

Low-valent Molybdenum Porphyrin Derivatives: Synthesis and X-Ray Crystal Structures of Dinitrosyl- and Methanol(nitrosyl)-meso-tetra-*p*-tolylporphyrinatomolybdenum(II) Benzene Solvates

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Summary Reduction by zinc amalgam of dichloromolybdenum meso-tetra-*p*-tolylporphyrin [Mo(ttp)Cl₂] under NO leads to two low-valent nitrosyl molybdenum porphyrin derivatives Mo(ttp)(NO)₂·C₆H₆ and Mo(NO)(MeOH)·2C₆H₆; the molecular structures of both compounds were established by X-ray diffraction.

ONLY a few low-valent early transition metal porphyrin derivatives are known as the chemistry in the higher oxidation states of these metals is dominated by strong M=O bonds.¹ With such metals the classical synthetic methods used in metalloporphyrin chemistry lead, in general, to oxometal complexes.² We now report the preparation of two nitrosyl molybdenum porphyrins, Mo(ttp)(NO)₂·C₆H₆ (**1**) and Mo(ttp)(NO)(MeOH)·2C₆H₆ (**2**), and the X-ray structures of both compounds (ttp is the dianion of meso-tetra-*p*-tolylporphyrin).

Reduction by zinc amalgam in benzene of the dichloromolybdenum(IV) derivative³ Mo(ttp)Cl₂ under NO led to a green solution from which crystals of Mo(ttp)(NO)₂·C₆H₆ (**1**) [ν(NO) 1740 and 1600 cm⁻¹]⁴ could be isolated. When this green benzene solution was chromatographed on Al₂O₃ with CH₂Cl₂ (containing traces of methanol) as eluant it became red and Mo(ttp)(NO)(MeOH)·2C₆H₆ (**2**) [ν(NO) 1540 cm⁻¹]⁴ crystallized. Moreover, under NO the mononitrosyl derivative (**2**) reverts progressively to the dinitrosyl compound (**1**). This reaction can be easily followed by absorption spectroscopy; in CH₂Cl₂, the spectrum of (**2**) shows bands at 425 nm (10⁻³ ε 871), 551 (36),

586 (18), and 622 (8) nm, whereas (**1**) gives a hyperporphyrin-type spectra; the Soret band of (**2**) at 425 nm is replaced by two intense bands at 390 (513) and 468 nm (407) in the spectrum of (**1**).

Compound (**1**) is diamagnetic whereas (**2**) is paramagnetic and behaves as a low spin *d*⁵ species (*S* = 1/2), μ_{eff} = 1.71 B.M.⁵ The room temperature X-band e.s.r. powder spectrum shows a six-line signal characteristic of a low spin *d*⁵ species with ^{95,97}Mo (*I* = 5/2) hyperfine splitting: <*g*> = 1.968, <*A*^{95,97}Mo> = -99.66. These values and the absence of a ¹⁴N hyperfine structure are consistent with the localization of the unpaired electron in the molybdenum *d*_{xy} level.⁶

Similar routes to that just described with NO led to other low-valent molybdenum porphyrin derivatives: under CO, a dicarbonyl complex Mo(ttp)(CO)₂ has been isolated [ν(CO) 1940 and 1850 cm⁻¹], and in the presence of mono- and di-substituted acetylenes, complexes of the type Mo(ttp)(R-C≡C-R') (R = H, R' = Me, Ph, etc) have been obtained.⁷

The structures of (**1**) and (**2**) have been determined by X-ray crystallography. Both compounds were solvated by benzene molecules. *Crystal data*: (**1**): Mo(ttp)(NO)₂·C₆H₆, triclinic, space group *P* $\bar{1}$, *a* = 16.605(5), *b* = 13.131(4), *c* = 10.330(3) Å, α = 91.70(5), β = 91.84(5), γ = 94.49(5)°, *U* = 2243.1 Å³, *Z* = 2, 3135 independent reflections with *I* > 3σ(*I*), 2θ ≤ 100°, Cu-K_α radiation. (**2**): Mo(ttp)(NO)(MeOH)·2C₆H₆, monoclinic, space group *P*2₁/*m*, *a* = 12.691(4), *b* = 17.008(6), *c* = 12.083(4) Å, β = 98.86(3)°, *U* = 2576.9 Å³, *Z* = 2, 2679 independent

reflections with $I > 4\sigma(I)$ (step scan techniques, $2\theta \leq 110^\circ$, Cu- K_α radiation). The structures were solved by the heavy atom method and refined by least-square techniques. Present R_1 and R_2 values are 0.077 and 0.099 for (1), and 0.060 and 0.083 for (2).†

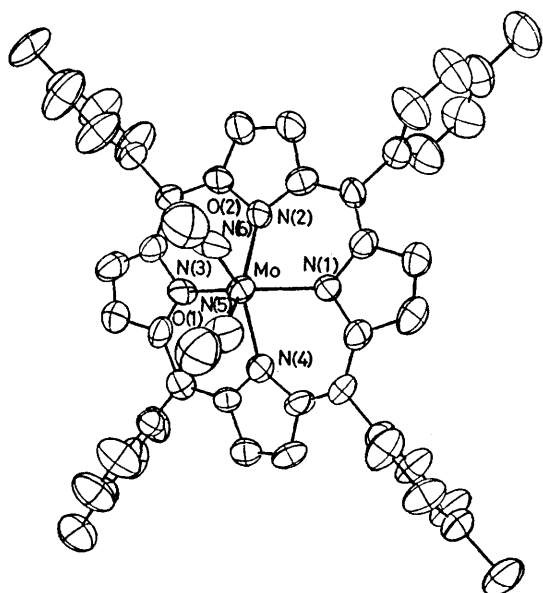


FIGURE 1. The structure of $\text{Mo}(\text{ttp})(\text{NO})_2$. Bond lengths: Mo-N(1), 2.140(8); Mo-N(2), 2.185(9); Mo-N(3), 2.130(8); Mo-N(4), 2.204(8) Å. Bond angles: N(1)-Mo-N(3), 144.0(4); N(2)-Mo-N(4), 122.0(4)°. Important intramolecular contacts: N(5)···N(4), 2.50(1); N(6)···N(2), 2.56(1); N(5)···N(6), 2.15(2); O(1)···O(2), 2.89(2) Å.

In (1), molybdenum is hexaco-ordinated and bonded to the four porphyrinato nitrogens and to the two nitrosyl nitrogens (Figure 1). What is surprising for a porphyrin derivative, although it is not completely unexpected for an $\{\text{M}(\text{NO})\}^{10}$ complex,⁸ is that the two NO ligands are in a *cis* position with respect to one another. The molybdenum is thus displaced by 0.99 Å from the porphyrinato skeleton towards the nitrosyls. The averaged Mo-N-O bond angle is 158.0(8)° and the mean Mo-N(NO) bond distance is 1.70(1) Å. Moreover, the nitrosyl groups are bent towards each other: $\angle \text{N}(5)\text{-Mo-N}(6) = 78.4(5)^\circ$ and $\angle \text{O}(1)\text{-Mo-O}(2) = 60.0(3)^\circ$ and are thus in an *atracto* conformation.⁹ As in $\text{Mo}(\text{ttp})(\text{O}_2)_2^{10}$ and $\text{Ti}(\text{oep})(\text{O}_2)$ (oep

= dianion of octaethylporphyrin),¹¹ the nitrosyl groups partially eclipse two porphyrinato nitrogens N(2) and N(4), and thus two types of Mo-N(porph.) distances are present: Mo-N(1) and Mo-N(3) with a mean value of 2.135(8) Å, and Mo-N(2) and Mo-N(4) with an average of 2.194(8) Å.

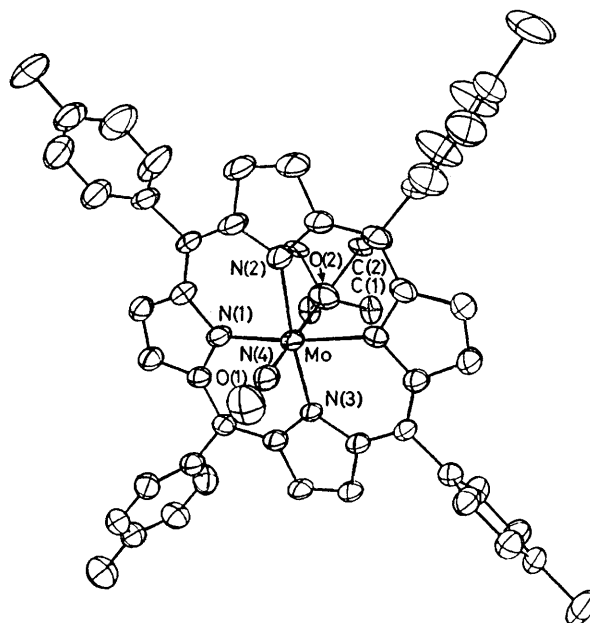


FIGURE 2. The structure of $\text{Mo}(\text{ttp})(\text{NO})(\text{MeOH})$. The four-fold positional disorder of the methanol methyl carbon is shown. Bond angles: average N(4)-Mo-N(1,2,3), 96.4(3); average O(2)-Mo-N(1,2,3), 83.5(2); O(2)-Mo-N(4), 179.6(3)°.

In (2), the molecule contains a mirror plane passing through the pyrrole nitrogens N(2) and N(3), the molybdenum atom, the nitrosyl group N(4)O(1), and the oxygen O(2) of methanol (Figure 2). The methyl carbon exhibits four-fold positional disorder. The axial NO is linear with an Mo-N-O angle of 179.8(4)° and an Mo-N(NO) bond distance of 1.746(6) Å. The molybdenum lies 0.28 Å out of the mean plane of the 24-atom porphyrinato core towards the nitrosyl ligand. The Mo-O(MeOH) distance is 2.284(5) Å, and the average Mo-N(porph.) distance is 2.091(4) Å.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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