Inorganica Chimica Acta, 33 (1979) L133–L134
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Variable Electron Population of Discrete Metal Atom Clusters of the M_3X_{13} Type

AVI BINO, F. ALBERT COTTON*, and ZVI DORI*†

Department of Chemistry, Texas A & M University, College Station, Tex. 77843, U.S.A.

Received December 27, 1978

The M_3X_{13} type of metal atom cluster (Fig. 1) was discovered as a *non*-discrete component of the compound $Zn_2Mo_3O_8$ and occurs also in several closely similar mixed metal oxides [1]. A simple but effective analysis of the metal-to-metal (M–M) bonding [2] showed that the MO's concerned are as follows:

$$\underbrace{1a_1 \quad 1e}_{\text{bonding}} \qquad 2a_1 \qquad \underbrace{2e \quad 3e \quad 1a_2}_{\text{anti bonding}}$$

This implies that the predominent tendency in such systems will be to use six electrons in a $(1a_1)^2(1e)^4$ configuration to form three M–M single bonds. $Zn_2Mo_3O_8$ exactly satisfies this prescription. Nb_3Cl_8, characterized shortly thereafter as another *non*-discrete M_3X_{13} structure, has 7 electrons, but can be understood readily on the above bonding picture by assigning the additional electron to the non-bonding $2a_1$ orbital.

Only very recently has the M_3X_{13} structure been discovered in discrete form. The first example [3] was the $[W_3O_4F_9]^{5-}$ ion [4] and we recently reported [5] the very stable and easily prepared compound $Cs_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]\cdot 4H_2O\cdot 1/2H_2C_2O_4$. In both of these there is a set of M–M single bonds based on the $(1a_1)^2(1e)^4$ configuration. We now report the first example of an M_3X_{13} structure with an 8-electron M–M bond system; it is also the first example of a discrete M_3X_{13} entity deviating from the simple 6-electron system of M–M single bonds.

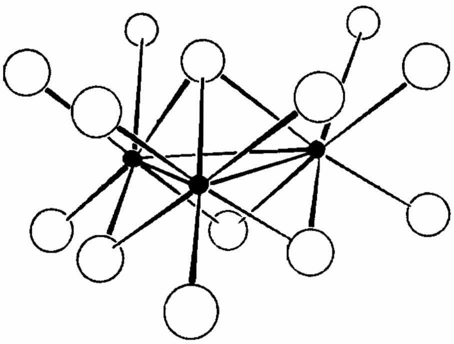

Figure 1. The M_3X_{13} structure. Small black circles represent the three metal atoms, which are bonded to one another to form an equilateral triangle.

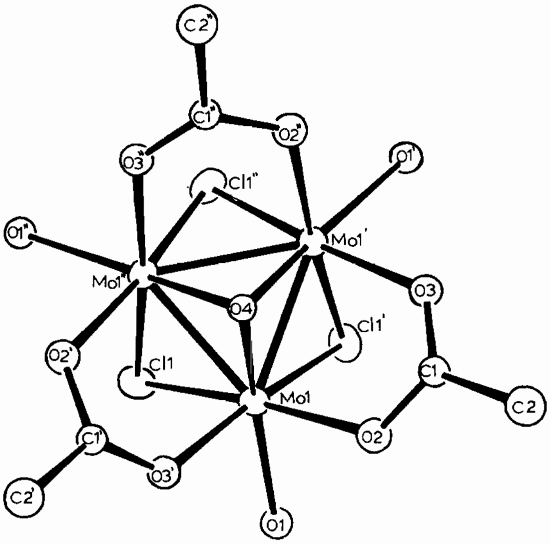

Figure 2. The structure of the $[Mo_3O_4(O_2CCH_3)_3(H_2O)_3]^{2+}$ ion.

Experimental

Dichlorotetracarbonylmolybdenum was dissolved in a 1:1 mixture of acetic acid and acetic anhydride under nitrogen and the solution was stirred for 4 h at room temperature. The red solution was diluted with water, absorbed on a DOWEX 50W cation exchange column and eluted with 2 *M* $HClO_4$. As the orange eluate was allowed to evaporate slowly, the color changed to deep blue and dark blue crystals were deposited.

These crystals were found to belong to space group $P6_3$ with a = 8.906(6) Å, c = 15.162(4) Å and Z = 2. The structure was solved and showed the formula to be $[MO_3OCl_3(O_2CCH_3)_3(H_2O)_3](ClO_4)Cl$. The trinuclear cation, **1**, has the structure shown in Fig. 2. Crystallographic symmetry C_3 is imposed, but effectively the symmetry is C_{3v}. Thus, there are two crystallographically independent Mo–Cl distances, but these are equal within the experimental uncertainties with values of 2.428(5) and 2.425(5) Å. Similarly the Mo–O(2) and Mo–O(3) distances are essentially equal with values of 2.06(1) and 2.07(1) Å, respectively. The Mo–O(4) distances are 2.03(1) Å, while Mo–O(1) = 2.13(1) Å.

---

*Authors to whom correspondence should be addressed.

†Permanently in the Department of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel.

This structure closely resembles that of the anion $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$, 2, but shows several significant and interesting differences: (1) instead of chelating oxalato ions there are bridging acetato ions; (2) in place of three μ_2–O atoms there are three μ_2–Cl atoms. These qualitative differences indicate further the inherent stability of this type of structure despite changes in detail. (3) The one truly significant quantitative difference between the structures of **1** and **2** is in the Mo–Mo distances which have the values 2.550(2) and 2.486(1) Å, respectively. This difference may be in part due to the replacement of the μ_2–O atoms by the larger μ_2–Cl atoms. However, there is another possible cause.

A reckoning of metal valences in **1** and **2** quickly shows that there are *eight* electrons available for M–M orbitals in the former, in contrast to the *six* available in the latter. The persistence of the M_3X_{13} type structure despite this change in the number of electrons is simply and satisfactorily explained by the availability of the essentially non-bonding $2a_1$ orbital. It is therefore possible to assign eight instead of six electrons without any major disturbance of the metal-to-ligand or metal-to-metal bonding. It is possible that the $2a_1$ orbital might have slightly antibonding character in the M–M sense, thus providing an additional explanation for the small increase in Mo–Mo distances in **1** as compared to **2**.

Our studies of this and related systems are continuing and this compound will be more fully described at a later time.

Acknowledgement

We thank the National Science Foundation for financial support.

References

1 W. H. McCarroll, L. Katz and R. Ward, *J. Am. Chem. Soc., 79,* 5410 (1957). See also W. H. McCarroll, *Inorg. Chem., 16,* 3351 (1977) for later references.
2 F. A. Cotton, *Inorg. Chem., 3,* 1217 (1964).
3 We regret the oversight in our recent note (Ref. 5) of the slightly earlier work of Mattes and Mennemann described in ref. 4. It may also be noted that the $[Mo_3S(S_2)_6]^{2-}$ of Müller, *et al.* [6] is also of essentially the same structure type.
4 K. Mennemann and R. Mattes, *Angew. Chem., 88,* 92 (1976); *idem., Z. anorg. allg. Chem., 437,* 175 (1977).
5 A. Bino, F. A. Cotton and Z. Dori, *J. Am. Chem. Soc., 100,* 5252 (1978).
6 A. Müller, S. Sarkar, R. G. Bhattacharyya, S. Pohl and M. Dartmann, *Angew. Chem., 90,* 564 (1978).