X-Ray Crystal Structure of Hexakis(dimethylamino)dimolybdenum. A New Compound with a Metal-to-metal Triple Bond

By Malcolm Chisholm
(*Department of Chemistry, Princeton University, Princeton, New Jersey* 08540)
and F. Albert Cotton,* Bertram A. Frenz, and Larry Shive
(*Department of Chemistry, Texas A&M University, College Station, Texas* 77843)

Summary The compound $Mo_2(NMe_2)_6$ is shown by *X*-ray crystallography to contain centrosymmetric molecules (virtual symmetry S_6, differing little from D_{3d}) with a triple bond between the metal atoms [Mo–Mo = 2·214(2)]

Although there are now many reports[1] on compounds containing quadruple bonds between transition metal atoms, our knowledge of compounds with triple bonds is still relatively sketchy. The first such bond was discovered[2] in the mixed-valence compound of rhenium, $Re_2Cl_5(dth)_2$ (dth = $MeSCH_2CH_2SMe$); the presence of only the σ- and two π-components, but no δ-component, was evidenced by the staggered rotational configuration.

Direct structural evidence for other triple bonds has subsequently been presented in only two cases, *viz.*, $[(MeC)_5Cr(CO)_2]_2$[3] and $(Me_3SiCH_2)_6Mo_2$,[4] so far as we know. We therefore examined the structure of $(Me_2N)_6Mo_2$, a new compound with a triple bond and containing a type of ligand different to any previously present, namely the Me_2N group, which may be capable of appreciable π interaction with the metal atom. Some of the properties of this compound have already been reported.[5]

The structure was determined by conventional single-crystal *X*-ray methods, using counter-diffractometer data and refined to reliability indices of $R_1 = 0·057$ and $R_2 = 0·075$. *Crystal data:* space group, $P2_1/c$; $a = 11·461(3)$; $b = 12·052(4)$; $c = 15·409(3)$ Å; $\beta = 101·83(2)°$; $Z = 4$. There are two crystallographically independent molecules, which differ slightly but not in any chemically significant way in their dimensions. Each molecule lies on a crystallographic centre of inversion. The Figure shows the structure

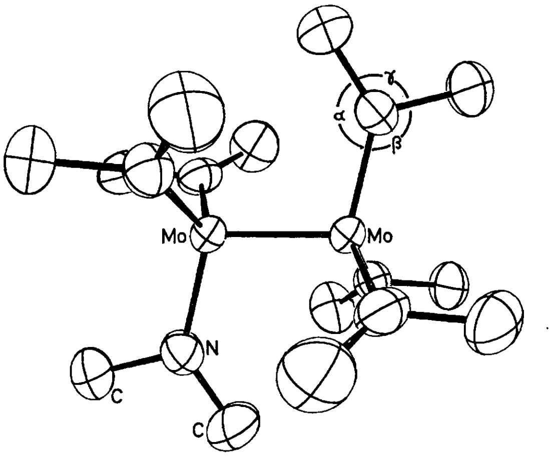

Figure. The molecular structure of $Mo_2(NMe_2)_6$. The important dimensions, averaged over the two independent molecules and over the symmetry-related bonds and angles within each one are: Mo–Mo, 2·214(2); Mo–N, 1·98(1); N–C (both sets together), 1·48(2) Å; ∠Mo–Mo–N, 103·7(3)°; α, 133(1)°; β, 116(1)°; γ, 110(1)°.

and gives important dimensions averaged for the two molecules.

The general features of the molecular structure, namely, the short Mo–Mo distance, the absence of bridging groups, and the staggered configuration all indicate that we are dealing here with an authentic triple bond. However, the structural details raise a number of interesting questions.

The configuration about each nitrogen atom is planar to within experimental error. Crystallographically, the molecules are centrosymmetric. If the Mo–Mo axis is taken to define the vertical direction, the skeletal planes of the six NMe_2 groups are each tilted from the vertical by about 6° so that the D_{3d} symmetry which would obtain if they were strictly vertical is reduced to S_6. The structure is thus consistent with the observation[5] that in solution the methyl groups are of two types (by n.m.r.) at low temperatures. The collapse and merging of the two resonances can be attributed to the rotation, singly or in concert, of the NMe_2 groups so as to interchange the proximal and distal methyl groups. The large chemical shift difference between the protons of the two sorts of methyl groups can now easily be correlated with their very different spatial relationships to the triple bond which would be expected to manifest marked diamagnetic anisotropy.

The Mo–Mo distance in this case [2·211(2) and 2·217(2) Å averaging to 2·214(2) Å] is considerably longer than the only previously reported Mo–Mo triple bond distance,[4] *viz.*, 2·167 Å in $Mo_2(CH_2SiMe_3)_6$. The latter is, in fact, surprisingly short, coming nearly into the range[1b] (2·09—2·15 Å) for Mo–Mo quadruple bonds, whereas the present distance appears to be more consistent with the lower bond order.

It is not certain what role π bonding between the Mo and N atoms may play in the structure of $Mo_2(NMe_2)_6$. The planarity of the $MoNC_2$ groups seems to suggest that some such π bonding occurs. The mean Mo–N bond length, when compared with the Mo–C bond length in $Mo_2(CH_2SiMe_3)_6$ with suitable allowance made for the inherently different covalent radii of $C(sp^3)$ and $N(sp^2)$ appears to be shortened by only 0·03—0·04 Å, however. Nevertheless, since there are six such Mo–N bonds, the total effect of even slight π bonding in each one could significantly affect the Mo–Mo bond.

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