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(Nitrate- κ O)oxido(5,10,15,20-tetra-phenylporphyrinato- κ^4 N)molybdenum(V) benzene solvate

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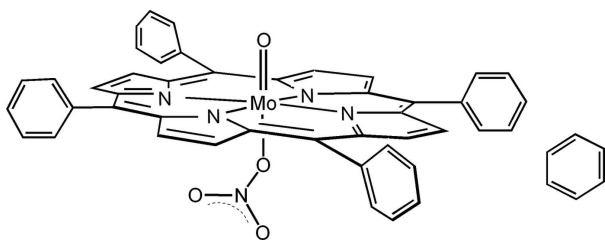
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 Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; disorder in main residue; R factor = 0.049; wR factor = 0.108; data-to-parameter ratio = 12.9.

In the title compound, $[\text{Mo}(\text{C}_{44}\text{H}_{28}\text{N}_4)(\text{NO}_3)\text{O}]\cdot\text{C}_6\text{H}_6$, the porphyrin ring is centrosymmetric. The Mo atom, oxide ion and nitrate ion are equally disordered over two sites, such that the Mo atom is displaced by 0.366 (1) Å towards the oxide ion from the 24-atom mean plane of the porphyrin, and also makes a long Mo—O bond to a nitrate O atom. A centrosymmetric benzene solvent molecule is situated between adjacent porphyrin molecules.

Related literature

For the structure of $(\text{TPP})\text{Mo}(\text{O})(\text{ONO}_2)$ (TPP is the tetraphenylporphyrinate dianion) with CH_2Cl_2 as the solvate, see: Okubo *et al.* (1999). For the crystal structures of related molybdenum(V)-oxo porphyrin complexes, see: Harada *et al.* (2004); Kim *et al.* (1987); Hamstra *et al.* (1999); Fujihara *et al.* (2002); Ledon & Mentzen (1978); Liu *et al.* (2001); Imamura & Furusaki (1990); Cheng & Scheidt (1996).



Experimental

Crystal data

 $[\text{Mo}(\text{C}_{44}\text{H}_{28}\text{N}_4)(\text{NO}_3)\text{O}]\cdot\text{C}_6\text{H}_6$
 $M_r = 864.76$

 Triclinic, $P\bar{1}$
 $a = 8.6846$ (14) Å

 $b = 11.2895$ (18) Å
 $c = 11.7180$ (18) Å
 $\alpha = 61.617$ (5)°
 $\beta = 79.283$ (6)°
 $\gamma = 76.354$ (6)°
 $V = 978.6$ (3) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.39$ mm⁻¹
 $T = 120$ (2) K
 $0.16 \times 0.08 \times 0.02$ mm

Data collection

 Bruker SMART APEX CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2007)
 $T_{\min} = 0.938$, $T_{\max} = 0.994$

 10263 measured reflections
 3836 independent reflections
 3395 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.108$
 $S = 1.16$
 3836 reflections
 298 parameters

 3 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.43$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.47$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|---------------------|-----------|--------|-----------|
| Mo1—O1 | 1.678 (9) | Mo1—N2 | 2.139 (2) |
| Mo1—N1 ¹ | 2.039 (2) | Mo1—N1 | 2.159 (2) |
| Mo1—N2 ² | 2.044 (2) | Mo1—O2 | 2.227 (9) |

 Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2799).

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supplementary materials

Acta Cryst. (2008). E64, m1337 [doi:10.1107/S1600536808030705]

(Nitrato- κ O)oxido(5,10,15,20-tetraphenylporphyrinato- κ^4 N)molybdenum(V) benzene solvate

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Comment

In this paper, we report the structure of the title compound, (I), a six-coordinate nitrate molybdenum(V)-oxo tetraphenylporphyrin with benzene as solvate, and the new approach to synthesize the compound using oxochloromolybdenum tetraphenylporphyrin as the precursor. The structure of the related compound with CH_2Cl_2 as solvate has been reported previously (Okubo *et al.* 1999).

The molecular structure of (I) is shown in Fig. 1. Both the metal complex and the benzene molecule were found to sit on a crystallographic center of symmetry. The porphyrin core of the compound has a slight wave shape. The Mo atom is displaced by 0.366 (1) Å from the 24-atom mean porphyrin plane toward the oxo ion. The nitrate ligand binds to the molybdenum atom through one of its oxygen atoms. Selected bond lengths are given in Table 1. The Mo(V)=O distance of 1.678 (9) Å in (I) is in the range of those [1.658 (2)–1.722 (6) Å] reported previously for other molybdenum(V)-oxo porphyrin complexes (Harada *et al.*, 2004; Kim *et al.*, 1987; Hamstra *et al.*, 1999; Fujihara *et al.*, 2002; Ledon & Mentzen, 1978; Liu *et al.*, 2001; Imamura & Furusaki, 1990; Cheng & Scheidt, 1996). The O=Mo—O linkage in (I) is essentially linear with a bond angle of 174.4 (16)°. A benzene molecule is situated between two adjacent porphyrin molecules with 1:1 benzene/porphyrin stoichiometry.

Experimental

To a toluene solution (20 ml) of (TPP)Mo(O)Cl (0.015 g, 0.020 mmol) (Ledon & Mentzen, 1978) under nitrogen was added LiAlH_4 (0.0016 g, 0.42 mmol) (Aldrich Chemical Company, used as received). Then, nitric oxide (98%; Matheson Gas, purified by passing through KOH pellets and a cold trap (dry ice/acetone) to remove higher nitrogen oxides) was bubbled through the mixture for 15 min. The mixture was stirred for an additional 30 min and filtered. A dark green solid was obtained after removal of solvent under vacuum. A suitable dark green prism-shaped crystal of (I) was grown by slow evaporation of a benzene solution of the product at room temperature under nitrogen.

Refinement

The H atoms were positioned geometrically (C—H = 0.95 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The metal, the oxo ion and the nitrate group are disordered by 50% across the center of symmetry.

Figures

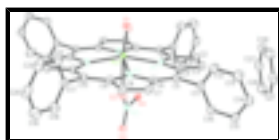


Fig. 1. The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level (H atoms omitted for clarity). The unlabelled atoms of the complex and the benzene molecule are generated by the symmetry operations (1-x, 1-y, 1-z) and (-x, -y, 1-z), respectively.

(Nitrato- κ O)oxido(tetraphenylporphyrinato- κ^4 N)molybdenum(V) benzene solvate

Crystal data

| | |
|---|---|
| $[\text{Mo}(\text{C}_{44}\text{H}_{28}\text{N}_4)(\text{NO}_3)\text{O}]\cdot\text{C}_6\text{H}_6$ | $Z = 1$ |
| $M_r = 864.76$ | $F_{000} = 443$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.467 \text{ Mg m}^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation |
| $a = 8.6846 (14) \text{ \AA}$ | $\lambda = 0.71073 \text{ \AA}$ |
| $b = 11.2895 (18) \text{ \AA}$ | Cell parameters from 7414 reflections |
| $c = 11.7180 (18) \text{ \AA}$ | $\theta = 3.2\text{--}26.3^\circ$ |
| $\alpha = 61.617 (5)^\circ$ | $\mu = 0.39 \text{ mm}^{-1}$ |
| $\beta = 79.283 (6)^\circ$ | $T = 120 (2) \text{ K}$ |
| $\gamma = 76.354 (6)^\circ$ | Prism, green |
| $V = 978.6 (3) \text{ \AA}^3$ | $0.16 \times 0.08 \times 0.02 \text{ mm}$ |

Data collection

| | |
|---|--|
| Bruker SMART APEX CCD diffractometer | 3836 independent reflections |
| Radiation source: fine-focus sealed tube | 3395 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.023$ |
| $T = 120(2) \text{ K}$ | $\theta_{\text{max}} = 26.0^\circ$ |
| ω scans | $\theta_{\text{min}} = 2.0^\circ$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2007) | $h = -10 \rightarrow 10$ |
| $T_{\text{min}} = 0.938$, $T_{\text{max}} = 0.994$ | $k = -13 \rightarrow 13$ |
| 10263 measured reflections | $l = -14 \rightarrow 14$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.049$ | H-atom parameters constrained |
| $wR(F^2) = 0.108$ | $w = 1/[\sigma^2(F_o^2) + (0.032P)^2 + P]$ |
| $S = 1.16$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 3836 reflections | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 298 parameters | $\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$ |
| 3 restraints | $\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|-------------|-------------|----------------------------------|-----------|
| Mo1 | 0.47549 (6) | 0.53402 (4) | 0.48115 (5) | 0.02365 (15) | 0.50 |
| O1 | 0.354 (3) | 0.668 (2) | 0.380 (2) | 0.031 (3) | 0.50 |
| O2 | 0.652 (3) | 0.356 (2) | 0.598 (2) | 0.035 (3) | 0.50 |
| N3 | 0.6402 (5) | 0.2554 (5) | 0.7138 (5) | 0.0285 (10) | 0.50 |
| O4 | 0.5111 (4) | 0.2409 (4) | 0.7791 (4) | 0.0340 (9) | 0.50 |
| O3 | 0.7618 (5) | 0.1698 (4) | 0.7537 (4) | 0.0369 (9) | 0.50 |
| N1 | 0.3480 (3) | 0.3743 (2) | 0.5196 (2) | 0.0283 (5) | |
| N2 | 0.6227 (2) | 0.4736 (2) | 0.3433 (2) | 0.0275 (5) | |
| C1 | 0.2198 (3) | 0.3414 (3) | 0.6109 (3) | 0.0289 (6) | |
| C2 | 0.1423 (3) | 0.2553 (3) | 0.5895 (3) | 0.0335 (6) | |
| H2 | 0.0503 | 0.2181 | 0.6382 | 0.040* | |
| C3 | 0.2241 (3) | 0.2368 (3) | 0.4875 (3) | 0.0323 (6) | |
| H3 | 0.1994 | 0.1845 | 0.4516 | 0.039* | |
| C4 | 0.3545 (3) | 0.3100 (3) | 0.4433 (2) | 0.0272 (6) | |
| C5 | 0.4674 (3) | 0.3184 (3) | 0.3386 (2) | 0.0275 (6) | |
| C6 | 0.5898 (3) | 0.3952 (3) | 0.2919 (2) | 0.0275 (6) | |
| C7 | 0.7039 (3) | 0.4052 (3) | 0.1842 (3) | 0.0310 (6) | |
| H7 | 0.7085 | 0.3621 | 0.1307 | 0.037* | |
| C8 | 0.8043 (3) | 0.4869 (3) | 0.1715 (3) | 0.0314 (6) | |
| H8 | 0.8924 | 0.5105 | 0.1083 | 0.038* | |
| C9 | 0.7534 (3) | 0.5311 (3) | 0.2710 (3) | 0.0294 (6) | |
| C10 | 0.8261 (3) | 0.6181 (3) | 0.2904 (3) | 0.0288 (6) | |
| C11 | 0.4563 (3) | 0.2361 (3) | 0.2711 (3) | 0.0287 (6) | |
| C12 | 0.3794 (4) | 0.2953 (3) | 0.1587 (3) | 0.0498 (9) | |
| H12 | 0.3345 | 0.3897 | 0.1219 | 0.060* | |
| C13 | 0.3678 (5) | 0.2168 (3) | 0.0993 (3) | 0.0553 (10) | |
| H13 | 0.3158 | 0.2583 | 0.0214 | 0.066* | |
| C14 | 0.4304 (4) | 0.0806 (3) | 0.1518 (3) | 0.0380 (7) | |
| H14 | 0.4194 | 0.0271 | 0.1121 | 0.046* | |
| C15 | 0.5086 (3) | 0.0221 (3) | 0.2614 (3) | 0.0354 (6) | |
| H15 | 0.5536 | -0.0722 | 0.2976 | 0.042* | |
| C16 | 0.5226 (3) | 0.1001 (3) | 0.3206 (3) | 0.0326 (6) | |
| H16 | 0.5789 | 0.0588 | 0.3962 | 0.039* | |

supplementary materials

| | | | | |
|-----|-------------|-------------|-------------|-------------|
| C17 | 0.9593 (3) | 0.6766 (3) | 0.1930 (3) | 0.0300 (6) |
| C18 | 1.1139 (4) | 0.6125 (3) | 0.2087 (3) | 0.0480 (8) |
| H18 | 1.1393 | 0.5289 | 0.2842 | 0.058* |
| C19 | 1.2343 (4) | 0.6692 (4) | 0.1146 (4) | 0.0599 (10) |
| H19 | 1.3417 | 0.6248 | 0.1263 | 0.072* |
| C20 | 1.1979 (4) | 0.7891 (4) | 0.0050 (3) | 0.0495 (9) |
| H20 | 1.2803 | 0.8280 | -0.0590 | 0.059* |
| C21 | 1.0445 (4) | 0.8521 (3) | -0.0122 (3) | 0.0480 (8) |
| H21 | 1.0194 | 0.9340 | -0.0892 | 0.058* |
| C22 | 0.9241 (4) | 0.7975 (3) | 0.0823 (3) | 0.0412 (7) |
| H22 | 0.8172 | 0.8433 | 0.0707 | 0.049* |
| C26 | 0.0430 (5) | -0.0977 (4) | 0.6200 (4) | 0.0581 (10) |
| H26 | 0.0726 | -0.1658 | 0.7037 | 0.070* |
| C27 | -0.0779 (4) | 0.0081 (4) | 0.6088 (4) | 0.0515 (9) |
| H27 | -0.1319 | 0.0135 | 0.6850 | 0.062* |
| C28 | -0.1220 (4) | 0.1060 (4) | 0.4897 (4) | 0.0566 (9) |
| H28 | -0.2066 | 0.1794 | 0.4823 | 0.068* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Mo1 | 0.0272 (3) | 0.0225 (3) | 0.0250 (3) | -0.0065 (2) | 0.0001 (2) | -0.0135 (3) |
| O1 | 0.043 (4) | 0.030 (6) | 0.011 (5) | -0.001 (4) | 0.002 (3) | -0.006 (5) |
| O2 | 0.035 (4) | 0.038 (6) | 0.026 (8) | -0.004 (4) | -0.008 (5) | -0.008 (5) |
| N3 | 0.024 (2) | 0.033 (3) | 0.039 (3) | -0.005 (2) | 0.002 (2) | -0.026 (3) |
| O4 | 0.035 (2) | 0.028 (2) | 0.037 (2) | -0.0094 (16) | 0.0041 (17) | -0.0134 (18) |
| O3 | 0.036 (2) | 0.029 (2) | 0.044 (2) | -0.0025 (17) | -0.0056 (18) | -0.0156 (19) |
| N1 | 0.0291 (12) | 0.0361 (13) | 0.0240 (11) | -0.0124 (10) | 0.0033 (9) | -0.0160 (10) |
| N2 | 0.0271 (12) | 0.0343 (13) | 0.0255 (11) | -0.0119 (9) | 0.0022 (9) | -0.0156 (10) |
| C1 | 0.0284 (14) | 0.0314 (14) | 0.0267 (14) | -0.0088 (11) | 0.0002 (11) | -0.0123 (12) |
| C2 | 0.0318 (15) | 0.0360 (16) | 0.0354 (16) | -0.0125 (12) | 0.0014 (12) | -0.0167 (13) |
| C3 | 0.0351 (15) | 0.0309 (15) | 0.0348 (15) | -0.0095 (12) | -0.0004 (12) | -0.0172 (13) |
| C4 | 0.0297 (14) | 0.0276 (14) | 0.0252 (13) | -0.0069 (11) | -0.0018 (11) | -0.0120 (11) |
| C5 | 0.0311 (14) | 0.0268 (14) | 0.0251 (13) | -0.0055 (11) | -0.0026 (11) | -0.0117 (11) |
| C6 | 0.0306 (14) | 0.0264 (14) | 0.0237 (13) | -0.0040 (11) | -0.0020 (11) | -0.0102 (11) |
| C7 | 0.0389 (16) | 0.0281 (14) | 0.0264 (14) | -0.0062 (12) | 0.0014 (12) | -0.0140 (12) |
| C8 | 0.0344 (15) | 0.0308 (15) | 0.0267 (14) | -0.0086 (12) | 0.0042 (11) | -0.0122 (12) |
| C9 | 0.0301 (14) | 0.0334 (15) | 0.0252 (14) | -0.0080 (11) | 0.0008 (11) | -0.0135 (12) |
| C10 | 0.0268 (14) | 0.0320 (14) | 0.0267 (14) | -0.0079 (11) | 0.0017 (11) | -0.0125 (12) |
| C11 | 0.0310 (14) | 0.0313 (14) | 0.0266 (14) | -0.0109 (11) | 0.0038 (11) | -0.0149 (12) |
| C12 | 0.075 (2) | 0.0312 (16) | 0.0470 (19) | 0.0034 (16) | -0.0252 (17) | -0.0198 (15) |
| C13 | 0.083 (3) | 0.0436 (19) | 0.047 (2) | 0.0021 (18) | -0.0304 (19) | -0.0239 (17) |
| C14 | 0.0465 (18) | 0.0402 (17) | 0.0360 (16) | -0.0147 (14) | 0.0011 (13) | -0.0224 (14) |
| C15 | 0.0397 (16) | 0.0299 (15) | 0.0363 (16) | -0.0106 (12) | 0.0029 (13) | -0.0148 (13) |
| C16 | 0.0373 (16) | 0.0329 (15) | 0.0275 (14) | -0.0085 (12) | -0.0033 (12) | -0.0123 (12) |
| C17 | 0.0328 (15) | 0.0342 (15) | 0.0290 (14) | -0.0126 (12) | 0.0038 (11) | -0.0183 (12) |
| C18 | 0.0372 (18) | 0.0411 (18) | 0.049 (2) | -0.0083 (14) | 0.0055 (14) | -0.0095 (15) |
| C19 | 0.0358 (19) | 0.058 (2) | 0.072 (3) | -0.0119 (16) | 0.0178 (17) | -0.025 (2) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C20 | 0.061 (2) | 0.048 (2) | 0.048 (2) | -0.0306 (17) | 0.0262 (17) | -0.0293 (17) |
| C21 | 0.069 (2) | 0.0421 (18) | 0.0316 (17) | -0.0245 (17) | 0.0027 (15) | -0.0112 (14) |
| C22 | 0.0448 (18) | 0.0402 (17) | 0.0358 (17) | -0.0139 (14) | -0.0026 (14) | -0.0122 (14) |
| C26 | 0.064 (2) | 0.046 (2) | 0.056 (2) | -0.0140 (18) | -0.0220 (19) | -0.0079 (17) |
| C27 | 0.0438 (19) | 0.062 (2) | 0.057 (2) | -0.0220 (17) | -0.0022 (16) | -0.0294 (19) |
| C28 | 0.047 (2) | 0.046 (2) | 0.082 (3) | 0.0000 (16) | -0.0212 (19) | -0.031 (2) |

Geometric parameters (Å, °)

| | | | |
|--------------------------------------|------------|--------------------------|-----------|
| Mo1—O1 | 1.678 (9) | C10—C17 | 1.493 (4) |
| Mo1—N1 ⁱ | 2.039 (2) | C11—C16 | 1.373 (4) |
| Mo1—N2 ⁱ | 2.044 (2) | C11—C12 | 1.380 (4) |
| Mo1—N2 | 2.139 (2) | C12—C13 | 1.391 (4) |
| Mo1—N1 | 2.159 (2) | C12—H12 | 0.9500 |
| Mo1—O2 | 2.227 (9) | C13—C14 | 1.367 (4) |
| O2—N3 | 1.30 (2) | C13—H13 | 0.9500 |
| N3—O4 | 1.232 (6) | C14—C15 | 1.361 (4) |
| N3—O3 | 1.241 (6) | C14—H14 | 0.9500 |
| N1—C1 | 1.377 (3) | C15—C16 | 1.391 (4) |
| N1—C4 | 1.382 (3) | C15—H15 | 0.9500 |
| N1—Mo1 ⁱ | 2.039 (2) | C16—H16 | 0.9500 |
| N2—C9 | 1.377 (3) | C17—C18 | 1.366 (4) |
| N2—C6 | 1.385 (3) | C17—C22 | 1.381 (4) |
| N2—Mo1 ⁱ | 2.044 (2) | C18—C19 | 1.391 (4) |
| C1—C10 ⁱ | 1.398 (4) | C18—H18 | 0.9500 |
| C1—C2 | 1.436 (4) | C19—C20 | 1.370 (5) |
| C2—C3 | 1.352 (4) | C19—H19 | 0.9500 |
| C2—H2 | 0.9500 | C20—C21 | 1.356 (5) |
| C3—C4 | 1.432 (4) | C20—H20 | 0.9500 |
| C3—H3 | 0.9500 | C21—C22 | 1.387 (4) |
| C4—C5 | 1.400 (4) | C21—H21 | 0.9500 |
| C5—C6 | 1.395 (4) | C22—H22 | 0.9500 |
| C5—C11 | 1.507 (3) | C26—C27 | 1.363 (5) |
| C6—C7 | 1.428 (4) | C26—C28 ⁱⁱ | 1.374 (5) |
| C7—C8 | 1.354 (4) | C26—H26 | 0.9500 |
| C7—H7 | 0.9500 | C27—C28 | 1.360 (5) |
| C8—C9 | 1.436 (4) | C27—H27 | 0.9500 |
| C8—H8 | 0.9500 | C28—C26 ⁱⁱ | 1.374 (5) |
| C9—C10 | 1.404 (4) | C28—H28 | 0.9500 |
| C10—C1 ⁱ | 1.398 (4) | | |
| O1—Mo1—N1 ⁱ | 101.6 (11) | C9—C8—H8 | 126.2 |
| O1—Mo1—N2 ⁱ | 100.8 (9) | N2—C9—C10 | 126.3 (2) |
| N1 ⁱ —Mo1—N2 ⁱ | 90.76 (8) | N2—C9—C8 | 108.4 (2) |
| O1—Mo1—N2 | 99.3 (8) | C10—C9—C8 | 125.3 (2) |
| N1 ⁱ —Mo1—N2 | 88.93 (8) | C1 ⁱ —C10—C9 | 125.7 (2) |
| N2 ⁱ —Mo1—N2 | 159.56 (3) | C1 ⁱ —C10—C17 | 117.6 (2) |

supplementary materials

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| O1—Mo1—N1 | 98.5 (11) | C9—C10—C17 | 116.7 (2) |
| N1 ⁱ —Mo1—N1 | 159.74 (3) | C16—C11—C12 | 118.7 (3) |
| N2 ⁱ —Mo1—N1 | 88.23 (8) | C16—C11—C5 | 120.4 (2) |
| N2—Mo1—N1 | 85.07 (8) | C12—C11—C5 | 120.9 (2) |
| O1—Mo1—O2 | 174.4 (16) | C11—C12—C13 | 120.0 (3) |
| N1 ⁱ —Mo1—O2 | 77.5 (8) | C11—C12—H12 | 120.0 |
| N2 ⁱ —Mo1—O2 | 84.8 (7) | C13—C12—H12 | 120.0 |
| N2—Mo1—O2 | 75.2 (7) | C14—C13—C12 | 120.6 (3) |
| N1—Mo1—O2 | 82.2 (8) | C14—C13—H13 | 119.7 |
| N3—O2—Mo1 | 132.5 (17) | C12—C13—H13 | 119.7 |
| O4—N3—O3 | 121.0 (5) | C15—C14—C13 | 119.6 (3) |
| O4—N3—O2 | 121.1 (11) | C15—C14—H14 | 120.2 |
| O3—N3—O2 | 117.8 (10) | C13—C14—H14 | 120.2 |
| C1—N1—C4 | 107.7 (2) | C14—C15—C16 | 120.1 (3) |
| C1—N1—Mo1 ⁱ | 126.60 (17) | C14—C15—H15 | 119.9 |
| C4—N1—Mo1 ⁱ | 124.54 (17) | C16—C15—H15 | 119.9 |
| C1—N1—Mo1 | 123.63 (17) | C11—C16—C15 | 120.8 (3) |
| C4—N1—Mo1 | 127.31 (17) | C11—C16—H16 | 119.6 |
| C9—N2—C6 | 107.7 (2) | C15—C16—H16 | 119.6 |
| C9—N2—Mo1 ⁱ | 126.73 (17) | C18—C17—C22 | 119.2 (3) |
| C6—N2—Mo1 ⁱ | 124.14 (17) | C18—C17—C10 | 122.1 (3) |
| C9—N2—Mo1 | 123.49 (17) | C22—C17—C10 | 118.7 (3) |
| C6—N2—Mo1 | 127.58 (17) | C17—C18—C19 | 120.3 (3) |
| N1—C1—C10 ⁱ | 126.1 (2) | C17—C18—H18 | 119.9 |
| N1—C1—C2 | 108.4 (2) | C19—C18—H18 | 119.9 |
| C10 ⁱ —C1—C2 | 125.4 (2) | C20—C19—C18 | 120.0 (3) |
| C3—C2—C1 | 107.7 (2) | C20—C19—H19 | 120.0 |
| C3—C2—H2 | 126.2 | C18—C19—H19 | 120.0 |
| C1—C2—H2 | 126.2 | C21—C20—C19 | 120.0 (3) |
| C2—C3—C4 | 107.9 (2) | C21—C20—H20 | 120.0 |
| C2—C3—H3 | 126.0 | C19—C20—H20 | 120.0 |
| C4—C3—H3 | 126.0 | C20—C21—C22 | 120.3 (3) |
| N1—C4—C5 | 125.5 (2) | C20—C21—H21 | 119.9 |
| N1—C4—C3 | 108.3 (2) | C22—C21—H21 | 119.9 |
| C5—C4—C3 | 126.2 (2) | C17—C22—C21 | 120.2 (3) |
| C6—C5—C4 | 126.0 (2) | C17—C22—H22 | 119.9 |
| C6—C5—C11 | 117.1 (2) | C21—C22—H22 | 119.9 |
| C4—C5—C11 | 116.9 (2) | C27—C26—C28 ⁱⁱ | 120.0 (3) |
| N2—C6—C5 | 125.8 (2) | C27—C26—H26 | 120.0 |
| N2—C6—C7 | 108.2 (2) | C28 ⁱⁱ —C26—H26 | 120.0 |
| C5—C6—C7 | 126.0 (2) | C28—C27—C26 | 120.6 (4) |
| C8—C7—C6 | 108.1 (2) | C28—C27—H27 | 119.7 |
| C8—C7—H7 | 125.9 | C26—C27—H27 | 119.7 |
| C6—C7—H7 | 125.9 | C27—C28—C26 ⁱⁱ | 119.3 (3) |
| C7—C8—C9 | 107.5 (2) | C27—C28—H28 | 120.3 |
| C7—C8—H8 | 126.2 | C26 ⁱⁱ —C28—H28 | 120.3 |

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| N1 ⁱ —Mo1—O2—N3 | 126 (3) | C3—C4—C5—C6 | 176.7 (3) |
| N2 ⁱ —Mo1—O2—N3 | 34 (2) | N1—C4—C5—C11 | 178.0 (2) |
| N2—Mo1—O2—N3 | -142 (3) | C3—C4—C5—C11 | -3.8 (4) |
| N1—Mo1—O2—N3 | -55 (2) | C9—N2—C6—C5 | 179.1 (2) |
| Mo1—O2—N3—O4 | 4(3) | Mo1 ⁱ —N2—C6—C5 | 11.8 (4) |
| Mo1—O2—N3—O3 | 179.8 (15) | Mo1—N2—C6—C5 | -13.2 (4) |
| O1—Mo1—N1—C1 | -82.6 (9) | C9—N2—C6—C7 | -0.2 (3) |
| N1 ⁱ —Mo1—N1—C1 | 105.4 (2) | Mo1 ⁱ —N2—C6—C7 | -167.48 (17) |
| N2 ⁱ —Mo1—N1—C1 | 18.0 (2) | Mo1—N2—C6—C7 | 167.58 (17) |
| N2—Mo1—N1—C1 | 178.7 (2) | C4—C5—C6—N2 | 1.7 (4) |
| O2—Mo1—N1—C1 | 103.0 (7) | C11—C5—C6—N2 | -177.8 (2) |
| O1—Mo1—N1—C4 | 82.4 (9) | C4—C5—C6—C7 | -179.2 (3) |
| N1 ⁱ —Mo1—N1—C4 | -89.6 (2) | C11—C5—C6—C7 | 1.3 (4) |
| N2 ⁱ —Mo1—N1—C4 | -177.0 (2) | N2—C6—C7—C8 | 0.5 (3) |
| N2—Mo1—N1—C4 | -16.4 (2) | C5—C6—C7—C8 | -178.7 (3) |
| O2—Mo1—N1—C4 | -92.0 (7) | C6—C7—C8—C9 | -0.7 (3) |
| O1—Mo1—N1—Mo1 ⁱ | 172.0 (9) | C6—N2—C9—C10 | 179.9 (3) |
| N1 ⁱ —Mo1—N1—Mo1 ⁱ | 0.0 | Mo1 ⁱ —N2—C9—C10 | -13.2 (4) |
| N2 ⁱ —Mo1—N1—Mo1 ⁱ | -87.39 (11) | Mo1—N2—C9—C10 | 11.6 (4) |
| N2—Mo1—N1—Mo1 ⁱ | 73.28 (10) | C6—N2—C9—C8 | -0.2 (3) |
| O2—Mo1—N1—Mo1 ⁱ | -2.4 (7) | Mo1 ⁱ —N2—C9—C8 | 166.65 (18) |
| O1—Mo1—N2—C9 | 84.7 (11) | Mo1—N2—C9—C8 | -168.61 (17) |
| N1 ⁱ —Mo1—N2—C9 | -16.9 (2) | C7—C8—C9—N2 | 0.6 (3) |
| N2 ⁱ —Mo1—N2—C9 | -106.2 (2) | C7—C8—C9—C10 | -179.6 (3) |
| N1—Mo1—N2—C9 | -177.5 (2) | N2—C9—C10—C1 ⁱ | 1.8 (4) |
| O2—Mo1—N2—C9 | -94.2 (8) | C8—C9—C10—C1 ⁱ | -178.0 (3) |
| O1—Mo1—N2—C6 | -81.3 (11) | N2—C9—C10—C17 | -175.5 (2) |
| N1 ⁱ —Mo1—N2—C6 | 177.2 (2) | C8—C9—C10—C17 | 4.8 (4) |
| N2 ⁱ —Mo1—N2—C6 | 87.9 (2) | C6—C5—C11—C16 | 96.5 (3) |
| N1—Mo1—N2—C6 | 16.6 (2) | C4—C5—C11—C16 | -83.0 (3) |
| O2—Mo1—N2—C6 | 99.8 (8) | C6—C5—C11—C12 | -83.6 (3) |
| O1—Mo1—N2—Mo1 ⁱ | -169.1 (11) | C4—C5—C11—C12 | 96.9 (3) |
| N1 ⁱ —Mo1—N2—Mo1 ⁱ | 89.31 (11) | C16—C11—C12—C13 | 1.2 (5) |
| N2 ⁱ —Mo1—N2—Mo1 ⁱ | -0.003 (2) | C5—C11—C12—C13 | -178.7 (3) |
| N1—Mo1—N2—Mo1 ⁱ | -71.32 (10) | C11—C12—C13—C14 | 0.7 (6) |
| O2—Mo1—N2—Mo1 ⁱ | 11.9 (8) | C12—C13—C14—C15 | -1.8 (5) |
| C4—N1—C1—C10 ⁱ | 177.8 (3) | C13—C14—C15—C16 | 0.9 (5) |
| Mo1 ⁱ —N1—C1—C10 ⁱ | 9.8 (4) | C12—C11—C16—C15 | -2.1 (4) |
| Mo1—N1—C1—C10 ⁱ | -14.7 (4) | C5—C11—C16—C15 | 177.9 (3) |
| C4—N1—C1—C2 | -0.9 (3) | C14—C15—C16—C11 | 1.0 (4) |
| Mo1 ⁱ —N1—C1—C2 | -168.85 (18) | C1 ⁱ —C10—C17—C18 | 92.1 (3) |
| Mo1—N1—C1—C2 | 166.57 (17) | C9—C10—C17—C18 | -90.4 (3) |
| N1—C1—C2—C3 | 0.4 (3) | C1 ⁱ —C10—C17—C22 | -89.6 (3) |

supplementary materials

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| C10 ⁱ —C1—C2—C3 | -178.3 (3) | C9—C10—C17—C22 | 87.8 (3) |
| C1—C2—C3—C4 | 0.3 (3) | C22—C17—C18—C19 | 0.6 (5) |
| C1—N1—C4—C5 | 179.5 (2) | C10—C17—C18—C19 | 178.8 (3) |
| Mo1 ⁱ —N1—C4—C5 | -12.2 (4) | C17—C18—C19—C20 | -0.7 (6) |
| Mo1—N1—C4—C5 | 12.7 (4) | C18—C19—C20—C21 | -0.4 (6) |
| C1—N1—C4—C3 | 1.1 (3) | C19—C20—C21—C22 | 1.5 (5) |
| Mo1 ⁱ —N1—C4—C3 | 169.33 (17) | C18—C17—C22—C21 | 0.5 (4) |
| Mo1—N1—C4—C3 | -165.80 (17) | C10—C17—C22—C21 | -177.8 (3) |
| C2—C3—C4—N1 | -0.8 (3) | C20—C21—C22—C17 | -1.6 (5) |
| C2—C3—C4—C5 | -179.3 (3) | C28 ⁱⁱ —C26—C27—C28 | 0.3 (6) |
| N1—C4—C5—C6 | -1.5 (4) | C26—C27—C28—C26 ⁱⁱ | -0.3 (6) |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$.

Fig. 1

