

Synthesis and Molecular Structure of Di- and Tetra-nuclear Nitrido(oxo) Molybdenum(vi) Compounds containing Trimethylsiloxy and N-base Ligands

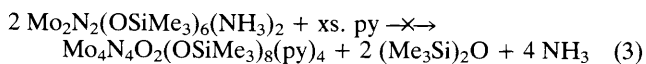
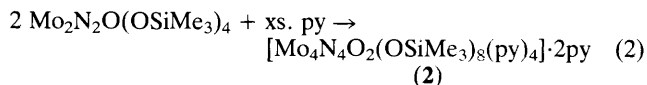
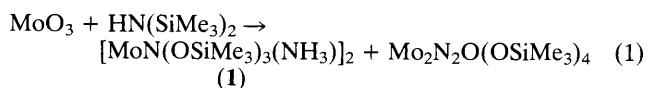
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The compounds $\text{Mo}_2\text{N}_2(\text{OSiMe}_3)_6(\text{NH}_3)_2$ (**1**) and $[\text{Mo}_4\text{N}_4\text{O}_2(\text{OSiMe}_3)_8(\text{py})_4]\cdot 2\text{py}$ (**2**) prepared from a co-condensation reaction between MoO_3 and $(\text{Me}_3\text{Si})_2\text{NH}$ [and also a solution synthesis for (**1**)] have been characterized spectroscopically and crystallographically, (py = pyridine).

This communication contributes to two areas. Firstly, unique synthetic routes to molybdenum(vi) nitride siloxides, and secondly, unusual molybdenum(vi) nitride structures.

The title compounds $\text{Mo}_2\text{N}_2(\mu\text{-OSiMe}_3)_2(\text{OSiMe}_3)_4(\text{NH}_3)_2$ (**1**) and $[\text{Mo}_4(\mu\text{-N})_4(\mu\text{-O})_2(\text{OSiMe}_3)_8(\text{py})_4]\cdot 2\text{py}$ (**2**) (py = pyridine) are prepared from the co-condensation reaction of MoO_3 with hexamethyldisilazane followed by addition of pyridine to obtain (**2**) [equations (1) and (2)].^{†‡} The reaction is believed to proceed through the co-ordination of the hexamethyldisilazane *via* nitrogen to a vacant Mo site followed by a N → O silyl group migration. The possibility of the N-base-assisted formation of (**2**) from (**1**) cannot be excluded. However, addition of pyridine to the hexane solution of (**1**) followed by crystallization did not lead to the formation of (**2**) [equation (3)].

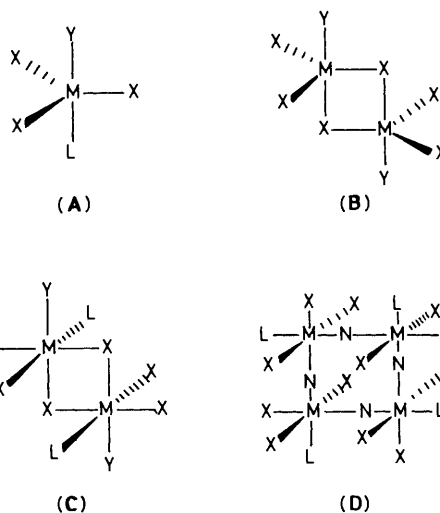


[†] Selected spectroscopic data: (**1**), ¹H n.m.r. (400 MHz, in [²H₆]benzene, reference to solvent protio impurity), δ 0.381 (s, 27H), 1.804 (s, br., 3H); i.r. ν(Mo≡N) 1049s, ν(N-H) 3401m, 3350m, 3234m, 3156m cm⁻¹; [ND₃ substituted analogue, ν(Mo≡N) 1051s, ν(N-D) 2538m, 2490m, 2367m, 2317m cm⁻¹] *m/z* (negative chemical ionisation), 379 [MoN(OSiMe₃)₃]⁻.

(**2**), ¹H n.m.r. (400 MHz, in [²H₈]toluene, reference to 2.09 p.p.m. of the solvent), δ 0.061 (s, 36H), 0.247 (s, 36H), 6.796 (m, 12H), 7.008 (m, 6H), 8.821 (m, 12H); i.r. ν(Mo≡N) 1026m, 1051m; *m/z* (negative chemical ionisation), 379 [MoN(OSiMe₃)₃]⁻.

[‡] Crystal data for (**1**): C₁₈H₆₀N₄O₆Si₆Mo₂, *M* = 789.09, monoclinic, space group *P*2₁/*a*, *a* = 10.851(4), *b* = 16.082(3), *c* = 12.282(4) Å, β = 109.14(2)°, *U* = 2025(1) Å³, *Z* = 2, *D*_c = 1.29 g cm⁻³, μ(Mo-Kα) = 8.09 cm⁻¹, crystal dimensions 0.2 × 0.2 × 0.05 mm. 2528 Observed reflections [*I* > 3σ(*I*)], 2θ_{max} = 50.0°, *R* = 0.055, *R*_w = 0.070.

(**2**): C₄₄H₉₂N₈O₁₀Si₈Mo₄·2(C₅H₅N), *M* = 1659.90, monoclinic, space group *C*2/*c*, *a* = 26.060(20), *b* = 14.250(6), *c* = 24.524(6) Å, β = 116.66(3)°, *U* = 8141(11) Å³, *Z* = 4, *D*_c = 1.35 g cm⁻³, μ(Mo-Kα) = 7.52 cm⁻¹, crystal dimensions 0.3 × 0.3 × 0.2 mm. 3259 Observed reflections [*I* > 3σ(*I*)], 2θ_{max} = 50.1°, *R* = 0.054, *R*_w = 0.065. Data were collected by the 2θ-ω scan method for (**1**) and ω scan method for (**2**) at 23 °C using a Rigaku AFC6 diffractometer. The structures were solved by the direct method and refined by full-matrix least-squares calculations using the 'TEXSAN, Tetryx Structural Analysis Package' from the Molecular Structure Corp., College Station, TX, U.S.A. Absorption and decay corrections were applied to both structure solutions. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Y = N or NO, X = ligand, L = Lewis base.

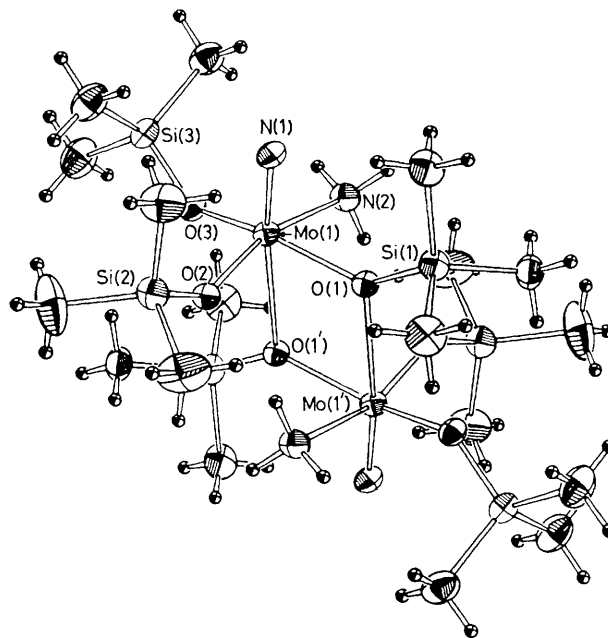


Figure 1. ORTEP drawing of $\text{Mo}_2\text{N}_2(\text{OSiMe}_3)_6(\text{NH}_3)_2$ (**1**), showing 20% thermal ellipsoids for the non-hydrogen atoms. Selected bond distances (Å) and angles (°): Mo(1)–N(1), 1.626(6); Mo(1)–N(2), 2.272(6); Mo(1)–O(1), 1.981(4); Mo(1)–O(2), 1.922(4); Mo(1)–O(3), 1.920(5); Mo(1)–O(1'), 2.669(4); N(1)–Mo(1)–O(1), 102.3(2); N(1)–Mo(1)–O(2), 103.0(2); N(1)–Mo(1)–O(3), 100.0(2); N(1)–Mo(1)–N(2), 95.0(3); N(1)–Mo(1)–O(1'), 171.6(2); O(3)–Mo(1)–O(1), 151.4(2); O(3)–Mo(1)–O(2), 99.2(2); O(3)–Mo(1)–N(2), 81.8(2); O(3)–Mo(1)–O(1'), 81.3(2); O(2)–Mo(1)–O(1), 93.2(2); O(2)–Mo(1)–N(2), 161.4(2); O(2)–Mo(1)–O(1'), 84.9(2); O(1)–Mo(1)–N(2), 78.5(2); O(1)–Mo(1)–O(1'), 74.2(2); Mo(1)–O(1)–Mo(1'), 105.8(2); N(2)–Mo(1)–O(1'), 76.9(2).

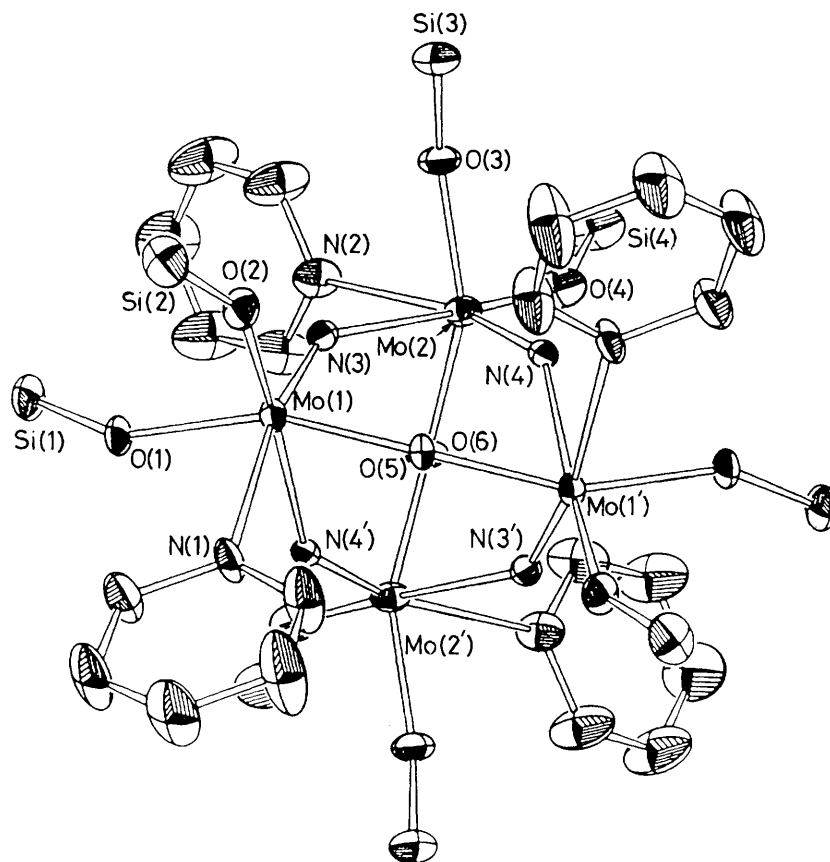
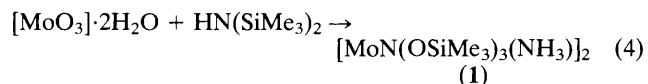


Figure 2. ORTEP drawing for $[\text{Mo}_4\text{N}_4\text{O}_2(\text{OSiMe}_3)_8(\text{py})_4]\cdot 2\text{py}$ showing 20% thermal ellipsoids. Hydrogens and methyl carbon atoms are omitted for clarity. Selected bond distances (\AA) and angles ($^\circ$): Mo(1)–N(1), 2.458(9); Mo(2)–N(2), 2.48(1); Mo(1)–N(3), 1.685(8); Mo(1)–N(4'), 2.157(8); Mo(1)–O(5), 1.908(3); Mo(2)–N(4), 1.688(8); Mo(2)–N(3), 2.152(8); Mo(2)–O(6), 1.909(3); N(3)–Mo(1)–O(5), 92.4(3); N(3)–Mo(1)–N(4), 86.1(3); O(5)–Mo(1)–N(4), 81.4(3); N(4)–Mo(2)–O(6), 92.2(3); N(4)–Mo(2)–N(3), 86.0(3); O(6)–Mo(2)–N(3), 81.4(3); Mo(1)–O(5)–Mo(1'), 146.3(5); Mo(2)–O(6)–Mo(2'), 146.6(5); Mo(1)–N(3)–Mo(2), 144.2(4); Mo(2')–N(4)–Mo(1), 144.0(4).

A high yield, one step synthesis of compound (**1**) has been achieved by the reaction of $[\text{MoO}_3]\cdot 2\text{H}_2\text{O}^1$ with hexamethyldisilazane at 85°C (typically 60–80% yield) [equation (4)].



Group VI transition metal nitrosyl alkoxides show structures of type (**A**), (**B**), and (**C**).^{2–4} However, for group VI transition metal nitride alkoxides,^{5–7} the only structure observed is the columnar, linear-chain polymer, type (**A**) with L a nitrido group from another molecule. When the basic four-co-ordinate unit, $\text{MoN}(\text{OR})_3$, is further supported by a co-ordinating ligand, structures (**C**) and (**D**) are expected. Until now, no report of a type (**C**) structure for a molybdenum(vi) nitride has appeared. Structure (**D**) is exclusively observed in nitrido halide molybdenum compounds^{8–12} with the general formula $[\text{MoNX}_3(\text{L})]_4$ where X is a halide and L an O-donating ligand.

Title compound (**1**) (Figure 1), type (**C**), is the first structurally characterized compound of this type for nitrido molybdenum compounds. Molybdenum atoms are in a distorted octahedral environment with the nitrido group in an apical position. The dimer molecule is composed of two five-co-ordinate monomeric fragments weakly bridging through two siloxy groups which are trans to $\text{Mo}\equiv\text{N}$ of another

fragment. The Mo–O bond distances for the two terminally bonded siloxy groups are identical (Mo–O = 1.921 \AA); however, that to the bridging siloxy group is slightly longer, [Mo(1)–O(1), 1.981(4) \AA], presumably owing to bridge formation.

The Mo(1)–O(1') bond distance [2.669(4) \AA] is too long to be a normal single bond, rather the bond may be described as a weak Mo ← O dative bond. This weak dative bond is easily broken in hydrocarbon solution at ambient temperature, which is confirmed by the sharp singlet OSiMe₃ resonance in the ¹H n.m.r. spectrum. This weak bridging bond results from the *trans* influence of the multiply bonded nitrido group¹² and possibly from the steric effect of the bulky siloxy group. The atoms, Mo(1), O(1), Si(1), Mo(1'), O(1'), and Si(1') are essentially in the same plane.

Title compound (**2**) (Figure 2) shows some interesting structural aspects and is the first example, to our knowledge, of a transition metal cage compound supported both by μ_2 -O and μ_2 -N bridges.¹³ Four molybdenum atoms are placed at the vertices of a perfect tetrahedron with the average Mo–Mo distance of 3.654(4) \AA and the average Mo–Mo–Mo angle of 60.00(9) $^\circ$. The bridging N and O are placed on the planes which contain two molybdenums and the centroid of the tetrahedron. This perfect Mo₄ tetrahedron clearly shows the bridging nature of the N and O in the same molecule. The asymmetric bond distances of Mo–N [1.69(1) and 2.15(1) \AA] are similar to the values observed for the cyclic tetramers of

[MoNX₃(L)]₄[structure (D)].⁸⁻¹⁰ In contrast to the asymmetric bond distances for Mo≡N, the molecule possesses a symmetric Mo-O [1.91(1) Å] bridge. Surprisingly, the bond angles, Mo-N-Mo [144.1(5)° av.] and Mo-O-Mo [146.5(11)° av.], are similar to each other, the Mo-N-Mo bond angles being far from appropriate for the almost linear geometry observed for the cyclic tetramers.⁸⁻¹⁰ The Mo-N(py) bond distance (2.47 Å av.) is quite long compared to those of other molybdenum compounds^{14,15} which is again a consequence of the *trans* influence of the nitrido group. This molecule may be viewed as a pairing of the two five-co-ordinate oxo-bridged dinuclear fragments in a cross-wise manner exclusively through the Mo≡N → Mo bonding.

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