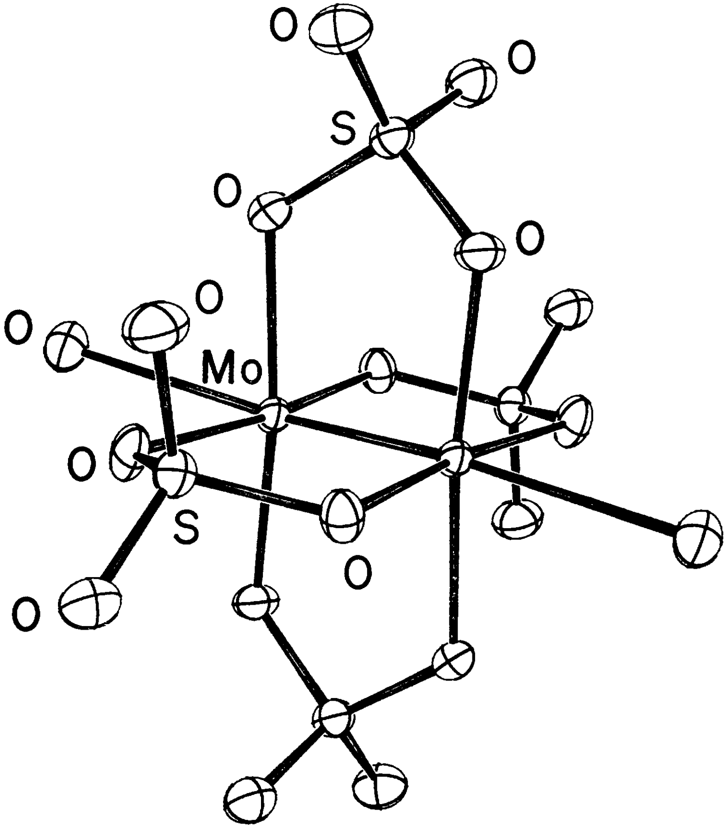

Figure 8 *The structure of the* $Mo_2(SO_4)_4{}^{n-}$ *entity which occurs with* $n = 4$ *in* $K_4[Mo_2(SO_4)_4],2H_2O$ *and* $n = 3$ *in* $K_3[Mo_2(SO_4)_4],3.5H_2O$. *There are oxygen atoms in the coaxial positions.*

$g_\parallel = 1.903$. The e.s.r. spectra show that the spin Hamiltonian has axial symmetry and that the unpaired electron is evenly distributed over two magnetically equivalent molybdenum atoms. Qualitative arguments show[40] that the quadruple-bond formulation in quantitative form (See Section 4) would require that both g values be <2, as observed.

Before leaving molybdenum, it should be mentioned that not only does this element seem, on present knowledge, to be the most prolific former of quadruple bonds, but it also has a marked tendency to form triple bonds. The two best-characterized examples are $Mo_2[CH_2Si(CH_3)_3]_6$[76] and $Mo_2[N(CH_3)_2]_6$.[77,78] The structure of the latter is shown in Figure 9, and the metal–metal distances in the two compounds are listed in Table 2. A similar compound,[79] $Mo_2[OC(CH_3)_3]_6$, presumably has the same sort of structure. The substance $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$

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[79] M. H. Chisholm, personal communication.

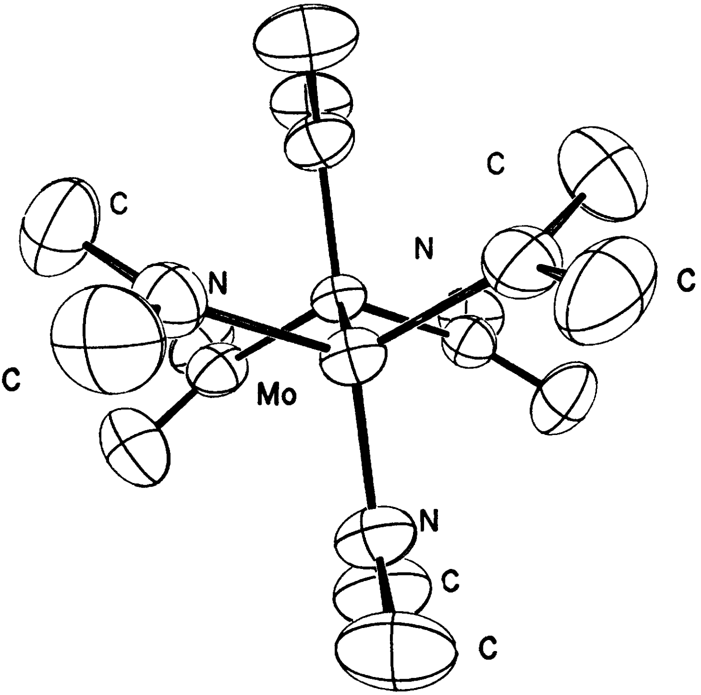

Figure 9 *The molecular structure of* $Mo_2[N(CH_3)_2]_6$. *The view is almost down the molecular three-fold axis.*

has been briefly described;[80] it presumably has a triple Mo–Mo bond by analogy with $\{[\eta^5\text{-}C_5(CH_3)_5]Cr(CO)_2\}_2$.[81]

Tungsten.—The great readiness of molybdenum to form M–M bonds of orders 3 to 4 naturally led to the hope that tungsten would also have a rich chemistry of similar compounds. This has not proved to be the case so far. The reaction of $W(CO)_6$ with glacial acetic acid does not appear to give $W_2(O_2CCH_3)_4$, but instead some sort of trinuclear species,[82,83] possibly $W_3(O_2CCH_3)_9O$. With a number of other acids, *e.g.* $C_6H_5CO_2H$, $C_6F_5CO_2H$, $C_3H_7CO_2H$, and $C_3F_7CO_2H$, compounds of the correct stoicheiometry have been obtained,[82] but none of them have formed crystals, and none are therefore substantiated structurally. The triply-bonded tungsten compound[76] $W_2[CH_2Si(CH_3)_3]_6$ has been prepared and reported to form crystals isomorphous with those of the molybdenum compound.

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[80] R. C. Job and M. D. Curtis, *Inorg. Chem.*, 1973, **12**, 2510.

[81] J. Potenza, P. Giordano, D. Mastropaolo, A. Efraty, and R. B. King, *J.C.S. Chem. Comm.*, 1972, 1333.

[82] F. A. Cotton and M. Jeremic, *Synth. Inorg. Metal-Org. Chem.*, 1971, **1**, 265.

[83] T. A. Stephenson and D. Whittaker, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 569.

A triply-bonded tungsten compound, $W_2[N(CH_3)_2]_6$, can be made but has not yet been fully purified {separated from $W[N(CH_3)_2]_6$} or structurally characterized.[79]

If the inaccessibility and intractability of compounds with quadruple W–W bonds results from relative weakness of those bonds, which is not necessarily the case, we must naturally try to understand why this bond should be significantly weaker than those in the Mo_2^{4+} and Re_2^{6+} cases. The answer is not yet obvious to this writer. A decrease in stability from Mo_2^{4+} to W_2^{4+} might be attributed to the presence of the $4f^{14}$ shells in the latter impeding the close approach necessary for the δ-overlap to be effective. However, this factor would not be expected to diminish greatly on moving to Re_2^{6+}; at least I do not think so. Further efforts towards the preparation of tungsten compounds would seem to be pertinent.

Chromium.—Though in many other cases multiple M–M bonds found in compounds of the second- and third-rows have no parallel in the first-row elements, such is not the case here; there are numerous compounds containing the Cr_2^{4+} entity. Those structurally characterized are listed in Table 3.

Table 3 *Compounds containing multiple bonds between chromium atoms which have confirmed structures*

Cr_2 *Entity*	*Compound*	Cr–Cr *Distance*/Å	*Ref.*
(*a*) *Bond Order* 4			
$Cr_2(O_2CCH_3)_4,2H_2O$	$Cr_2(O_2CCH_3)_4,2H_2O$	2.3855(5)	84
$[Cr_2(CO_3)_4]^{4-}$	$Mg_2Cr_2(CO_3)_4,6H_2O$	2.22(?)	86
$[Cr_2(C_4H_8)_4]^{4-}$	$Li_4Cr_2(C_4H_8)_4$,4THF	1.975(5)	90
$[Cr_2(CH_3)_8]^{4-}$	$Li_4Cr_2(CH_3)_8$,4THF	1.980(5)	89
$Cr_2(allyl)_4$	$Cr_2(allyl)_4$	1.97(?)	87, 88
(*b*) *Bond Order* 3			
$\{[\eta^5\text{-}C_5(CH_3)_5]Cr(CO)_2\}_2$		2.276(2)	81

It is fitting to begin by mentioning $Cr_2(O_3CCH_3)_4,2H_2O$, first reported[1] in 1844 but only in 1970 accurately described as to structure and bonding.[84] The Cr–Cr distance is 2.39 Å and the compound is isostructural and isoelectronic with $Mo_2(O_2CCH_3)_4$, except for the presence of the coaxial water molecules. It is therefore reasonable to propose that it contains a quadruple bond. This would require that the compound be diamagnetic, and it probably is. Reported susceptibilities for this and a large number of other $Cr_2(O_2CR)_4L_2$ compounds[85] are

[84] F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pipal, and D. A. Ucko, *J. Amer. Chem. Soc.*, 1970, **92**, 2926; *Acta Cryst.*, 1971, **B27**, 1664.

[85] S. Herzog and W. Kalies, *Z. anorg. Chem.*, 1964, **329**, 83; 1966, **351**, 237 and other references cited therein.

[86] R. Ouakes, Y. Maouche, M.-C. Perucaud, and P. Herpin, *Compt. rend.*, 1973, **276**, *C*, 281.

[87] G. Albrecht and D. Stock, *Z. Chem.*, 1967, **7**, 321.

[88] T. Aoki, A. Furusaki, Y. Tomiie, K. Ono, and K. Tanaka, *Bull. Chem. Soc. Japan*, 1969, **42**, 545.

[89] J. Krausse, G. Marx, and G. Schödl, *J. Organometallic Chem.*, 1970, **21**, 159.

[90] J. Krausse and G. Schödl, *J. Organometallic Chem.*, 1971, **27**, 59.

always weakly paramagnetic, with apparent magnetic moments of 0.50—0.85 BM. It seems quite likely that this is due to traces of chromium(III) compounds as impurities, although there is also the possibility that the δ-bond is so weak that a $\delta\delta^*$ triplet state is detectably populated. It is possible that this uncertainty could be resolved by an e.p.r. study.

As will be seen presently, there are other structurally characterized compounds with Cr–Cr quadruple bonds, and one with a triple bond, in which the Cr–Cr distances are much shorter than that in the acetate. This simply illustrates the fact that quadruple bonds can vary in strength and that bond multiplicity is not a direct or single-valued index of bond strength. This situation prevails for bonds of other orders as well. There are, for example, wide variations in the strengths of single bonds, as illustrated by the series C–C (356 kJ mol^{-1}), N–N (160 kJ mol^{-1}), O–O (146 kJ mol^{-1}), and F–F (158 kJ mol^{-1}). In the case of $Cr_2(O_2CCH_3)_4,2H_2O$ the relatively strong binding of the coaxial ligands (Cr–O, 2.27 Å) is probably related to the relative weakness of the Cr–Cr bond. In $Mo_2(O_2CR)_4$ compounds, where the Mo–Mo bonds are very short, coaxial ligands are either absent or only weakly attached. The exact interplay between these two factors is not clear, but a reciprocal relationship between the strengths of the two bonds does appear to exist.

An interesting compound which is similar to the acetate is $Mg_2Cr_2(CO_3)_4,6H_2O$. This contains the $[Cr_2(CO_3)_4(H_2O)_2]^{4-}$ ion, where the carbonate ions play the same bridging role as do the acetate ions in the acetate and the H_2O molecules serve as coaxial ligands.[86] In this case the Cr–Cr bond length is 2.22 Å and the Cr–OH_2 bond length is 2.32 Å, shorter and longer, respectively, than the corresponding bonds in the acetate.

We turn now to several compounds in which there are extremely short Cr–Cr bonds. These 'superbonds' are the shortest metal-to-metal bonds known. $Cr_2(allyl)_4$ has a structure[87,88] analogous to that[68] of $Mo_2(allyl)_4$ (Figure 6), with a Cr–Cr distance of only about 1.97 Å. There is also a $[Cr_2(CH_3)_8]^{4-}$ ion with a structure[89] essentially identical to that of $[Mo_2(CH_3)_8]^{4-}$ (see Figure 7); the Cr–Cr distance is 1.980(5) Å. A closely related species is the $[Cr_2(C_4H_8)_4]^{4-}$ ion, in which there are four chelating —$(CH_2)_4$— units, two on each Cr atom.[90] The Cr–Cr bond here is the shortest M–M bond presently known, with a length of 1.975(5) Å.

In addition to the structurally characterized compounds of dichromium(II) just mentioned there are a number of other reported compounds which seem certain to contain Cr–Cr quadruple bonds. Aside from the numerous carboxylato-bridged species other than the acetate,[85,91] there are several organometallic compounds. The compound $Cr_2[(CH_2)_2P(CH_3)_2]_4$[92] presumably contains a Cr–Cr quadruple bond and eight Cr–C bonds, but it is not known whether the structure is (a) or (b) of Figure 10, or possibly the variant of (a) in which the two

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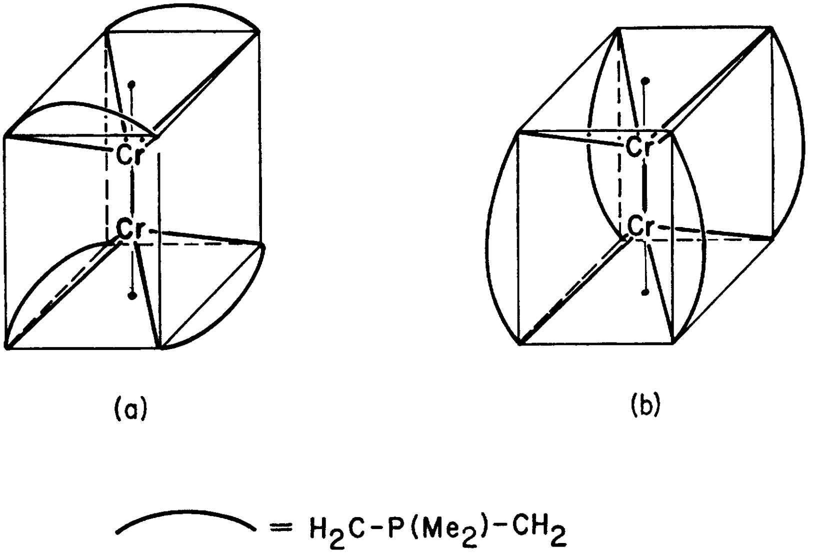
[91] P. Sharrock, T. Thiopanides, and F. Brisse, *Canad. J. Chem.*, 1973, **51**, 2963.

[92] E. Kurras, U. Rosenthal, H. Mennenya, G. Oehme and G. Engelhardt, *Z. Chem.*, 1974, **14**, 160.



(a) (b)

Figure 10 *Two possible structures for* $Cr_2[(CH_2)_2P(CH_3)_2]_4$.

sets of chelate rings are eclipsed rather than staggered. Compounds which may contain $[Cr_2(C_5H_{10})_4]^{4-}$ have been reported.[90] The compounds $Li_2Cr(\textit{o}\text{-}C_6H_4O)_2$, 2Ether and several similar ones[93] may well contain a $[Cr_2(\textit{o}\text{-}C_6H_4O)_4]^{4-}$ ion in which the $\textit{o}\text{-}C_6H_4O^{2-}$ ions occupy a set of positions similar to those of bridging carboxy-groups. There is also $Cr(\textit{o}\text{-}C_6H_4OMe)_2$,[94] which could contain dinuclear molecules, though its low solubility perhaps indicates a polymeric structure.

It should be noted, to complete the picture regarding chromium(II), that there are also many compounds, including important ones, which do *not* have metal–metal bonds according to magnetic or crystallographic data, or both. These include CrI_2,[95] $CrCl_2,4H_2O$,[96] several with the formula $M^I_2Cr(SO_4)_2,xH_2O$ where M^I is an alkali metal,[97] some $M^I_2CrCl_4$ compounds,[98] $M^I_2CrBr_4(H_2O)_2$,[99] and $Cr[N(SiMe_3)_2]_2(THF)_2$.[100] There is no evidence for the existence of a dinuclear aquo-ion (through no effort to detect it is recorded). It has been proposed[101] that the rate-controlling step in the redox and substitution reactions of

[93] F. Hein, R. Weiss, B. Heyn, K. H. Barth, and D. Tille, *Monatsber. Deut. Akad. Wiss. Berlin*, 1959, **1**, 541.

[94] F. Hein and D. Tille, *Z. anorg. Chem.*, 1964, **329**, 72.

[95] F. Besrest and S. Jaulmes, *Acta Cryst.*, 1973, **B29**, 1560.

[96] H. G. von Schnering and B. H. Brand, *Z. anorg. Chem.*, 1973, **402**, 159.

[97] A. Earnshaw, L. F. Larkworthy, K. C. Patel, and G. Beech, *J. Chem. Soc.* (*A*), 1969, 1334.

[98] H. J. Seifert and K. Klatyk, *Z. anorg. Chem.*, 1964, **334**, 113.

[99] L. F. Larkworthy and A. Yavari, *J.C.S. Chem. Comm.*, 1973, 632.

[100] D. C. Bradley, M. B. Hursthouse, C. W. Newing, and A. J. Welch, *J.C.S. Chem. Comm.*, 1972, 567.

[101] R. D. Cannon and J. S. Lind, *J.C.S. Chem. Comm.*, 1973, 904.

$Cr_2(O_2CCH_3)_4(H_2O)_2$ in aqueous media is the dissociation:

$$Cr_2(O_2CCH_3)_4 \rightleftarrows 2\ Cr(O_2CCH_3)_2$$

It thus appears that complexes of the dinuclear cation Cr_2^{4+} play a very important role in the chemistry of chromium(II), but is not as dominant as is Mo_2^{4+} in the chemistry of molybdenum(II). The latter, of course, also has an extensive cluster chemistry[102] involving Mo_6 clusters with Mo–Mo single bonds, and this has no parallel whatever in the chemistry of chromium(II).

Two compounds containing triple Cr–Cr bonds have been reported. The first was $(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_4$, which consists of two $(\eta^5\text{-}C_5Me_5)Cr(CO)_2$ units joined by a Cr–Cr bond which is 2.276(2) Å long.[103] On the reasonable assumption that each chromium atom is to have an 18-electron configuration, this should be considered a triple bond. Very recently it has been shown[104] that the presumably isostructural $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4$ forms readily on thermolysis of the highly strained $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$.[105]

Heteronuclear Quadruple Bonds.—The possibility of forming mixed metal species $[MM'(O_2CR)_4]$, containing two Group VI metals, is very obvious, but little has yet been published. The isolation of $CrMo(O_2CCH_3)_4$ has been reported.[106] The structure has not yet been determined, but if a band in the Raman spectrum (and also in the i.r.) at 392 is assigned to Cr–Mo stretching, then the Cr–Mo force constant is only about 2/3 that for Mo–Mo in $Mo_2(O_2CCH_3)_4$. McCarley and co-workers[107] have also prepared this compound as well as several $MoW(O_2CR)_4$ compounds and shown that both $Mo_2(O_2CR)_4$ and $MoW(O_2CR)_4$ species can be oxidized by halogens to such products as $Mo_2(O_2CR)_4{}^+I_3{}^-$ and $MoW(O_2CR)_4I$.

Ruthenium and Iron.—About ruthenium we know only enough to suggest that there may be significant things still to learn. In 1966 Stephenson and Wilkinson[108] reported the preparation of a series of compounds with the unusual stoicheiometry $Ru_2(O_2CR)_4Cl$, and having magnetic susceptibilities suggesting the presence of three unpaired electrons per formula unit. The true nature of these compounds was established *X*-ray crystallographically[109] a few years later; the significant portion of the structure of the butyrato-compound is shown in Figure 11. The very short Ru–Ru distance, 2.281(4) Å, implies that a very strong M–M bond is present. An orbital scheme was also proposed to explain the presence of three unpaired electrons within the general framework of the quadruple-bond scheme.

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[102] F. A. Cotton, *Accounts Chem. Res.*, 1969, **2**, 240.

[103] J. Potenza, P. Giordano, D. Mastrapaolo, A. Efraty, and R. B. King, *J.C.S. Chem. Comm.*, 1972, 1333.

[104] P. Hackett, P. S. O'Neill, and A. R. Manning, *J.C.S. Dalton*, 1974, 1625.

[105] R. D. Adams, D. E. Collins, and F. A. Cotton, *J. Amer. Chem. Soc.*, 1974, **96**, 749.

[106] C. D. Garner and R. G. Senior, *J.C.S. Chem. Comm.*, 1974, 580.

[107] R. E. McCarley, R. J. Hoxmeier, and V. Katovic, personal communication.

[108] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2285.

[109] M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1.

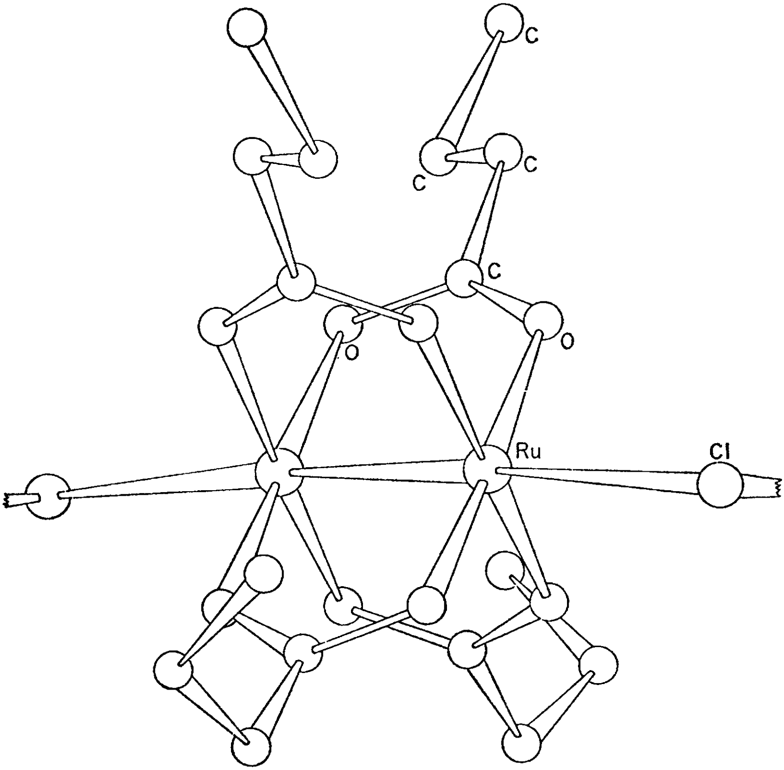

Figure 11 *A portion of the structure of* $Ru_2(O_2CC_3H_7)_4Cl$. *The long, angular* Cl *bridges between* $Ru_2(O_2C_3H_7)_4{}^+$ *units are to be noted.*

Very recently, $Ru_2(O_2CC_3H_7)_4Cl$ has been more thoroughly investigated.[110] The magnetic susceptibility from 60 to 300 K and the e.p.r. spectrum in solution show conclusively that $Ru_2(O_2CC_3H_7)_4{}^+$ has a quartet ground state and that the unpaired electrons are equally shared by the two metal atoms, thus ruling out any mixed-oxidation-state (Ru^{II}, Ru^{III}) formulation. It was also shown that one-electron reduction to $Ru_2(O_2CC_3H_7)_4$ occurs quasi-reversibly at potentials in the range 0.00 to −0.34 V, depending on solvent. The product, presumably $Ru_2(O_2CC_3H_7)_4$, appears to be diamagnetic; a crystalline specimen of this could not be obtained. Stephenson and Wilkinson[108] had also tried, unsuccessfully, to isolate crystalline samples of various compounds, *e.g.* $Ru_2(O_2CCH_3)_4(H_2O)$ $Ru(O_2CR)_2(py)_4$, and $Ru(O_2CR)_2(py)_2$, which appear to contain Ru in the oxidation state II. It would seem, however, that under appropriate conditions it should be possible to do so. A compound of apparent composition

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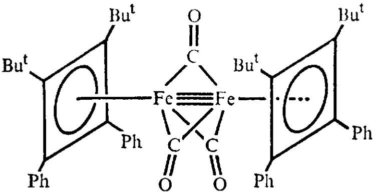
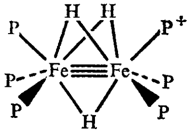
[110] F. A. Cotton and E. Pedersen, *Inorg. Chem.*, in the press.

$Ru_2(O_2CCH_3)_{4.5}(H_2O)_{1.5}$ was also reported, and its structure would be of interest.

Although no compounds with quadruple bonds are known, iron ranks a close second to chromium among first-row metals in forming multiple M–M bonds. Two compounds, (1) and (2), containing Fe–Fe triple bonds have been reported.



(1)



(2)

Compound (1)[111] has an Fe–Fe distance of 2.177(3) Å, which is about 0.1 Å shorter than the triple bond in the very similar $[(\eta^5\text{-}Me_5C_5)Cr(CO)_2]_2$. In (2)[112] each set of three P atoms belongs to a $HC(CH_2PPh_2)_3$ ligand and the accompanying anion is BPh_4^-. The Fe–Fe distance here is 2.34 Å. We have here another good example of the fact that bond multiplicity is simply a qualitative measure of the number of electron-pair interactions and not an index of bond strength (or length). In compound (2), there seem likely to be three bond components, $\sigma + 2\pi$, but they are weaker than in (1).

There are three compounds containing Fe–Fe double bonds. The first,[113] (3), has an M–M distance of 2.215 Å. Compound (4)[114] is a homologue of (3) and has nearly the same distance, 2.225(3) Å. Compound (5),[115] with different bridging groups, has a distinctly longer Fe–Fe distance, 2.326(4) Å. It is interesting to note that the latter is scarcely shorter than the length (2.37 Å) of the formal single bond in (6),[116] though the latter is definitely anomalous among single Fe–Fe bonds, which are generally 2.5—2.8 Å long.

Rhodium.—Dirhodium tetra-acetate dihydrate is a compound which contains the shortest known[84] Rh–Rh bond, 2.3855(5) Å. On the basis of comparisons with many Rh–Rh single bonds, which have lengths in the range 2.68 Å[117] to 2.94 Å,[118] it has been suggested[118] that this bond must be a multiple one, probably with an order of 3. Recently two compounds, (7) and (8), with double bonds have been

[111] S.-I. Murahashi, *et al*, *J.C.S. Chem. Comm.*, 1974, 563.

[112] P. Dapporto, G. Fallani, S. Midollini, and L. Sacconi, *J. Amer. Chem. Soc.*, 1973, **95**, 2021.

[113] K. Nicholas, L. S. Bray, R. E. Davis, and R. Pettit, *Chem. Comm.*, 1971, 608.

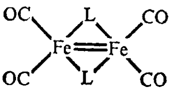
[114] H.-J. Schmitt and M. L. Ziegler, *Z. Naturforsch.*, 1973, **28b**, 508.

[115] J. Calderon, S. Fontana, E. Frauendorfer, V. W. Day, and S. D. A. Iske, *J. Organometallic Chem.*, 1974, **64**, C16.

[116] P. E. Baikie and O. S. Mills, *Inorg. Chim. Acta*, 1967, **1**, 55.

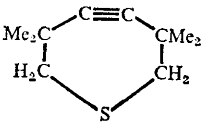
[117] O. S. Mills and J. P. Nice, *J. Organometallic Chem.*, 1967, **10**, 337.

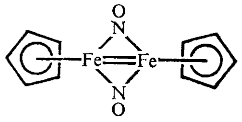
[118] K. G. Caulton and F. A. Cotton, *J. Amer. Chem. Soc.*, 1971, **93**, 1914.



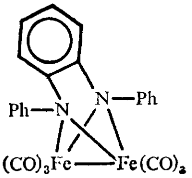
(3) L = $Bu^tC{\equiv}CBu^t$

(4) L =





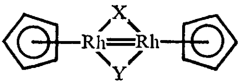
(5)



(6)

described.[119] Since these bonds have lengths of 2.46 and 2.55 Å, the previous proposal receives further support.

The structure of $Rh_2(O_2CCH_3)_4(PPh_3)_2$, which is analogous to that of the tetra-acetate dihydrate, has been determined.[120] The phosphines are fairly strongly bonded [Rh–P = 2.479(4) Å] and the Rh–Rh bond is longer than in the hydrate, namely 2.449(2) Å.



(7) X = CO; Y = CPh_2

(8) X = Y = CPh_2

A number of formate complexes, mostly of the type $[Rh(O_2CH)_2L]_2$, have been reported.[121] The basis for the dinuclear formula is an unpublished *X*-ray crystallographic study of the compound with L = $0.5H_2O$, which is said to 'contain $[Rh(O_2CH)_2(H_2O)]_2$ and $[Rh(O_2CH)_2]_2$ units alternating in an infinite chain,' but no bond distances are disclosed.

The preparation of the aquo-ion $Rh_2^{4+}(aq)$ has also been described.[122] This has been obtained in solution by reduction of $Rh(H_2O)_5Cl^+$ with Cr^{2+}; no solid compound has been isolated. It is oxidized slowly by air and reacts rapidly with various ligands, for example with acetate ion to generate what appears to be $Rh_2(O_2CCH_3)_4$.

4 Electronic Structures

It is obvious that for moderately complex molecules containing atoms of very high atomic numbers, *e.g.* $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$, conventional MO calcu-

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[119] H. Ueda, Y. Kai, N. Yauoka, and N. Kasai, 21st Symposium on Organometallic Chemistry, Japan, 1973, Abstract No. 214.

[120] J. Halpern and G. Khare, personal communication.

[121] I. I. Chernyaev, E. V. Shenderetskaya, A. G. Maiorova, and A. A. Karyagina, *Russ. J. Inorg. Chem.*, 1965, **10**, 290, and earlier work cited therein.

[122] F. Maspero and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 7361.

lations are barely, if at all, feasible. Therefore, until very recently, theoretical discussion of the electronic structures of quadruply bonded dinuclear species, and others closely related, has been of an essentially qualitative nature, and there was no important development beyond the basic qualitative proposals made by this writer some 9 years ago. Experimental approaches to questions of electronic structure have also been few. Aside from some early attempts to interpret a few electronic spectra[22,53,123] the measurement of bond lengths has been the only experimental method consistently used.

In the past few years this picture has begun to change. The SCF scattered-wave Xα (SCF–SW–Xα) method of calculation[124] appears to afford a practicable avenue of theoretical approach, and experimental studies employing e.p.r. measurements of paramagnetic species generated electrochemically, as well as

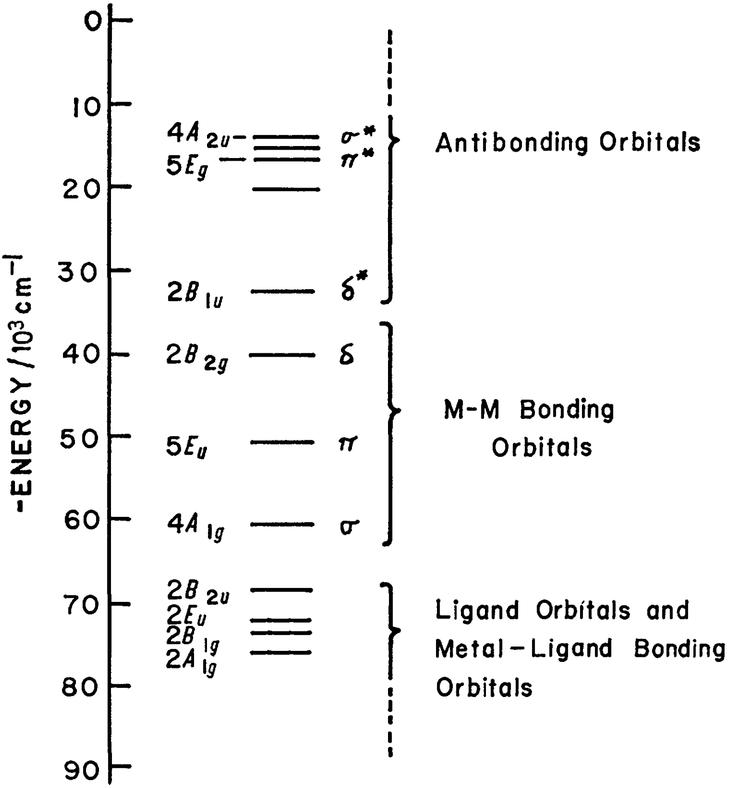

Figure 12 *A portion of the energy-level diagram for* $Mo_2Cl_8^{4-}$ *according to an SCF–SW–Xα calculation by Norman and Kolari. Levels shown are those with at least* 20% *metal character.*

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[123] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1967, **6**, 924.

[124] K. H. Johnson, *Adv. Quantum. Chem.*, 1973, **7**, 143.

more sophisticated measurements and interpretations of optical spectra, have begun to appear.

The $Mo_2Cl_8^{4-}$ ion has been treated by the SCF–SW–Xα method by Norman and Kolari.[125] Their results strikingly confirm all of the essential features of the original proposal[3] concerning the quadruple bond. Figure 12, which is adapted from the work of Norman and Kolari,[125] shows some of their results. It is evident that a little above the metal–ligand and ligand lone-pair orbitals, and below the anti-bonding orbitals, is a set of Mo–Mo bonding orbitals, in the order σ, π, δ,

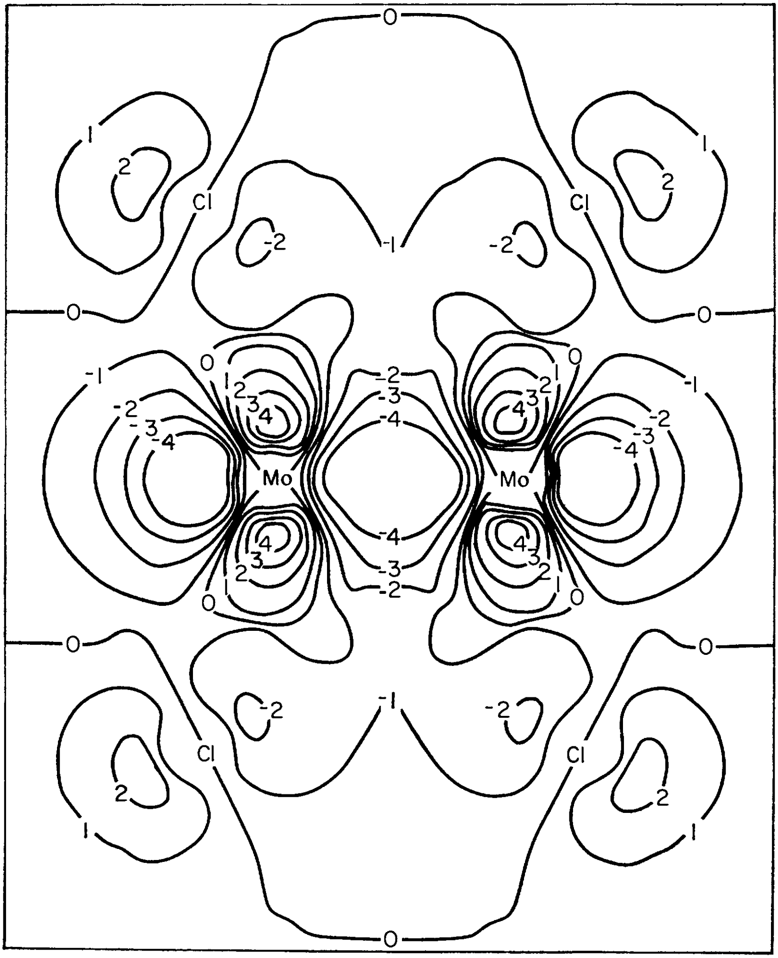

Figure 13 *The* Mo–Mo σ ($4\,A_{1g}$) *bonding orbital, in the* xy *plane, of* $Mo_2Cl_8^{4-}$ *according to the SCF–SW–Xα calculation of Norman and Kolari.*

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[125] (*a*) J. G. Norman, jun. and H. J. Kolari, *J.C.S. Chem. Comm.*, 1974, 303; (*b*) *J. Amer. Chem. Soc.*, in the press.

precisely as expected. The δ^*-orbital is not far above the δ-orbital, also as expected, since this is the weakest component of the quadruple bond.

Perhaps the most important result of this calculation is that the σ-, π-, and δ-orbitals are found to have mainly metal d character (76–93%), so that the original crude approximation[3] of describing the quadruple bond in terms of σ , π-, and δ-overlaps of pure d-orbitals is, in essence, validated. Figures 13–15 show contour diagrams of the σ-, π-, and δ-bonding orbitals. The σ-($4A_{1g}$)orbital (Figure 13) arises mainly from an overlap of metal $4d_{z^2}$ functions. The outer lobes and equatorial rings of the $4d_{z^2}$ functions are σ anti-bonding with respect to

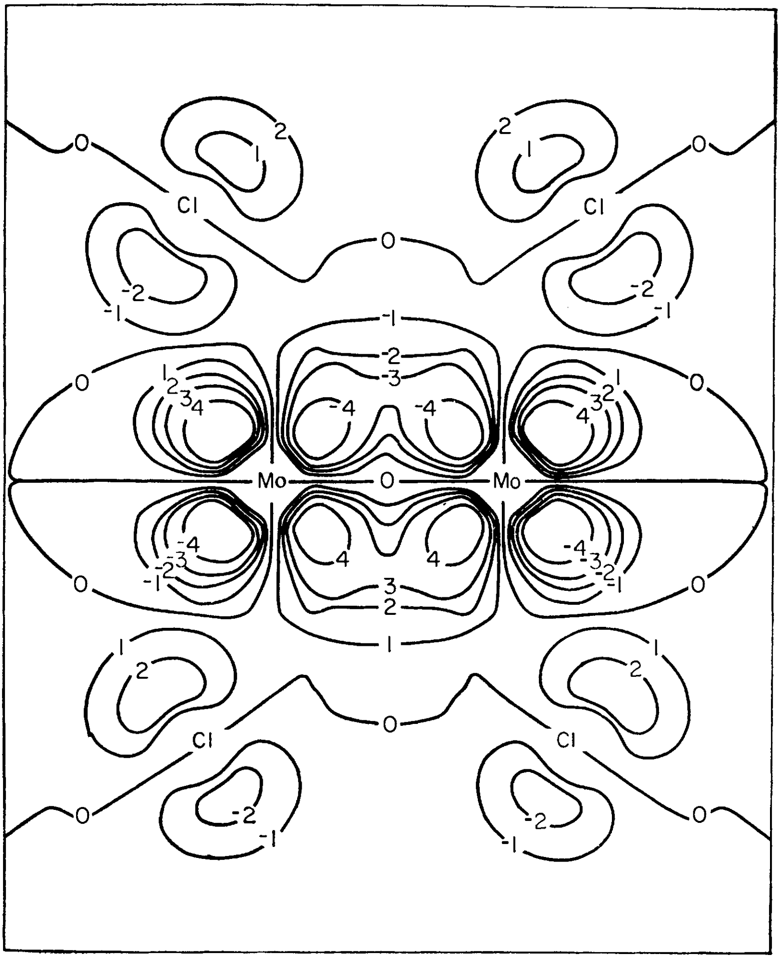

Figure 14 *One of the* Mo–Mo $\pi(5E_u)$ *bonding wavefunctions of* $Mo_2Cl_8^{4-}$, *from the SCF–SW–Xα calculation of Norman and Kolari.*

Mo–Cl interactions, as shown by the nodes between Mo and Cl atoms, but there is some appreciable overlap with the Cl $3p$ orbitals to give a bonding contribution as well. This σ-orbital has the lowest (76 %) metal d character of those forming the quadruple bond. The π-orbitals, one of which is shown in Figure 14, are obviously the result of $4d\pi$–$4d\pi$ overlap. Finally, Figure 15 shows one of four equivalent sections through the maximum electron density of the δ-orbital. This one has the highest metal d character (93 %) and looks just as one would expect for a $4d\delta$–$4d\delta$ overlap.

In addition to the basic description of the quadruple bond,[3] which the

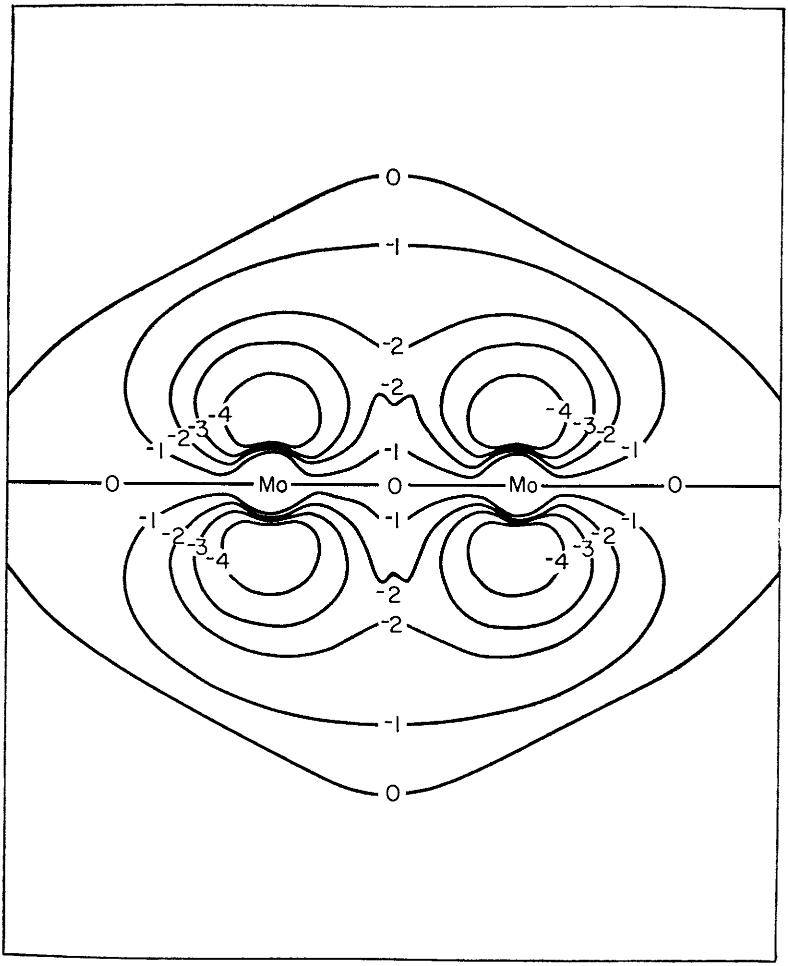

Figure 15 *A section through one of the maximal planes (halfway between the* xz *and* yz *planes) of the* Mo–Mo $\delta(2B_{2g})$ *bonding orbital of* $Mo_2Cl_8^{4-}$ *from the SCF–SW–X*α *calculation of Norman and Kolari.*

SCF–SW–Xα calculations so strikingly confirm, this writer subsequently suggested that there might also be two essentially non-bonding σ-orbitals, directed outwards along the M–M axis, and formed mainly from metal s- and p_z-orbitals, and that at least one of these would have an energy similar to those of the δ- and δ^*-orbitals. The SCF–SW–Xα calculation does not support this suggestion. While this is of no importance in describing the ground state of $Mo_2Cl_8^{4-}$, or other systems in which there are eight or fewer M–M bonding electrons, it is important with regard to the excited states of these molecules and for all species such as $Tc_2Cl_8^{3-}$, $Ru_2(O_2CR)_4^+$, and $Rh_2(O_2CCH_3)_4(H_2O)_2$, in which there are more than eight electrons. The molecular and electronic structures of these species have previously been rationalized by the writer in ways which employed at least one of these σ non-bonding orbitals, but, as Norman and Kolari suggest, it may not be too difficult to rationalize them in other ways.

One case, however, that at present seems to offer difficulty is $Re_2Cl_4(PEt_3)_4$, which has the structure[126] shown in Figure 16. This contains two more electrons than $Re_2Cl_8^{2-}$ or $Re_2Cl_6(PEt_3)_2$ and is subject to considerable internal crowding that should tend to stretch the Re–Re bond. If the two additional electrons occupy the δ^*-orbital, thus nullifying the δ-bond, as the diagram of Figure 12 would suggest, it is not easy to understand why the Re–Re distance of 2.232(6) Å is not significantly longer than those in $Re_2Cl_8^{2-}$ [2.241(7) Å] and $Re_2Cl_6(PEt_3)_2$ [2.222(3) Å].

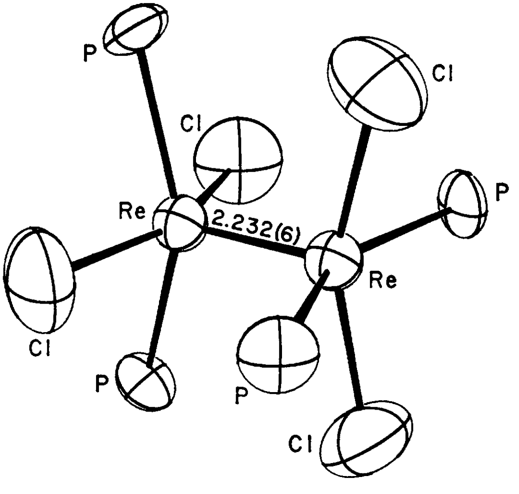

Figure 16 *The structure of* $Re_2Cl_4(PEt_3)_4$, *with the ethyl groups omitted for clarity.*

From the spectroscopic side, there is evidence to support the level scheme of

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[126] F. A. Cotton, B. A. Frenz, J. R. Ebner, and R. A. Walton, *J.C.S. Chem. Comm.*, 1974, 4.

Norman and Kolari. They have shown that the observed bands in the visible and u.v. spectra of $Mo_2Cl_8^{4-}$ can be satisfactorily assigned using their diagram; in so doing they assign the lowest observed band to the $\delta \rightarrow \delta^*$ transition, whereas, if a non-bonding σ-orbital were to lie below the δ^*-orbital, this transition would be assigned to $\delta \rightarrow \sigma$. For $Re_2Cl_8^{2-}$ and $Re_2Cl_6(PEt_3)_2$, Cowman and Gray[127] have offered experimental evidence which favours assigning the lowest observed band to the $\delta \rightarrow \delta^*$ transition in these species, too. The writer had previously rejected that assignment because the transition is extremely weak although a $\delta \rightarrow \delta^*$ transition is orbitally allowed.

Recent work in the writer's laboratory[40] involving an e.p.r. study of species with unpaired electrons that must occupy orbitals above the δ-orbital also gives results that cast doubt upon the earlier proposal that a σ non-bonding orbital is next above the δ-orbital.

This is not the place to pursue the interesting but currently controversial question of the detailed electronic structures of the quadruply bonded and related species. There are many other data bearing on the question. The foregoing discussion merely serves to show that this aspect of the field as well as chemical aspects remain challenging subjects for further research.

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[127] C. D. Cowman and H. B. Gray, *J. Amer. Chem. Soc.*, 1973, **95**, 8177.