

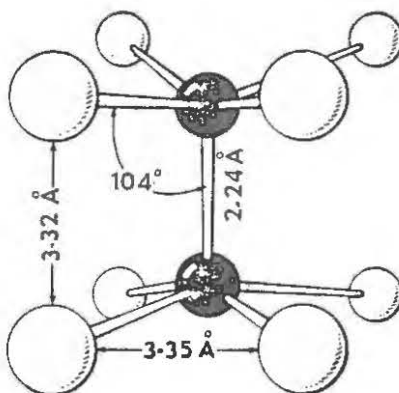
## Quadruple Bonds in Group VI Metal Complexes

Deborah Main

Literature Seminar

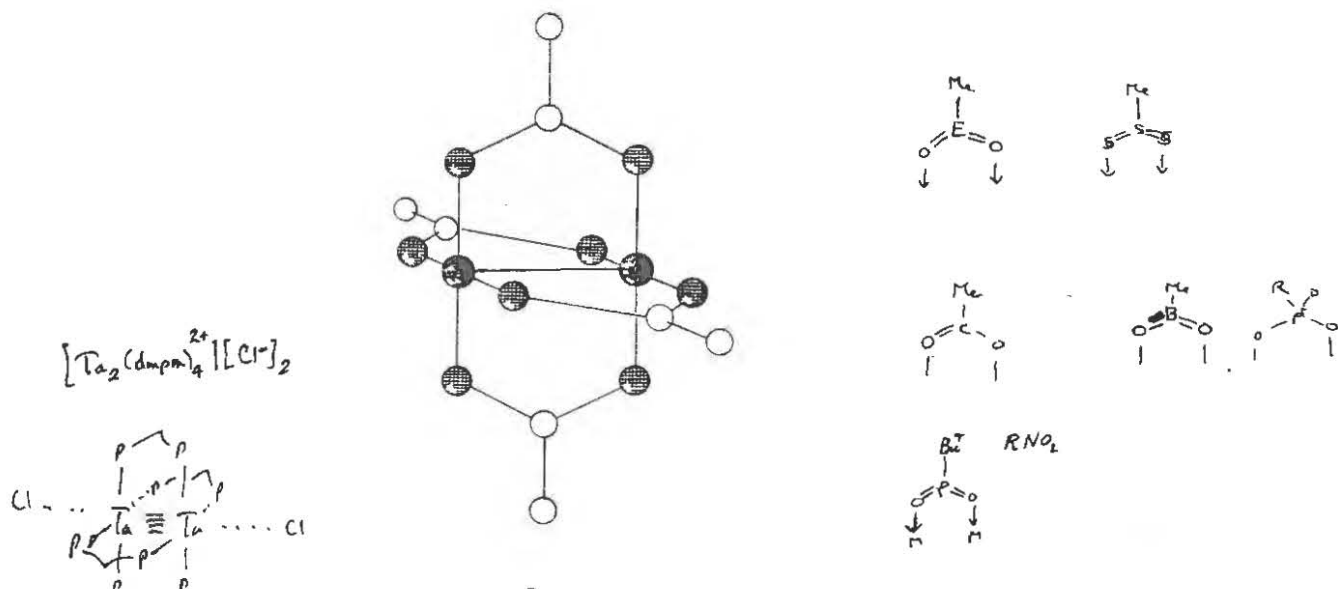
April 7, 1983

Although the first discovery of a compound containing a quadruple bond can be traced back as far as 1844 when Eugene Peligot first synthesized  $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ , it was not until 1964 that quadruple bonds were recognized to exist. This recognition came when the structure of  $\text{KReCl}_4 \cdot \text{H}_2\text{O}$  was reported to contain the dimeric unit  $[\text{Re}_2\text{Cl}_8]^{2-}$  (1) [1]. The bonding and electronic structure of  $[\text{Re}_2\text{Cl}_8]^{2-}$  was interpreted in terms of a quadruple bond consisting of one  $\sigma$ -, two  $\pi$ -, and one  $\delta$ -component between the rhenium atoms. Since then, the chemistry surrounding this important class of coordination complexes has developed very rapidly [2-6].



1

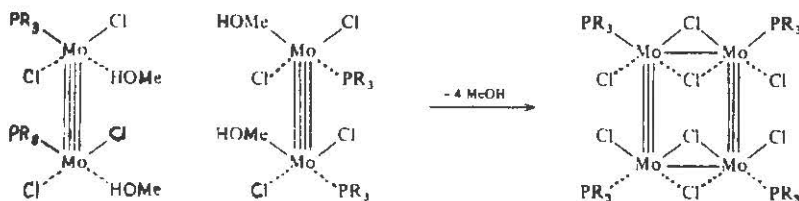
Today, there are five elements known to participate in quadruple bonding, three of which belong to Group VIB, namely, chromium, molybdenum, and tungsten. Of the quadruply bonded compounds known, the carboxylate complexes,  $\text{M}_2(\text{O}_2\text{CR})_4$  (2) are probably regarded as the single most important class because they have traditionally been the starting materials for the synthesis of almost all other derivatives (except for the case of  $\text{M}=\text{W}$ ).



Peligot's original synthesis of  $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$  involving addition of  $\text{NaO}_2\text{CCH}_3$  to an aqueous solution of  $\text{Cr}^{2+}$  is still one of the easiest and most efficient means of preparing  $\text{Cr}_2(\text{O}_2\text{CR})_4$  compounds [7], although new methods have been introduced [8]. The molybdenum carboxylates can be prepared by heating  $\text{Mo}(\text{CO})_6$  with carboxylic acid in various solvents such as diglyme, toluene, and 1,2-dichlorobenzene [9] or by reduction of  $\text{MoO}_3$  [10]. However, preparation of the tungsten analogs,  $\text{W}_2(\text{O}_2\text{CR})_4$ , have been extraordinarily elusive, as have  $\text{W}_2^{4+}$  compounds in general. Only recently has success been reported with the preparation of  $\text{W}_2(\text{O}_2\text{CCF}_3)_4$  [11].  $\text{W}_2\text{Cl}_8(\text{THF})_4$  is reduced to  $\text{W}_2\text{Cl}_4(\text{THF})_4$  with two equivalents of sodium amalgam at  $-20^\circ\text{C}$  followed by addition of sodium trifluoroacetate and subsequent workup.

The rapid growth of compounds containing quadruple M-M bonds can largely be attributed to the desire to produce new compounds with bridging ligands which are stereoelectronically similar to the carboxylates. Research in this area has led to the discovery of certain ligands which yield "supershort" M-M bonds [12-14]. Examples of compounds containing such ligands include  $\text{Cr}_2(2,6-(\text{OCH}_3)_2\text{C}_6\text{H}_3)_4$  ( $\text{Cr}-\text{Cr} = 1.847 \text{ \AA}$ ),  $\text{Cr}_2-(\text{CH}_2\text{NC}(\text{Ph})\text{NCH}_2)_4$  ( $\text{Cr}-\text{Cr} = 1.843 \text{ \AA}$ ),  $\text{Cr}_2((\text{CH}_2)_2\text{P}(\text{CH}_3)_2)_4$  ( $\text{Cr}-\text{Cr} = 1.895 \text{ \AA}$ ), and the compound containing the shortest known M-M bond,  $\text{Cr}_2(2-\text{OCH}_3-5-\text{CH}_3\text{C}_6\text{H}_3)_4$  ( $\text{Cr}-\text{Cr} = 1.828 \text{ \AA}$ ). The factors responsible for such shortness in the Cr-Cr bond have been investigated but are presently unknown.

Dinuclear quadruply bonded complexes undergo a variety of reactions: oxidative addition, reductive elimination, Lewis base association and dissociation, and insertion-deinsertion reactions. Recent work by McCarley and co-workers has led to perhaps the most intriguing of all reactions, namely, the dimerization of two such species to give tetranuclear complexes (Scheme 1) [15].  $\text{Mo}_4\text{Cl}_8(\text{PEt}_3)_4$  was the first such compound prepared and structurally characterized. It was found to contain a rectangular array of metal atoms with alternating single-triple metal-metal bonds [15]. Since then, several new tetranuclear compounds have been synthesized [16-18].



Scheme 1

References

1. Cotton, F. A.; Harris, C. B. Inorg. Chem. 1965, 4, 330-3.
2. Cotton, F. A. Chem. Soc. Rev. 1975, 4, 27-53.
3. Cotton, F. A. Accts. Chem. Res. 1978, 11, 225-32.
4. Trogler, W. C.; Gray, H. B. Accts. Chem. Res. 1978, 11, 232-9.
5. Templeton, J. L. Prog. Inorg. Chem. 1979, 26, 211-300.
6. Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms," John Wiley, & Sons: New York, 1982; pp. 1-452.
7. Ocone, L. R.; Block, B. P. Inorg. Synth. 1966, 125-30.
8. Cotton, F. A.; Extine, M. W.; Rice, G. W. Inorg. Chem. 1978, 17, 176-86.
9. Stephenson, T. A.; Bannister, E.; Wilkinson, G. J. Chem. Soc. 1964, 2538-41.
10. Bins, A.; Gibson, D. J. Am. Chem. Soc. 1980, 102, 4277-8.
11. Sattelberger, A. P.; McLaughlin, K. W.; Huffman, J. C. J. Am. Chem. Soc. 1981, 103, 2880-2.
12. Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. Inorg. Chem. 1979, 18, 1143-9.
13. Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. Inorg. Chem. 1979, 18, 1149-51.
14. Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. Inorg. Chem. 1979, 18, 1152-61.
15. McGinnis, R. N.; Ryan, T. R.; McCarley, R. E. J. Am. Chem. Soc. 1978, 100, 7900-2.
16. Ryan, T. R.; McCarley, R. E. Inorg. Chem. 1982, 21, 2072-9.
17. Cotton, F. A.; Powell, G. L. Inorg. Chem. 1983, 22, 871-3.
18. McCarley, R. E.; Ryan, T. R.; Torardi, C. C. In "Reactivity of Metal-Metal Bonds", ACS Symp. Ser. No. 155; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; pp. 41-60.