

A *Trans* Diperoxomolybdenum(VI) Porphyrin. Synthesis and Crystal Structure

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Recently the synthesis of several oxomolybdenum (V) derivatives $O=Mo(X)P$ and $(O=MoP)_2O$ have been reported ($X = F, Cl, OH, OOH$, and $P = TPP$ or OEP).¹⁻⁵ Reduction by hydrazine of the hydroxo species ($X = OH$) in pyridine led Fleischer¹ to the oxomolybdenum(IV) complex $O=Mo(py)TPP$. The simple oxomolybdenum(IV) derivative was also obtained by Buchler⁵ by reaction of OEP with molybdenum(III) trisacetylacetonate.

We were interested in the possibility of generating dioxygen complexes of molybdenum porphyrin. To a solution of $O=Mo(OH)TPP$ (1 mmol) in dichloromethane (150 ml) was added excess hydrogen peroxide. The mixture was stirred for 4-6 hours at 20 °C and after decanting to remove unreacted H_2O_2 the residual solution was concentrated and passed through a column packed with Al_2O_3 using CH_2Cl_2 as eluant. Precipitation by pentane gave the product in a good yield (ca. 90%). Chemical analysis indicated the formula $C_{44}H_{28}N_4O_4Mo$ (MoO_4TPP).

Well formed crystals suitable for X-ray examination were only obtained using tetraparatolylporphin instead of tetraphenylporphin. Accordingly all succeeding results refer to this latter molybdenum porphyrin complex. A deuteriochloroform solution gave a sharp spectrum in the nmr, thus showing the complex to be diamagnetic: $\delta(CDCl_3; Me_4Si)$: a singlet at 2.73 (H methyls), two doublets centered at 7.64 and 8.20 (H phenyls), a singlet at 9.03 (H pyrroles). In CH_2Cl_2 it gave a green solution with three broad visible absorptions at 616 nm ($\epsilon: 20 \times 10^3$), 576 (11×10^3) and 444 (25×10^4). Its ir spectrum showed two intense bands at 964 and 685 cm^{-1} while the intense absorption at 900 cm^{-1} present in the initial molybdenum complex ($Mo=O$ vibration) had disappeared.

The X-ray crystal structure was solved by the heavy atom method. *Crystal data*: Space group $I\bar{4}$ with $a = b = 14.669(4)$, $c = 9.571(3)$ Å; $Z = 2$; $D_c = 1.336$, $D_m = 1.32$ g cm^{-3} . Three-dimensional data were recorded on an automatic diffractometer (Philips PW 1100) using $Cu-K\alpha$ radiation and the structure refinement was by full-matrix least-squares techniques with anisotropic thermal parameters for the nonhydrogen atoms. The present value of

the discrepancy index R is 0.041 for the 906 non zero independent reflections having $\sigma(I)/I < 0.33$.

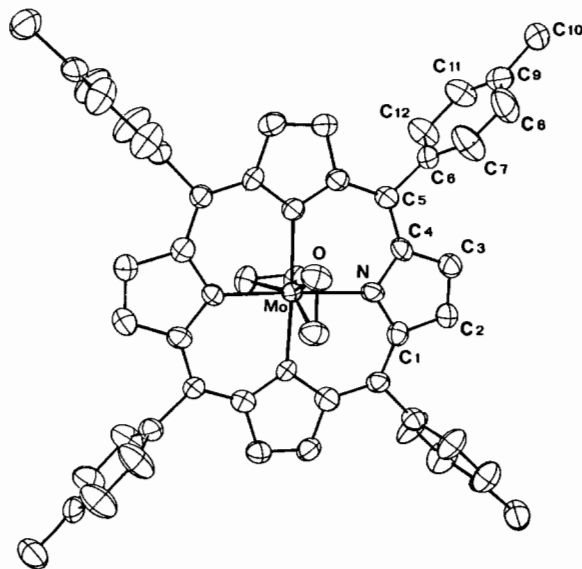


Figure. A perspective view of the molecule.

The Figure shows a perspective view of the complex which has S_4 symmetry. The molybdenum is octa-coordinated with the oxygen atoms of two peroxo groups and with the nitrogen atoms of the porphyrin ligand. The nitrogen atoms lie at ± 0.19 Å from the crystallographic (001) plane. The oxygen atoms are ± 1.83 Å away from this plane in an eclipsed position with respect to the nitrogen atoms. The Mo-N bond lengths are 2.096(4) Å and the Mo-O distances 1.958(4) Å. The oxygen-oxygen bond length is 1.399(6) Å and appears to be significantly shorter than those of 1.44-1.49 Å determined in a peroxotitaniumoctaethylporphyrin⁶ and in several peroxomolybdenum compounds.⁷

The individual pyrrole rings are planar within ± 0.02 Å. The molecular symmetry is such that two of the pyrrole rings are bent up and two are bent down by 3° from the (001) plane. As is normal for metallotetraphenylporphin complexes,⁸ the phenyl rings are rotated considerably out of the plane of the macrocycle ($\phi = 84.2^\circ$).

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