Synthesis and Structural Characterization of the Metalloporphyrin Dimer, [Mo(TPP)]$_2$, the First Product from the Reaction of Mo(CO)$_6$ with H$_2$TPP (tetraphenylporphyrin)

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The properties and crystal structure of [Mo(TPP)]$_2$, obtained from the reaction of Mo(CO)$_6$ and H$_2$TPP (tetraphenylporphyrin), are discussed.

The first report of the synthesis of molybdenum porphyrins, from the reaction of Mo(CO)$_6$ with H$_2$TPP (tetraphenylporphyrin), to yield Mo(O)(OH)(TPP) appeared fifteen years ago.[1] This reaction has become the accepted starting point for the preparation of all other molybdenum porphyrin com-

pounds. Herein we present [1]H n.m.r. and X-ray crystallographic evidence that the initial product from this reaction, prior to the Al$_2$O$_3$ chromatographic purification, is actually the metal–metal bonded dimer, [Mo(TPP)]$_2$. This compound and other cofacially metal–metal bonded porphyrin deriva-

tives have considerable theoretical interest from a bonding and reactivity viewpoint because of steric repulsions of the porphyrin ligands.
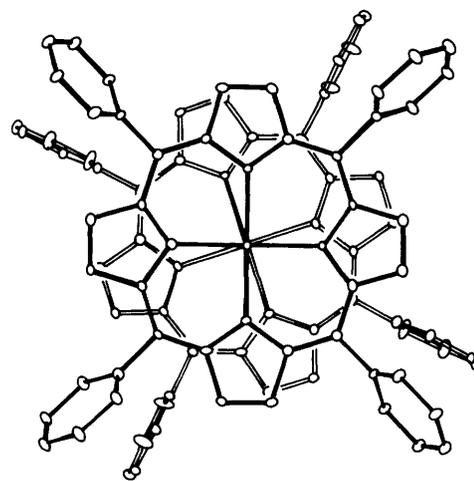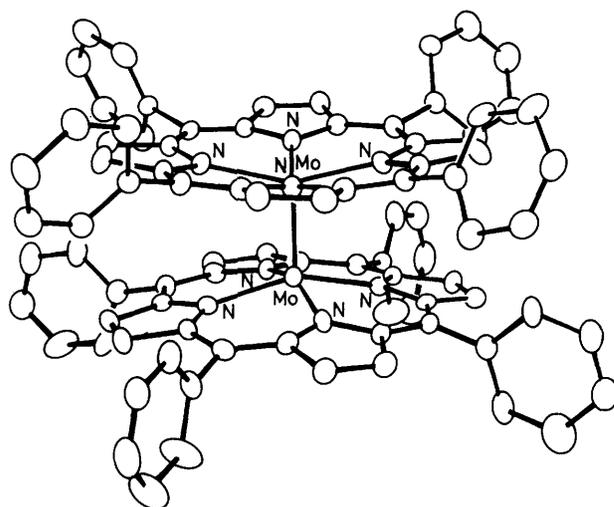
[Mo(TPP)]$_2$ is stable indefinitely in the solid state and moderately stable in solution. Chloroform solutions showed no significant decomposition after several hours; at 60 °C, benzene solutions start to decompose to O=Mo(TPP). Passing solutions over alumina, as described in the original purification procedure, leads to reaction and formation of O=M(OH)(TPP). A closely related complex, [Mo(TTP)]$_2$, prepared either from the vacuum pyrolysis of Mo(TTP)(PhC≡CPh)[2] or from the reaction of Mo(CO)$_4$Cl$_2$ with H$_2$TTP (tetratolylporphyrin)[3], has been reported. In contrast to the moderate stability of our [Mo(TPP)]$_2$, the [Mo(TTP)]$_2$ complex is described as very oxygen sensitive, a surprising finding in view of the similarity of properties expected for tetraphenyl and tetratolyl porphyrins.

The most pertinent features of the crystal structure† of [Mo(TPP)]$_2$, Figure 1, are summarized below: (1) The Mo–Mo distance of 2.239(1) Å is the longest that has been reported; most are in the range 2.07 to 2.18 Å.[4] (2) The two porphyrin cores are rotated 18° relative to one another. While this may lead to a significant reduction in the δ-bond order, larger rotations of Mo^{II}–Mo^{II} bonds, up to 40°, have been reported.[5] These parameters may be compared with the only other metal–metal bonded porphyrin dimer structurally characterized, [Ru(OEP)]$_2$ (OEP = octaethylporphyrinato), which only has a formal bond order of 2, and has a longer Ru–Ru distance, 2.408(1) Å with the two porphyrin rings rotated by 23.8°.[6] However, the currently accepted M.O. scheme for this complex does not lead to any rotational preference based on the metal–metal bonding. (3) Each porphyrin has a dome conformation with the Mo atoms displaced 0.458 Å from the N$_4$ co-ordination plane {compare with 0.30 Å for [Ru(OEP)]$_2$}. (4) The average distance between the N atoms of the two porphyrin skeletons is 3.208 Å. The observed metal–metal separation and porphyrin ring rotation is a minimum energy conformation, resulting from the balance between the attractive δ-bond interaction which is maximized in the eclipsed conformation and the sum of the non-bonding repulsions of the two porphyrin rings. (5) The relative orientation of all four phenyl rings of the two porphyrins is the same. However, the 'top' rings (Figure 1) are rotated 75° relative to the porphyrin plane while the 'bottom' rings are nearly perpendicular to the porphyrin plane (87° rotation). This appears to be the result of crystallographic packing considerations rather than any intrinsic property of the dimer molecules.

The ^{1}H n.m.r. spectra are complicated by (1) the distinguishability between o and o' as well as m and m' phenyl hydrogen atoms and (2) conformational isomers resulting from restricted rotation of the phenyl rings. The latter has two barriers: (a) rotation past the β-pyrrole hydrogens is large and does not occur on the n.m.r. time scale and (b) rotation of the top and bottom phenyl groups past one another. Using the

Figure 1. (a) ORTEP plot of [Mo(TPP)]$_2$ from the side illustrating the Mo–Mo bond and doming of the porphyrin ligand. Mo–Mo 2.239(1) Å; Mo–N(av.) 2.122(10) Å; distance of Mo from N$_4$ plane is 0.458 Å. (b) ORTEP plot as viewed down the Mo–Mo bond axis illustrating the 18° rotation of the two porphyrin ligands.

solid state crystal structure as a guide, it would appear that this barrier is not as large as that presented by the β-pyrrole hydrogen atoms. A mechanism for the simultaneous 'pseudo rotation' of all eight phenyl rings would be for rotation of the porphyrin rings by 36° about the Mo–Mo bond axis, through the maximum δ-bond interaction and back to the minimum energy conformation.

The ^{1}H n.m.r. of the bulk sample and also of the individual crystal used for the structure analysis confirms the diamagnetic nature of the complex and indicates that the solution contains a mixture of several conformers resulting from the afore described restricted rotation of the phenyl rings. The resonances for the major component occur at 6.90 (d, o'-Ph), 7.38 (t, m'-Ph), 7.77 (m, p-Ph), 7.92 (t, m-Ph), 8.51 (s, β-pyrrole-H), and 9.28 (d, o-Ph). These resonances exhibit a similar pattern to those reported for [Ru(TPP)]$_2$.[6] Appar-

ently, the longer Ru–Ru distance (2.408 Å) and larger separation between porphyrin rings as well as free rotation about the Ru–Ru bond does not result in locked conformations because only one species is observed in solution.

Variable temperature 270 MHz ^{1}H n.m.r. spectra of [Mo(TPP)]$_2$ in CD_2Cl_2 are consistent with the presence of conformational isomers and of a dynamic equilibrium involving rotation (more accurately, probably oscillations) of the porphyrin rings through the minimum of the δ-bond. As the temperature is lowered from room temperature to $-50\,°C$, the minor components first broaden (with some shifting) and are no longer observable. At $-60\,°C$ the major components also begin to broaden. The β-pyrrole protons which are non-equivalent in the solid state structure, appear as a singlet in solution, indicative of dynamic motion leading to equivalence on the n.m.r. time scale. The β-pyrrole resonance reaches its maximum broadening at $-75\,°C$ and then separates into two components at $-85\,°C$, confirming the non equivalence of the β-pyrrole hydrogens as the rotational motion is frozen out.

References

1 E. B. Fleischer and T. S. Srivastava, *Inorg. Chim. Acta*, 1971, **5**, 151.
2 J. P. Collman, C. E. Barnes, and L. K. Woo, *Proc. Natl. Acad. Sci. USA*, 1983, **80**, 7684.
3 J. P. Collman and L. K. Woo, *Proc. Natl. Acad. Sci. USA*, 1984, 2592.
4 F. A. Cotton and R. A. Walton, 'Multiple Bonds Between Metal Atoms,' John Wiley & Sons, New York, 1982, pp. 89—90.
5 F. L. Campbell, F. A. Cotton, and G. L. Powell, *Inorg. Chem.*, 1984, **23**, 4222.
6 J. P. Collman, C. E. Barnes, P. N. Swepston, and J. A. Ibers, *J. Am. Chem. Soc.*, 1984, **106**, 3500.