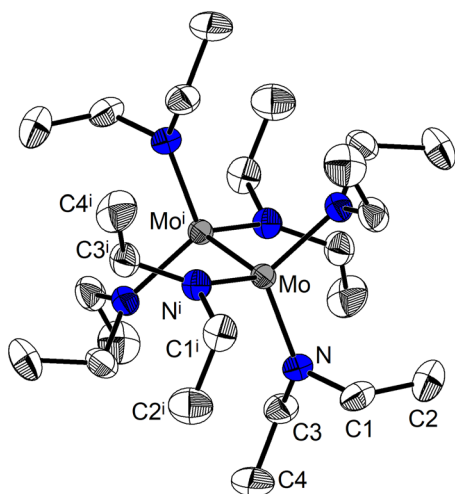


Tobias Brauner, Christoph Wagner and Kurt Merzweiler\*

# The crystal structure of Hexakis(diethylamido) dimolybdenum, $\text{Mo}_2(\text{NEt}_2)_6$



<https://doi.org/10.1515/ncrs-2021-0138>

Received April 12, 2021; accepted April 26, 2021;  
published online May 18, 2021

## Abstract

$\text{C}_{24}\text{H}_{60}\text{Mo}_2\text{N}_6$ , trigonal,  $R\bar{3}$  (no. 148),  $a = 16.7680(8)$  Å,  $c = 9.7523(4)$  Å,  $V = 2374.7(2)$  Å<sup>3</sup>,  $Z = 3$ ,  $R_{\text{gt}}(F) = 0.0205$ ,  $wR_{\text{ref}}(F^2) = 0.0517$ ,  $T = 213$  K.

CCDC no.: 2080037

The molecular structure is shown in the figure (Hydrogen atoms were omitted for clarity).

## Source of material

$\text{Mo}_2(\text{NEt}_2)_6$  was synthesized from  $\text{LiNEt}_2$  and  $\text{MoCl}_3(\text{THF})_3$  [1] by a slightly modified method according to Chisholm

\*Corresponding author: Kurt Merzweiler, Naturwissenschaftliche Fakultät II, Institut für Chemie, Martin-Luther-Universität Halle Wittenberg, Kurt-Mothes-Straße 2, 06120 Halle (Saale), Germany, E-mail: kurt.merzweiler@chemie.uni-halle.de. <https://orcid.org/0000-0001-6349-347X>

Tobias Brauner and Christoph Wagner, Naturwissenschaftliche Fakultät II, Institut für Chemie, Martin-Luther-Universität Halle Wittenberg, Kurt-Mothes-Straße 2, 06120 Halle (Saale), Germany. <https://orcid.org/0000-0001-6141-351X> (C. Wagner)

Table 1: Data collection and handling.

Crystal:	Yellow needle
Size:	$0.56 \times 0.07 \times 0.07$ mm
Wavelength:	Mo $K_{\alpha}$ radiation (0.71073 Å)
$\mu$ :	$0.81 \text{ mm}^{-1}$
Diffractometer, scan mode:	STOE IPDS 2, $\omega$ -scan
$\theta_{\text{max}}$ , completeness:	$26.0^\circ$ , >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	7139, 1039, 0.062
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 1007
$N(\text{param})_{\text{refined}}$ :	49
Programs:	SHELX [11, 12], Olex2 [13], Diamond [14], X-Area [15]

et al. [2]. Yellow single crystals of  $\text{Mo}_2(\text{NEt}_2)_6$  were obtained by sublimation at  $150^\circ\text{C}$  and  $10^{-5}$  mbar.

$^1\text{H-NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 1.11 (t, 36H,  $\text{CH}_3$ ,  $^3J_{\text{HH}} = 7.0$  Hz); 3.50 (q, 24H,  $\text{CH}_2$ ,  $^3J_{\text{HH}} = 7.0$  Hz),  $^{13}\text{C-NMR}$  (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 15.5 (s, 12 C,  $\text{CH}_3$ ); 51.9 (s; 12 C;  $\text{CH}_2$ ).

## Experimental details

Details of the crystal structure determination are collected in Table 1 and the results of structure calculation are listed in Table 2 with atomic coordinates.

The hydrogen atoms were placed on calculated positions and refined with a riding model. Their  $U_{\text{iso}}$  values were set to  $1.2 U_{\text{eq}}$  for  $\text{CH}_2$  groups and 1.5 for  $\text{CH}_3$  groups of the parent carbon atoms.

## Comment

Since the first synthesis of  $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$  around five decades ago [3], a large number of  $\text{Mo}_2\text{R}_6$  compounds comprising Mo–Mo triple bonds were synthesized and characterized by X-ray diffraction methods [4]. However, in the case of dialkylamide derivatives  $\text{Mo}_2(\text{NR}_2)_6$  X-ray structure determinations apart from that of the parent compound  $\text{Mo}_2(\text{NMe}_2)_6$  [5] are still rare. Some more structural data are available from complexes with  $\mu_2$ -bridging bis-amido ligands like  $\text{Mo}_2(\text{R}'\text{NCH}_2\text{CH}_2\text{NR}')_3$  ( $\text{R}' = \text{Me}$ ) [6],

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	U <sub>iso</sub> <sup>*</sup> /U <sub>eq</sub>
Mo	0.6667	0.3333	0.44755 (2)	0.02368 (11)
N	0.73519 (10)	0.46460 (10)	0.49924 (15)	0.0315 (3)
C1	0.76858 (15)	0.48126 (14)	0.6415 (2)	0.0414 (4)
H1	0.7292	0.4263	0.6961	0.050*
H2	0.7624	0.5322	0.6789	0.050*
C2	0.86725 (17)	0.50409 (19)	0.6573 (3)	0.0597 (6)
H3	0.8843	0.5141	0.7534	0.072*
H4	0.8738	0.4534	0.6229	0.072*
H5	0.9071	0.5594	0.6056	0.072*
C3	0.76863 (14)	0.54991 (13)	0.4211 (2)	0.0401 (4)
H6	0.7527	0.5344	0.3244	0.048*
H7	0.8359	0.5854	0.4277	0.048*
C4	0.72989 (19)	0.61003 (16)	0.4690 (3)	0.0585 (6)
H8	0.7549	0.6651	0.4128	0.070*
H9	0.6633	0.5761	0.4605	0.070*
H10	0.7467	0.6272	0.5640	0.070*

R' = i-Pr [7]), and mixed organyl/dialkylamide ligands, e.g. Mo<sub>2</sub>R'<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> (R' = benzyl, o-tolyl, p-tolyl [8], ethyl [9]).

The preparation of the title compound Mo<sub>2</sub>(NEt<sub>2</sub>)<sub>6</sub> was reported in 1976 [2]. Pale yellow single crystals suitable for X-ray diffraction were grown by sublimation in high vacuum.

Mo<sub>2</sub>(NEt<sub>2</sub>)<sub>6</sub> crystallizes in the trigonal system, space group  $R\bar{3}$  with three formula units per unit cell. The crystal structure consists of discrete molecules Mo<sub>2</sub>(NEt<sub>2</sub>)<sub>6</sub> without any unusual short intermolecular contacts. The Mo<sub>2</sub>(NEt<sub>2</sub>)<sub>6</sub> units are situated around a crystallographic center of inversion (Wyckoff site 3a). The asymmetric unit comprises one third of the molecule with the Mo atom situated on the  $\bar{3}$  axis and the remaining atoms at general positions. Thus, the Mo<sub>2</sub>(NEt<sub>2</sub>)<sub>6</sub> unit exhibits crystallographically imposed S<sub>6</sub> point symmetry, which implies a staggered conformation of the Mo(NEt<sub>2</sub>)<sub>3</sub> fragments. Generally, the staggered conformation is preferred for Mo<sub>2</sub>R<sub>6</sub> compounds with terminally binding ligands R [4]. In the case of  $\mu_2$ -bridging ligands steric strain usually forces eclipsed arrangements, i.e. Mo<sub>2</sub>(RNCH<sub>2</sub>CH<sub>2</sub>NR)<sub>3</sub> [10] (R = Me [5], i-Pr [6]).

Mo<sub>2</sub>(NEt<sub>2</sub>)<sub>6</sub> exhibits a Mo–Mo distance of 2.2277(4) Å which is close to that in Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> (2.21(2) Å) [1]. Comparable distances are found in the dimolybdenum hexaalkoxides Mo<sub>2</sub>(OR)<sub>6</sub> R = CH<sub>2</sub><sup>t</sup>Bu [9] with 2.222(2) Å and R = C(CF<sub>3</sub>)<sub>2</sub>CH<sub>3</sub> [10] with 2.2263(4) Å. Furthermore, the Mo–N distances (1.9723(1) Å) and the N–Mo–N angles (113.70(4)°) are in accordance with the observations in Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> (1.97(2)–2.00(1) Å and (113.5(2)–115.2(2)°). Like in the case of the NMe<sub>2</sub> derivative, the nitrogen atoms adopt a nearly planar coordination (sum of the angles around N: 359.6°).

The dihedral angle between the Mo<sub>2</sub>N plane and NC<sub>2</sub> plane is 16° and thus markedly larger than in case of Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> (0.3–3.6°). Obviously, this is a result of increased steric crowding in the NEt<sub>2</sub> derivative. The orientation of the ethyl groups with respect to the Mo–Mo triple bonds allows for a differentiation into proximal and distal groups. In the case of the proximal ethyl groups the Mo–N–C angles (133.1(1)°) are significantly larger than in the distal case (114.0(1)°). Similar disparities were observed for Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> (132° and 116°, resp.) [2].

**Author contributions:** All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

**Research funding:** We acknowledge the financial support within the funding programme Open Access Publishing by the German Research Foundation (DFG).

**Conflict of interest statement:** The authors declare no conflicts of interest regarding this article.

## References

1. Stoffelbach F., Saurenz D., Poli R. Improved preparations of molybdenum coordination compounds from tetrachlorobis(diethyl ether)molybdenum(IV). *Eur. J. Inorg. Chem.* 2001, 2001, 2699–2703.
2. Chisholm M. H., Cotton F. A., Frenz B. A., Reichert W. W., Shive L. W., Stults B. R. The molybdenum-molybdenum triple bond. 1. hexakis(dimethylamido)dimolybdenum and some homologs preparation, structure, and properties. *J. Am. Chem. Soc.* 1976, 98, 4469–4476.
3. Huq F., Mowat W., Shortland A., Skapski A. C., Wilkinson G. Crystal structure of hexakis(trimethylsilylmethyl)dimolybdenum. *J. Chem. Soc. D* 1971, 1079–1080, <https://doi.org/10.1039/c29710001079>.
4. Chisholm M. H., Hollandsworth C. B. X<sub>3</sub>M ≡ MX<sub>3</sub> compounds of molybdenum and tungsten. In *Multiple Bonds Between Metal Atoms*; Cotton F. A., Murillo C. A., Walton R. A., Eds.; Springer Science and Business Media Inc.: New York, 2005; pp. 203–210.
5. Blatchford T. P., Chisholm M. H., Folting K., Huffman J. C. Tris(N,N'-dimethylethylenediamido)dimolybdenum M ≡ M, A metallopropellane with a near-eclipsed central molybdenum nitride (Mo<sub>2</sub>N<sub>6</sub>) moiety. *Inorg. Chem.* 1980, 19, 3175–3176.
6. Armstrong W. H., Bonitatebus P. J. Crystal structure of tris(diisopropylethylenediamido)dimolybdenum(III) (Mo–Mo), C<sub>48</sub>H<sub>108</sub>Mo<sub>4</sub>N<sub>12</sub>. *Z. Kristallogr. N. Cryst. Struct.* 1999, 214, 241–242.
7. Chetcuti M. J., Chisholm M. H., Folting K., Haitko D. A., Huffman J. C., Janos J. 1,2-Dibenzyl- and 1,2-diaryltetrakis(dimethylamido) dimolybdenum and -ditungsten compounds M<sub>2</sub>R<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> M ≡ M, structural effects of Me<sub>2</sub>N-to-M π bonding. *J. Am. Chem. Soc.* 1983, 105, 1163–1170.
8. Chisholm M. H., Haitko D. A., Folting K., Huffman J. C. Preparation and characterization of 1,2-dialkyl compounds of dimolybdenum and ditungsten of formula M<sub>2</sub>R<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> M ≡ M. *J. Am. Chem. Soc.* 1981, 103, 4046–4053.

9. Chisholm M. H., Cotton F. A., Murillo C. A., Reichert W. W. The molybdenum-molybdenum triple bond. 2. Hexakis(alkoxy) dimolybdenum compounds: preparation, properties and structural characterization of hexakis(neopentoxy) dimolybdenum. *Inorg. Chem.* 1977, *16*, 1801–1808.
10. Bittner C., Ehrhorn H., Bockfeld D., Brandhorst K., Tamm M. Tuning the catalytic alkyne metathesis activity of molybdenum and tungsten 2,4,6-trimethylbenzylidyne complexes with fluoroalkoxide ligands  $\text{OC}(\text{CF}_3)_n \text{Me}_{3-n}$  ( $n = 0-3$ ). *Organometallics* 2017, *36*, 3398–3406.
11. Sheldrick G. M. SHELX – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
12. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
13. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
14. Brandenburg K. Visual crystal structure information system. (Ver. 4.6.4); Crystal Impact: Bonn, Germany, 2020.
15. X-AREA; STOE & Cie GmbH: Darmstadt (Germany), 2016.