Synthesis and structure of two isomers of a molybdenum(II) 2-butyne complex stabilized by bioinspired S,N-bidentate ligands

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The synthesis and structural determination of two isomers of the molybdenum(II) complex (η^2^-but-2-ynecarbonyl)(2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)benzenethiolato-C^2^N,S)molybdenum(II), [Mo(C_11H_12NOS)_2(C_4H_6)(CO)] or Mo(CO)(C_2Me_2)(S-Phoz)_2, are presented. The \( \text{N,N-cis-S,S-trans isomer 1} \) shows quite different bond lengths to the metal atom [Mo—N = 2.4715 (10) \text{ vs.} 2.3404 (11) Å; Mo—S = 2.4673 (3) \text{ vs.} 2.3665 (3) Å]. In the \( \text{N,N-trans-S,S-cis isomer 2} \), which is isotypic with the corresponding W complex, the Mo—N bond lengths [2.236 (2) and 2.203 (2) Å], as well as the Mo—S bond lengths [2.5254 (8) and 2.5297 (8) Å], are almost the same.

1. Introduction

In order to explore the interaction of Mo and W centres with acetylene (C_2H_2), which is accepted as a substrate by the tungsten-enzyme acetylene hydratase (Schink, 1985; Rosner & Schink, 1995), our group has focused on the synthesis of W^{II} and Mo^{II} complexes containing bioinspired S,N-bidentate ligands and their subsequent oxidation to the respective W^{IV} and Mo^{IV} complexes. Although N-donor ligands are not the closest structural mimics of the dithiolene ligands in the active site of acetylene hydratase (Seiffert et al., 2007) and other members of the dimethyl sulfoxide (DMSO) reductase enzyme family (Seelmann et al., 2020), the use of these ligands has resulted in the discovery of new reactivities at W centres (Vidovič et al., 2019; Ehweiner et al., 2021c), the isolation of a so-far-elusive Mo^{IV} C_2H_2 complex (Ehweiner et al., 2021a) and a detailed comparison of W and Mo complexes with a variety of coordinated alkynes (Ehweiner et al., 2021b). One of the early publications of our group in this research field focused on the reversible activation of C_2H_2 at a W^{IV} centre coordinated by two 2-(4,4-dimethylazolin-2-yl)thiophenolate (S-Phoz) ligands (Peschel et al., 2015a). Thereafter, the reversible binding of C_2Me_2 and C_2Ph_2 (Peschel et al., 2019) was investigated, with a particular focus on the flexibility of the S-Phoz ligand. The latter has also found application in Ni, Pd and Pt compounds (Peschel et al., 2015b; Holzer et al., 2018), as well as in Zn (Mugesh et al., 1999) and Fe (Bottini et al., 2010) complexes.

Herein we report an improved synthetic procedure for Mo(CO)_2(S-Phoz)_2, and the preparation and structural characterization of carbonyl(η^2^-1,2-dimethylethyne)[2-(4,4-dimethyl-

oxazolin-2-yl)benzenethiolato-C^2^N,S)molybdenum(II), Mo(CO)(C_2Me_2)(S-Phoz)_2, which forms two isomers (1 and 2) in solution, as well as in the solid state (see Scheme 1). This behaviour is different from that observed for the W variant.
which crystallized solely as the \(N,N\)-trans isomer and showed the presence of a second isomer in solution only to a minor extent.

2. Experimental

Synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk and glove-box techniques. Solvents were purified via a Pure Solv Solvent Purification System. Chemicals were purchased from commercial sources and used without further purification. The precursor Mo\(_2\)(CO)\(_3\)(NMeCO) was synthesized according to a literature procedure (Baker et al., 1986). For the synthesis of Mo\(_2\)(CO)\(_2\)(S-Phoz)\(_2\), a slight modification of a published procedure was used (Peschel et al., 2013).

\(^{1}\)H NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer at ambient temperature and are referenced to residual protons in the solvent. The multiplicity of peaks is denoted as singlet (\(s\)), doublet (\(d\)), doublet of doublets (\(dd\)) or multiplet (\(m\)). NMR solvents were stored over molecular sieves. Solid-state IR spectra were measured on a Bruker ALPHA ATR–FT–IR spectrometer at a resolution of 2 cm\(^{-1}\). The relative intensity of signals is declared as strong (\(s\)), medium (\(m\)) and weak (\(w\)). Electron impact mass spectroscopy (EI–MS) measurements were performed with an Agilent 5973 MSD mass spectrometer with a push rod.

2.1. Synthesis and crystallization

2.1.1. Preparation of Mo\(_2\)(CO)\(_2\)(S-Phoz)\(_2\). A solution of Li(S-Phoz) (853 mg, 4.00 mmol) in MeCN (8 ml) was added dropwise to a solution of Mo\(_2\)(CO)\(_3\)(NMeCO) (1.03 g, 2.00 mmol) in MeCN (8 ml). The resulting blood-red solution was stirred for 2 h at 35°C, whereupon the solvent was removed by evaporation. The residue was suspended in toluene (20 ml) and the resulting suspension was filtered through Celite. The blood-red filtrate was then evaporated to dryness. After repeated recrystallization from \(CH_2Cl_2/\)heptane at \(-25\) °C, Mo\(_2\)(CO)\(_2\)(S-Phoz)\(_2\) (yield 790 mg, 70%) was obtained as dark red crystals. NMR and IR data are in agreement with previously published results (Peschel et al., 2013).

2.1.2. Preparation of Mo\(_2\)(CO)\(_2\)(C\(_2\)Me\(_2\))(S-Phoz)\(_2\). A solution of \(CH_2Cl_2/\)heptane at \(-25\) °C, Mo\(_2\)(CO)\(_2\)(S-Phoz)\(_2\) (yield 790 mg, 70%) was obtained as dark red crystals. NMR and IR data are in agreement with previously published results (Peschel et al., 2013).

\[\text{Mo}(C_2H_4OS)_2(C_2H_4)(CO)\]

\[M_r = 590.59, Z = 4.\]

Experiments were carried out at 100 K with Mo \(K\alpha\) radiation using a Bruker APEXI CCD diffractometer. Absorption was corrected for by multi-scan methods (SADABS; Bruker, 2013). Refinement was on 332 parameters. Only H-atom displacement parameters were refined.

### Table 1

**Experimental details.**

For both structures: [Mo\(_2\)(C\(_2\)H\(_4\)OS\(_2\))(C\(_2\)H\(_4\))(CO)], \(M_r = 590.59, Z = 4\). Experiments were carried out at 100 K with Mo \(K\alpha\) radiation using a Bruker APEXI CCD diffractometer. Absorption was corrected for by multi-scan methods (SADABS; Bruker, 2013). Refinement was on 332 parameters. Only H-atom displacement parameters were refined.

| Crystal data | Monoclinic, \(P2_1/n\) | Monoclinic, \(P2_1/c\) |
|--------------|------------------------|------------------------|
| \(a, b, c\) (Å) | 10.6159 (5), 8.9300 (4), 27.3801 (12) | 9.1512 (4), 21.3515 (12), 13.1781 (7) |
| \(\beta\) (°) | 96.189 (2) | 98.483 (3) |
| \(V\) (Å\(^3\)) | 2580.5 (2) | 2546.7 (2) |
| \(\mu\) (mm\(^{-1}\)) | 0.70 | 0.71 |
| Crystal size (mm) | 0.18 × 0.18 × 0.10 | 0.23 × 0.07 × 0.07 |

| Data collection | \(\bar{T}_{min}, \bar{T}_{max}\) | 0.884, 1.000 | 0.776, 1.000 |
|----------------|-------------------------------|------------------------|------------------------|
| No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections | 30042, 11363, 9549 | 22009, 7415, 5339 |
| \(\bar{R}_{int}\) | 0.029 | 0.068 |
| \(\sin \theta/\lambda_{max}\) (Å\(^{-1}\)) | 0.807 | 0.703 |

| Refinement | \([R(F^2 > 2\sigma(F^2)), wR(F^2), S]\) | 0.028, 0.071, 1.04 | 0.043, 0.087, 1.01 |
|----------------|-----------------------------------------------|------------------------|------------------------|
| No. of reflections | 11363 | 7415 |
| \(\Delta F_{max}, \Delta F_{min}\) (e Å\(^{-3}\)) | 0.72, −0.64 | 0.52, −0.83 |

Computer programs: APEXI2 (Bruker, 2013), SAINT (Bruker, 2013), SHELX97 (Sheldrick, 2008), SHELX12014 (Sheldrick, 2015) and modified ORTEP (Johnson, 1965).

![Scheme 1](image-url)
crystals suitable for X-ray diffraction were obtained from CH$_2$Cl$_2$/heptane solutions at −35 °C. Crystals of both isomers (green plates of 1 and yellow needles of 2) were obtained from the same batch. The product is very sensitive to air and should be stored in a glove-box.

2.1.3. Analytical data. $^1$H NMR for 1 (CD$_2$Cl$_2$, 300 MHz, S,S-trans isomer, 34%): δ 8.07 (dd, $J = 8.1$, 1.1 Hz, 1H, PhH), 7.78–7.72 (m, 3H, PhH), 7.35 (dd, $J = 7.8$, 1.1 Hz, 1H, PhH), 7.32–7.27 (m, 2H, PhH), 7.21–7.01 (m, 1H, PhH), 4.46 (d, $J = 8.2$ Hz, 1H, CH$_2$), 4.18 (d, $J = 8.1$ Hz, 1H, CH$_2$), 4.11 (d, $J = 8.3$ Hz, 1H, CH$_2$), 3.78 (d, $J = 8.2$ Hz, 1H, CH$_2$), 2.70 (s, 3H, C$_2$CH$_3$), 2.55 (s, 3H, C$_2$CH$_3$), 1.89 (s, 3H, CH$_3$), 1.57 (s, 3H, CH$_3$), 1.44 (s, 3H, CH$_3$); $^1$H NMR for 2 (CD$_2$Cl$_2$, 300 MHz, N,N-trans isomer, 66%): δ 7.67–7.62 (m, 2H, PhH), 7.43 (dd, $J = 8.1$, 1.4 Hz, 1H, PhH), 7.21–7.01 (m, 4H, PhH), 6.90–6.84 (m, 1H, PhH), 4.11 (d, $J = 8.3$ Hz, 1H, CH$_2$), 3.93–3.90 (m, 3H, CH$_2$), 2.90 (s, 3H, C$_2$CH$_3$), 2.46 (s, 3H, C$_2$CH$_3$), 1.63 (s, 3H, CH$_3$), 1.34 (s, 3H, CH$_3$), 0.77 (s, 3H, CH$_3$), 0.58 (s, 3H, CH$_3$). IR (cm$^{-1}$): 2995 (w), 2962 (w), 2928 (w), 2916 (w), 2894 (w), 1898 (s, C=O), 1856 (m, C=O), 1590 (s), 1572 (s), 1539 (m, C=N), 1455 (m), 1357 (m), 1326 (m), 1280 (m), 1246 (m), 1208 (m), 1160 (m), 1139 (m), 1053 (s), 966 (m), 818 (m), 776 (m), 741 (s), 695 (m), 653 (m). EI–MS (70 eV) m/z: [M − 2CO + O]$^+$ 526.1.

2.2. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 1. The H atoms of the CH$_2$ groups were placed at positions with approximately tetrahedral angles and C–H distances of 0.99 Å, and common isotropic displacement parameters were refined for the H atoms of the same group. The H atoms of the arene rings were placed at the external bisectors of the C–C–C angles at C–H distances of 0.95 Å, and common isotropic displacement parameters were refined for the H atoms of the same ring. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotations around the C–C bonds, and with C–H distances of 0.98 Å.

3. Results and discussion

3.1. Crystal structure analysis

Isomers 1 and 2 crystallize without any solvent molecules in the monoclinic space groups P2$_1$/n and P2$_1$/c, respectively, and both have one metal complex in the asymmetric unit. In N,N-cis isomer 1 (Fig. 1), the Mo–N distance of the oxazole ring $trans$ to the butyne ligand [Mo1–N13 = 2.4715 (10) Å] is much longer than that $trans$ to the carbonyl ligand [Mo1–N33 = 2.3404 (11) Å] in N,N-trans isomer 2 (Fig. 2), these distances [Mo1–N13 = 2.236 (2) Å and Mo1–N33 = 2.203 (2) Å] are comparable to those observed in the dicarbonyl derivative [2.2333 (9) Å; Peschel et al., 2013] or in the isotypic W compound [W1–N13 = 2.2153 (16) Å and W1–N33 = 2.1862 (16) Å; Peschel et al., 2019]. In contrast to this,
the Mo—S distances of the benzenethiolate residues in isomer 1 are significantly different, although they are trans to one another, and both are clearly shorter [Mo1—S1 = 2.4673 (3) Å and Mo1—S2 = 2.3665 (3) Å] than in isomer 2 [Mo1—S1 = 2.5254 (8) Å and Mo1—S2 = 2.5297 (8) Å] or in the W compound [W—S = 2.5232 (4)—2.5243 (4) Å]. On the other hand, in both isomers, the distances are almost the same between the central atom and the butyne ligands [2.0310 (12)—2.0664 (12) Å versus 2.024 (3)—2.059 (3) Å] and to the carbonyl ligands [1.9417 (13) versus 1.953 (3) Å], although both are arranged in trans positions with respect to the N atoms of the oxazole rings in 1, and trans to the S atoms of the benzenethiolate groups in 2. In both isomers, the CO ligands [C3—O3 = 1.1555 (16) and 1.157 (3) Å] lie roughly in the best planes through the butyne ligands [C1—C2 = 1.2965 (18) and 1.314 (4) Å] and the Mo atoms.

Comparing all known structures of M(CO)(C2R2)(S-Phoz)2 complexes (Table 2), the following conclusions can be made: whereas N,N-trans conformations for R = H and CH3, and S,S-trans conformations for R = Ph were observed (Peschel et al., 2015a, 2019) for the W complexes, both conformations were found in the first two crystal structures of the analogous Mo complexes with R = CH3. In general, the Mo—N distances are clearly longer in the S,S-trans conformers, and slightly longer for the S-Phoz ligands trans to the alkylene ligands than those trans to the carbonyl ligand (e.g. M—N13 is larger than M—N33). In isomer 1, the Mo—N distance of the S-Phoz ligand trans to the butyne ligand is exceptionally large due to the wide C1—Mo1—N13 angle of 173.53 (4)° and large C—M—S1 angles. The Mo—S distances are the same in the N,N-trans conformers, but in the S,S-trans conformers, M—S1 is distinctly longer than M—S2. Therefore, the S-Phoz ligands whose oxazole rings are trans to the alkylene ligands are more weakly bound to the metal centre than the others. In all six complexes (Table 2), the M—C1 distance is significantly shorter than M—C2, presumably due to the carbonyl ligand near atom C2.

3.2. NMR spectroscopy

1H NMR spectra recorded in CD2Cl2 and CD3CN show a 1:2 ratio of the two isomers of Mo(CO)(C2Me2)(S-Phoz)2, while a 1:1 ratio is observed in CDCl3. The NMR data of isomer 2, which presumably adopt the N,N-trans configuration, are almost identical with those of the W analogue (Peschel et al., 2019), of which only the N,N-trans isomer was crystallized. In CD2Cl2 solutions, the two isomers of W(CO)(C2Me2)(S-Phoz)2 exhibit a 95:5 ratio, with a clear preference for the N,N-trans configuration of isomer 2.

3.3. IR spectroscopy

The IR spectrum of an average sample of Mo(CO)(C2Me2)(S-Phoz)2 shows a very strong band at 1898 cm⁻¹ which is attributed to the C≡O bond. Due to weaker π-backbonding of the Mo centre, this bond is stronger by 18 cm⁻¹ compared to that in the respective W compound (Peschel et al., 2019), which is in accordance with previous observations on Mo and W carbonyl complexes (Ehweiner et al., 2021a,b,c). Despite the existence of two isomers, only one C≡O bond is visible.

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Computing details

For both structures, data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELX97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: modified ORTEP (Johnson, 1965); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

**N,N-cis-(η²-But-2-yn)e-carbonylbis[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)benzenethiolato]molybdenum(II) (1)**

**Crystal data**

\[\text{[Mo(C₁₁H₁₂NOS)₂(C₄H₆)(CO)]}\]

- \(M_r = 590.59\)
- Monoclinic, \(P₂₁/n\)
- \(a = 10.6159\) (5) Å
- \(b = 8.9300\) (4) Å
- \(c = 27.3801\) (12) Å
- \(\beta = 96.189\) (2)°
- \(V = 2580.5\) (2) Å³
- \(Z = 4\)

**Data collection**

- Bruker APEXII CCD diffractometer
- Radiation source: Incoatec microfocus sealed tube
- Multilayer monochromator
- \(\varphi\) and \(\omega\) scans
- Absorption correction: multi-scan (SADABS; Bruker, 2013)
- \(T_{\text{min}} = 0.884, T_{\text{max}} = 1.000\)

**Refinement**

- Refinement on \(F^2\)
- Least-squares matrix: full
- \(R(F^2 > 2\sigma(F^2)) = 0.028\)
- \(wR(F^2) = 0.071\)
- \(S = 1.04\)
- 11363 reflections
- 332 parameters
- 0 restraints
- Primary atom site location: structure-invariant direct methods
- Secondary atom site location: difference Fourier map
- Hydrogen site location: inferred from neighbouring sites

\(F(000) = 1216\)

\(D_x = 1.520\) Mg m⁻³

Mo Kα radiation, \(\lambda = 0.71073\) Å

Cell parameters from 9935 reflections

\(\theta = 2.4-35.8°\)

\(\mu = 0.70\) mm⁻¹

\(T = 100\) K

Plate, green

\(0.18 \times 0.18 \times 0.10\) mm

30042 measured reflections

11363 independent reflections

9549 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.029\)

\(\theta_{\text{max}} = 35.0°, \theta_{\text{min}} = 1.5°\)

\(h = -17→17\)

\(k = -14→11\)

\(l = -44→42\)
Only H-atom displacement parameters refined

\[ w = \frac{1}{\sigma^2(F_o^2) + (0.0331P)^2 + 0.5019P} \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

\[ (\Delta/\sigma)_{\text{max}} = 0.008 \]
\[ \Delta \rho_{\text{max}} = 0.72 \text{ e Å}^{-3} \]
\[ \Delta \rho_{\text{min}} = -0.64 \text{ e Å}^{-3} \]

**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 \( F^2 > 2\sigma(F^2) \) 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.

The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH\(_2\) groups were put at positions with approx. tetrahedral angles and C-H distances of 0.99 Å, and common isotropic displacement parameters were refined for the H atoms of the same group (AFIX 23 of SHELXL). The H atoms of the phenyl rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same ring (AFIX 43 of SHELXL). The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotations around the C-C bonds, and C-H distances of 0.98 Å (AFIX 137 of SHELXL).

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

| \( \times \) | \( y \) | \( z \) | \( U_{\text{iso}}/U_{\text{eq}} \) |
|---|---|---|---|
| Mo1 | 0.89263 (2) | 0.62618 (2) | 0.60957 (2) | 0.00748 (3) |
| C10 | 0.79768 (14) | 0.34484 (15) | 0.53122 (5) | 0.0169 (2) |
| H101 | 0.8405 | 0.3231 | 0.5020 | 0.032 (3)* |
| H102 | 0.7171 | 0.3954 | 0.5213 | 0.032 (3)* |
| H103 | 0.7816 | 0.2510 | 0.5480 | 0.032 (3)* |
| C1 | 0.87961 (12) | 0.44360 (14) | 0.56508 (4) | 0.0118 (2) |
| C2 | 0.99846 (12) | 0.46043 (14) | 0.58069 (4) | 0.0116 (2) |
| C20 | 1.12488 (14) | 0.39396 (16) | 0.57708 (6) | 0.0196 (3) |
| H201 | 1.1150 | 0.2896 | 0.5663 | 0.065 (5)* |
| H202 | 1.1748 | 0.3975 | 0.6093 | 0.065 (5)* |
| H203 | 1.1685 | 0.4507 | 0.5533 | 0.065 (5)* |
| C3 | 1.07172 (12) | 0.65704 (14) | 0.62980 (4) | 0.0117 (2) |
| O3 | 1.17882 (9) | 0.67813 (12) | 0.63972 (4) | 0.01788 (19) |
| O11 | 0.93259 (10) | 0.95082 (11) | 0.74208 (3) | 0.01669 (18) |
| C12 | 0.94202 (12) | 0.82783 (14) | 0.71368 (4) | 0.0116 (2) |
| N13 | 0.88974 (10) | 0.83507 (11) | 0.66865 (3) | 0.00967 (17) |
| C14 | 0.84945 (12) | 0.99714 (13) | 0.66127 (4) | 0.01058 (19) |
| C15 | 0.84074 (13) | 1.04622 (14) | 0.71414 (4) | 0.0151 (2) |
| H151 | 0.8632 | 1.1533 | 0.7188 | 0.015 (3)* |
| H152 | 0.7545 | 1.0296 | 0.7237 | 0.015 (3)* |
| C16 | 0.72358 (12) | 1.01441 (14) | 0.63024 (5) | 0.0140 (2) |
| H161 | 0.7321 | 0.9824 | 0.5965 | 0.024 (3)* |
| H162 | 0.6973 | 1.1196 | 0.6302 | 0.024 (3)* |
| H163 | 0.6597 | 0.9525 | 0.6439 | 0.024 (3)* |
### Atomic displacement parameters (Å²)

|  | \(U_{11}\)   | \(U_{22}\)   | \(U_{33}\)   | \(U_{12}\) | \(U_{13}\) | \(U_{23}\) |
|---|-------------|-------------|-------------|-----------|----------|----------|
| Mo1 | 0.00739 (4) | 0.00758 (4) | 0.00757 (4) | 0.00003 (3) | 0.00130 (3) | -0.00047 (3) |
| C10 | 0.0187 (6)  | 0.0167 (6)  | 0.0149 (5)  | -0.0037 (5) | 0.0000 (4)  | -0.0055 (4)  |
| C1  | 0.0156 (6)  | 0.0095 (5)  | 0.0105 (4)  | -0.0010 (4) | 0.0020 (4)  | -0.0013 (4)  |
| Atom  | U11 (A²) | U22 (A²) | U33 (A²) | U12 (A²) | U13 (A²) | U23 (A²) |
|-------|----------|----------|----------|----------|----------|----------|
| C2    | 0.0134 (5) | 0.0106 (5) | 0.0113 (4) | 0.0013 (4) | 0.0036 (4) | −0.0019 (4) |
| C20   | 0.0141 (6) | 0.0183 (6) | 0.0274 (7) | 0.0035 (5) | 0.0063 (5) | −0.0073 (5) |
| C3    | 0.0134 (5) | 0.0110 (5) | 0.0108 (4) | 0.0002 (4) | 0.0021 (4) | −0.0020 (4) |
| O3    | 0.0106 (4) | 0.0223 (5) | 0.0205 (4) | −0.0016 (4) | 0.0008 (3) | −0.0043 (4) |
| O11   | 0.0243 (5) | 0.0138 (4) | 0.0110 (4) | 0.0063 (4) | −0.0023 (3) | −0.0052 (3) |
| C12   | 0.0127 (5) | 0.0112 (5) | 0.0109 (4) | 0.0016 (4) | 0.0015 (4) | −0.0021 (4) |
| N13   | 0.0106 (4) | 0.0086 (4) | 0.0098 (4) | 0.0009 (3) | 0.0011 (3) | −0.0003 (3) |
| C14   | 0.0123 (5) | 0.0082 (4) | 0.0112 (4) | 0.0011 (4) | 0.0011 (4) | −0.0010 (4) |
| C15   | 0.0205 (6) | 0.0119 (5) | 0.0128 (5) | 0.0063 (5) | 0.0011 (4) | −0.0017 (4) |
| C16   | 0.0137 (6) | 0.0118 (5) | 0.0163 (5) | 0.0027 (4) | 0.0003 (4) | 0.0010 (4) |
| C17   | 0.0171 (6) | 0.0118 (5) | 0.0201 (6) | −0.0038 (5) | 0.0042 (5) | −0.0016 (4) |
| S1    | 0.01297 (13) | 0.01097 (12) | 0.01060 (11) | −0.00069 (10) | 0.00153 (9) | 0.00193 (9) |
| C21   | 0.0122 (5) | 0.0142 (5) | 0.0096 (4) | 0.0022 (4) | 0.0019 (4) | 0.0015 (4) |
| C22   | 0.0125 (5) | 0.0143 (5) | 0.0096 (4) | 0.0031 (4) | 0.0007 (4) | 0.0000 (4) |
| C23   | 0.0178 (6) | 0.0204 (6) | 0.0134 (5) | 0.0035 (5) | −0.0031 (4) | −0.0033 (4) |
| C24   | 0.0200 (7) | 0.0277 (7) | 0.0179 (6) | 0.0063 (6) | −0.0065 (5) | −0.0030 (5) |
| C25   | 0.0229 (7) | 0.0256 (7) | 0.0177 (6) | 0.0096 (6) | −0.0042 (5) | 0.0049 (5) |
| C26   | 0.0204 (6) | 0.0161 (6) | 0.0165 (5) | 0.0041 (5) | −0.0003 (5) | 0.0038 (4) |
| O31   | 0.0087 (4) | 0.0192 (5) | 0.0189 (4) | −0.0033 (3) | −0.0008 (3) | 0.0071 (3) |
| C32   | 0.0088 (5) | 0.0101 (5) | 0.0114 (4) | −0.0017 (4) | 0.0012 (4) | −0.0012 (4) |
| N33   | 0.0087 (4) | 0.0090 (4) | 0.0104 (4) | −0.0010 (3) | 0.0020 (3) | 0.0002 (3) |
| C34   | 0.0090 (5) | 0.0118 (5) | 0.0127 (5) | −0.0022 (4) | 0.0028 (4) | 0.0011 (4) |
| C35   | 0.0103 (5) | 0.0175 (6) | 0.0182 (5) | −0.0040 (5) | 0.0006 (4) | 0.0063 (4) |
| C36   | 0.0167 (6) | 0.0152 (5) | 0.0156 (5) | −0.0013 (5) | 0.0070 (4) | 0.0005 (4) |
| C37   | 0.0146 (6) | 0.0099 (5) | 0.0201 (5) | −0.0026 (4) | 0.0022 (4) | 0.0028 (4) |
| S2    | 0.00911 (12) | 0.01204 (12) | 0.00983 (11) | −0.00215 (10) | 0.00123 (9) | 0.00168 (9) |
| C41   | 0.0105 (5) | 0.0092 (5) | 0.0089 (4) | −0.0001 (4) | 0.0023 (4) | −0.0009 (3) |
| C42   | 0.0112 (5) | 0.0099 (5) | 0.0096 (4) | −0.0012 (4) | 0.0006 (4) | 0.0003 (4) |
| C43   | 0.0142 (6) | 0.0170 (6) | 0.0145 (5) | −0.0014 (4) | −0.0017 (4) | 0.0030 (4) |
| C44   | 0.0177 (6) | 0.0207 (6) | 0.0157 (5) | −0.0007 (5) | −0.0030 (4) | 0.0066 (5) |
| C45   | 0.0191 (6) | 0.0155 (6) | 0.0131 (5) | −0.0001 (5) | 0.0020 (4) | 0.0047 (4) |
| C46   | 0.0147 (6) | 0.0126 (5) | 0.0116 (5) | −0.0009 (4) | 0.0030 (4) | 0.0019 (4) |

**Geometric parameters (Å, °)**

| Bond/Key   | Length/Angle (Å, °) |
|------------|---------------------|
| Mo1—C1     | 2.0310 (12)         |
| Mo1—C2     | 2.0664 (12)         |
| Mo1—C3     | 1.9417 (13)         |
| Mo1—N13    | 2.4715 (10)         |
| Mo1—N33    | 2.3404 (11)         |
| Mo1—S1     | 2.4673 (7)          |
| Mo1—S2     | 2.3665 (3)          |
| C1—C2      | 1.2965 (18)         |
| C1—C10     | 1.4899 (17)         |
| C10—H101   | 0.98                |
| C10—H102   | 0.98                |
| C10—H103   | 0.98                |
| C2—C20     | 1.4804 (19)         |

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C20—H201 0.98  C34—C37 1.5233 (18)
C20—H202 0.98  C34—C35 1.5285 (18)
C20—H203 0.98  C34—C36 1.5288 (17)
C3—O3 1.1555 (16)  C35—H351 0.99
O11—C12 1.3558 (15)  C35—H352 0.99
O11—C15 1.4494 (16)  C36—H361 0.98
C12—N13 1.2978 (15)  C36—H362 0.98
C12—C22 1.4710 (17)  C36—H363 0.98
N13—C14 1.5166 (15)  C37—H371 0.98
C14—C16 1.5120 (18)  C37—H372 0.98
C14—C15 1.5247 (16)  C37—H373 0.98
C14—C17 1.5322 (18)  S2—C41 1.7477 (12)
C15—H151 0.99  C41—C42 1.4029 (17)
C15—H152 0.99  C41—C46 1.4131 (16)
C16—H161 0.98  C42—C43 1.4177 (17)
C16—H162 0.98  C43—C44 1.3811 (18)
C16—H163 0.98  C43—H43 0.95
C17—H171 0.98  C44—C45 1.390 (2)
C17—H172 0.98  C44—H44 0.95
C17—H173 0.98  C45—C46 1.3810 (18)
S1—C21 1.7551 (13)  C45—H45 0.95
C21—C26 1.4046 (18)  C46—H46 0.95
C21—C22 1.4051 (18)

N13—Mo1—N33 92.41 (3)  H172—C17—H173 109.5
S1—Mo1—S2 162.979 (11)  C21—S1—Mo1 105.69 (4)
C1—Mo1—N13 173.53 (4)  C26—C21—C22 118.23 (12)
C2—Mo1—N13 146.80 (4)  C26—C21—S1 119.66 (10)
C3—Mo1—N33 168.19 (4)  C22—C21—S1 121.97 (9)
C3—Mo1—C1 106.63 (5)  C21—C22—C23 120.09 (11)
C3—Mo1—C2 69.81 (5)  C21—C22—C12 122.60 (11)
C1—Mo1—C2 36.88 (5)  C23—C22—C12 117.30 (12)
C1—Mo1—N33 83.79 (4)  C24—C23—C22 120.52 (13)
C2—Mo1—N33 120.63 (4)  C24—C23—H23 119.7
C3—Mo1—S2 85.88 (4)  C22—C23—H23 119.7
C1—Mo1—S2 99.36 (3)  C23—C24—C25 119.73 (13)
C2—Mo1—S2 98.42 (3)  C23—C24—H24 120.1
N33—Mo1—S2 86.95 (3)  C25—C24—H24 120.1
C3—Mo1—S1 91.22 (4)  C26—C25—C24 120.28 (13)
C1—Mo1—S1 97.54 (3)  C26—C25—H25 119.9
C2—Mo1—S1 96.29 (3)  C24—C25—H25 119.9
N33—Mo1—S1 92.90 (2)  C25—C26—C21 121.14 (13)
C3—Mo1—N13 77.70 (4)  C25—C26—H26 119.4
S2—Mo1—N13 85.62 (2)  C21—C26—H26 119.4
S1—Mo1—N13 77.38 (2)  C32—O31—C35 107.19 (9)
C1—C10—H101 109.5  N33—C32—O31 116.38 (10)
C1—C10—H102 109.5  N33—C32—C42 132.61 (11)
H101—C10—H102 109.5  O31—C32—C42 110.99 (10)
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|-----------|----------------------|-----------|
| C1—C10—H103         | 109.5     | C32—N33—C34          | 106.17 (10) |
| H101—C10—H103       | 109.5     | C32—N33—Mo1          | 128.30 (8)  |
| H102—C10—H103       | 109.5     | C34—N33—Mo1          | 125.49 (7)  |
| C2—C1—C10           | 139.10 (12) | C37—C34—N33         | 113.73 (10) |
| C2—C1—Mo1           | 73.04 (7)  | C37—C34—C35          | 108.63 (10) |
| C10—C1—Mo1          | 147.76 (10) | N33—C34—C35         | 102.17 (9)  |
| C1—C2—C20           | 142.05 (12) | C37—C34—C36          | 112.24 (10) |
| C1—C2—Mo1           | 70.08 (7)  | N33—C34—C36          | 108.73 (10) |
| C20—C2—Mo1          | 147.87 (10) | C35—C34—C36          | 110.91 (11) |
| C2—C20—H201         | 109.5     | O31—C35—C34          | 104.29 (10) |
| C2—C20—H202         | 109.5     | O31—C35—H351         | 110.9      |
| H201—C20—H202       | 109.5     | C34—C35—H351         | 110.9      |
| C2—C20—H203         | 109.5     | O31—C35—H352         | 110.9      |
| H201—C20—H203       | 109.5     | C34—C35—H352         | 110.9      |
| H202—C20—H203       | 109.5     | H351—C35—H352        | 108.9      |
| Mo1—C3—O3           | 176.84 (11) | C34—C36—H361      | 109.5      |
| C12—O11—C15         | 105.09 (9) | C34—C36—H362        | 109.5      |
| N13—C12—O11         | 117.01 (11) | H361—C36—H362      | 109.5      |
| N13—C12—C22         | 129.87 (11) | C34—C36—H363        | 109.5      |
| O11—C12—C22         | 113.06 (10) | H361—C36—H363       | 109.5      |
| C12—N13—C14         | 105.05 (9) | H362—C36—H363       | 109.5      |
| C12—N13—Mo1         | 123.36 (8) | C34—C37—H371        | 109.5      |
| C14—N13—Mo1         | 131.02 (7) | C34—C37—H372        | 109.5      |
| C16—C14—N13         | 113.06 (10) | C34—C37—H372        | 109.5      |
| C16—C14—C15         | 111.33 (10) | H371—C37—H372       | 109.5      |
| N13—C14—C15         | 101.12 (9) | C34—C37—H373        | 109.5      |
| C16—C14—C17         | 112.34 (10) | H371—C37—H373       | 109.5      |
| N13—C14—C17         | 109.12 (10) | H372—C37—H372       | 109.5      |
| C15—C14—C17         | 109.25 (10) | C41—S2—Mo1          | 117.58 (4)  |
| O11—C15—C14         | 103.06 (9)  | C42—C41—C46          | 118.72 (11) |
| O11—C15—H151        | 111.2     | C42—C41—S2          | 127.52 (9)  |
| C14—C15—H151        | 111.2     | C46—C41—S2          | 113.74 (9)  |
| O11—C15—H152        | 111.2     | C41—C42—C43        | 118.36 (11) |
| C14—C15—H152        | 111.2     | C41—C42—C32        | 125.16 (11) |
| H151—C15—H152       | 109.1     | C43—C42—C32        | 116.43 (11) |
| C14—C16—H161        | 109.5     | C44—C43—C42        | 121.73 (12) |
| C14—C16—H162        | 109.5     | C44—C43—H43        | 119.1      |
| H161—C16—H162       | 109.5     | C42—C43—H43        | 119.1      |
| C14—C16—H163        | 109.5     | C43—C44—C45        | 119.73 (12) |
| H161—C16—H163       | 109.5     | C43—C44—H44        | 120.1      |
| H162—C16—H163       | 109.5     | C45—C44—H44        | 120.1      |
| C14—C17—H171        | 109.5     | C46—C45—C44        | 119.55 (12) |
| C14—C17—H172        | 109.5     | C46—C45—H45        | 120.2      |
| H171—C17—H172       | 109.5     | C45—C46—C41        | 121.81 (12) |
| C14—C17—H173        | 109.5     | C45—C46—H46        | 119.1      |
| H171—C17—H173       | 109.5     | C41—C46—H46        | 119.1      |
| C1—C2—Mo1—C3        | −176.82 (9) | C22—C21—C26—C25    | 0.4 (2)    |
| Bond/Angle | Value (σ) |
|-----------|-----------|
| C10—C1—C2—C20 | 2.9 (3) |
| Mo1—C1—C2—C20 | 179.67 (19) |
| Mo1—C2—C1—C10 | 176.81 (17) |
| C15—O11—C12—N13 | 11.37 (15) |
| C15—O11—C12—C22 | 171.33 (11) |
| O11—C12—N13—C14 | 8.08 (15) |
| C22—C12—N13—C14 | 168.70 (13) |
| O11—C12—N13—Mo1 | 179.70 (8) |
| C15—O11—C12—C22 | 3.52 (19) |
| C12—N13—C14—C16 | 92.37 (12) |
| Mo1—N13—C14—C16 | 141.83 (11) |
| C12—N13—C14—C15 | 22.71 (13) |
| Mo1—N13—C14—C15 | 165.91 (8) |
| C12—N13—C14—C17 | 38.04 (13) |
| Mo1—N13—C14—C17 | 25.47 (12) |
| C16—C14—C15—O11 | 148.99 (11) |
| Mo1—S1—C21—C26 | 28.64 (12) |
| C17—C14—C15—O11 | 186.35 (12) |
| Mo1—S1—C21—C22 | 55.02 (10) |
| C26—C21—C22—C23 | 0.06 (18) |
| C1—C21—C22—C23 | 175.83 (10) |
| C26—C21—C22—C12 | 30.98 (19) |
| S1—C21—C22—C12 | 172.89 (11) |
| N13—C12—C22—C21 | 146.55 (14) |
| N13—C12—C22—C23 | 30.24 (16) |
| C21—C22—C23—C24 | 0.4 (2) |
| C12—C22—C23—C24 | 179.16 (13) |
| C22—C23—C24—C25 | 0.5 (2) |
| C23—C24—C25—C26 | 0.1 (2) |
| C24—C25—C26—C21 | 0.3 (2) |

**Supporting Information**

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N,N-*trans-(η²-But-2-yne)carbonylbis[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)benzenethiolato]molybdenum(II) (2)

**Crystal data**

\[
\text{[Mo(C}_{11}\text{H}_{12}\text{NOS})_{2}(\text{C}_{4}\text{H}_{6})(\text{CO})]} \]

\[
M_r = 590.59
\]

Monoclinic, \(P2_1/c\)

\[
a = 9.1512 \text{ (4) Å} \\
b = 21.3515 \text{ (12) Å} \\
c = 13.1781 \text{ (7) Å} \\
\beta = 98.4833 \text{ (3)°} \\
V = 2546.7 \text{ (2) Å}^3 \\
Z = 4
\]

\[F(000) = 1216\]

\[D_x = 1.540 \text{ Mg m}^{-3}\]

Mo Ka radiation, \(\lambda = 0.71073 \text{ Å}\)

Cell parameters from 3132 reflections

\[\theta = 2.4–26.8°\]

\[\mu = 0.71 \text{ mm}^{-1}\]

\[T = 100 \text{ K}\]

Needle, yellow

\[0.23 \times 0.07 \times 0.07 \text{ mm}\]
supporting information

Data collection

Bruker APEXII CCD
diffraclometer
Radiation source: Incoatec microfocus sealed tube
Multilayer monochromator
\( \varphi \) and \( \omega \) scans
Absorption correction: multi-scan
(SADABS; Bruker, 2013)

\[ T_{\text{min}} = 0.776, \quad T_{\text{max}} = 1.000 \]

Refinement

Refinement on \( F^2 \)
Least-squares matrix: full
\[ R[F^2 > 2\sigma(F^2)] = 0.043 \]
\[ wR(F^2) = 0.087 \]
7415 reflections
332 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
Only H-atom displacement parameters refined

\[ \Delta \rho_{\text{max}} = 0.52 \text{ e Å}^{-3} \]
\[ \Delta \rho_{\text{min}} = -0.83 \text{ e Å}^{-3} \]

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 \( F^2 > 2\sigma(F^2) \) 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.

The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints.
The H atoms of the CH2 groups were put at positions with approx. tetrahedral angles and C-H distances of 0.99 Å, and common isotropic displacement parameters were refined for the H atoms of the same group (AFIX 23 of SHELXL).
The H atoms of the phenyl rings were put at the external bisectors of the C-C-C angles at C-H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same ring (AFIX 43 of SHELXL).
The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotations around the C-C bonds, and C-H distances of 0.98 Å (AFIX 137 of SHELXL).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|    | x   | y    | z   | \( U_{\text{iso}}^*/U_{\text{eq}} \) |
|----|-----|------|-----|--------------------------------------|
| Mo1| 0.72006 (2) | 0.85241 (2) | 0.32592 (2) | 0.00779 (6) |
| C10 | 0.6039 (3) | 0.75606 (14) | 0.5024 (2) | 0.0153 (6) |
| H101 | 0.6362 | 0.7619 | 0.5760 | 0.029 (6)* |
| H102 | 0.6544 | 0.7197 | 0.4784 | 0.029 (6)* |
| H103 | 0.4969 | 0.7491 | 0.4899 | 0.029 (6)* |
| C1  | 0.6403 (3) | 0.81274 (14) | 0.4461 (2) | 0.0101 (6) |
| C2  | 0.6263 (3) | 0.87368 (14) | 0.4544 (2) | 0.0111 (6) |
| C20 | 0.5702 (3) | 0.92014 (14) | 0.5225 (2) | 0.0153 (6) |
|    | x         | y         | z         | U eq (A²) |
|----|-----------|-----------|-----------|-----------|
| H201 | 0.4685    | 0.9315    | 0.4945    | 0.026 (5)*|
| H202 | 0.6326    | 0.9576    | 0.5270    | 0.026 (5)*|
| H203 | 0.5724    | 0.9021    | 0.5910    | 0.026 (5)*|
| C3  | 0.6944 (3) | 0.94287 (14) | 0.3361 (2) | 0.0111 (6) |
| O3  | 0.6808 (2) | 0.99615 (10) | 0.34780 (16) | 0.0158 (4) |
| O11 | 1.16158 (19) | 0.91979 (10) | 0.45152 (16) | 0.0163 (5) |
| C12 | 1.0293 (3) | 0.91404 (14) | 0.3892 (2) | 0.0129 (6) |
| N13 | 0.9525 (2) | 0.86506 (11) | 0.40345 (18) | 0.0111 (5) |
| C14 | 1.0531 (3) | 0.82224 (14) | 0.4740 (2) | 0.0134 (6) |
| C15 | 1.1612 (3) | 0.87050 (15) | 0.5275 (2) | 0.0159 (6) |
| H151| 1.1270    | 0.8866    | 0.5904    | 0.018 (6)* |
| H152| 1.2610    | 0.8522    | 0.5459    | 0.018 (6)* |
| C16 | 1.1309 (3) | 0.77888 (15) | 0.4072 (2) | 0.0174 (7) |
| H161| 1.2006    | 0.7520    | 0.4510    | 0.019 (5)* |
| H162| 1.1847    | 0.8040    | 0.3625    | 0.019 (5)* |
| H163| 1.0575    | 0.7528    | 0.3650    | 0.019 (5)* |
| C17 | 0.9738 (3) | 0.78611 (16) | 0.5474 (2) | 0.0181 (7) |
| H171| 0.9163    | 0.8151    | 0.5836    | 0.023 (5)* |
| H172| 1.0461    | 0.7642    | 0.5973    | 0.023 (5)* |
| H173| 0.9073    | 0.7555    | 0.5092    | 0.023 (5)* |
| S1  | 0.85728 (7) | 0.87267 (4) | 0.17639 (6) | 0.01253 (15) |
| C21 | 0.9358 (3) | 0.94634 (14) | 0.2090 (2) | 0.0119 (6) |
| C22 | 1.0035 (3) | 0.96176 (14) | 0.3094 (2) | 0.0123 (6) |
| C23 | 1.0611 (3) | 1.02195 (15) | 0.3305 (3) | 0.0174 (7) |
| H23 | 1.1063    | 1.0319    | 0.3981    | 0.022 (4)* |
| C24 | 1.0534 (3) | 1.06682 (15) | 0.2551 (3) | 0.0212 (7) |
| H24 | 1.0889    | 1.1080    | 0.2709    | 0.022 (4)* |
| C25 | 0.9933 (3) | 1.05120 (15) | 0.1556 (2) | 0.0187 (7) |
| H25 | 0.9914    | 1.0814    | 0.1025    | 0.022 (4)* |
| C26 | 0.9359 (3) | 0.99211 (15) | 0.1327 (2) | 0.0162 (6) |
| H26 | 0.8957    | 0.9823    | 0.0639    | 0.022 (4)* |
| O31 | 0.30893 (19) | 0.78898 (10) | 0.14341 (16) | 0.0149 (4) |
| C32 | 0.4389 (3) | 0.78648 (14) | 0.2073 (2) | 0.0115 (6) |
| N33 | 0.5126 (2) | 0.83815 (11) | 0.22034 (17) | 0.0091 (5) |
| C34 | 0.4180 (3) | 0.88879 (14) | 0.1625 (2) | 0.0115 (6) |
| C35 | 0.3001 (3) | 0.84988 (15) | 0.0959 (2) | 0.0187 (6) |
| H351| 0.2008    | 0.8684    | 0.0954    | 0.020 (6)* |
| H352| 0.3212    | 0.8472    | 0.0245    | 0.020 (6)* |
| C36 | 0.5039 (3) | 0.92864 (14) | 0.0960 (2) | 0.0145 (6) |
| H361| 0.5788    | 0.9531    | 0.1400    | 0.017 (5)* |
| H362| 0.4360    | 0.9571    | 0.0541    | 0.017 (5)* |
| H363| 0.5523    | 0.9014    | 0.0512    | 0.017 (5)* |
| C37 | 0.3473 (3) | 0.92796 (14) | 0.2388 (2) | 0.0152 (6) |
| H371| 0.2912    | 0.9006    | 0.2786    | 0.025 (5)* |
| H372| 0.2806    | 0.9589    | 0.2015    | 0.025 (5)* |
| H373| 0.4246    | 0.9496    | 0.2852    | 0.025 (5)* |
| S2  | 0.77527 (7) | 0.74136 (3) | 0.27649 (6) | 0.01212 (15) |
| C41 | 0.6123 (3) | 0.69967 (14) | 0.2814 (2) | 0.0113 (6) |
### Atomic displacement parameters (Å²)

|   | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{12}$   | $U_{13}$   | $U_{23}$   |
|---|------------|------------|------------|------------|------------|------------|
| Mo1 | 0.0074 (9) | 0.00788 (11) | 0.00833 (12) | 0.00024 (9) | 0.00205 (7) | −0.00025 (10) |
| C10 | 0.0191 (13) | 0.0148 (15) | 0.0124 (16) | −0.0046 (11) | 0.0039 (11) | 0.0026 (12) |
| C1  | 0.0082 (11) | 0.0157 (15) | 0.0061 (14) | −0.0007 (10) | 0.0003 (9)  | 0.0018 (11) |
| C2  | 0.0069 (11) | 0.0175 (15) | 0.0085 (14) | 0.0012 (10)  | −0.0001 (10) | −0.0001 (11) |
| C20 | 0.0174 (13) | 0.0158 (16) | 0.0143 (16) | 0.0014 (11)  | 0.0076 (11) | −0.0044 (12) |
| C3  | 0.0086 (11) | 0.0140 (14) | 0.0106 (15) | −0.0005 (10) | 0.0008 (10) | 0.0014 (12) |
| O3  | 0.0153 (9)  | 0.0126 (11) | 0.0199 (12) | 0.0009 (8)   | 0.0038 (8)  | −0.0017 (9)  |
| O11 | 0.0099 (8)  | 0.0235 (12) | 0.0144 (12) | −0.0047 (8)  | −0.0015 (7) | 0.0004 (9)   |
| C12 | 0.0098 (11) | 0.0157 (15) | 0.0137 (16) | 0.0025 (10)  | 0.0033 (10) | −0.0024 (12) |
| N13 | 0.0087 (9)  | 0.0133 (13) | 0.0111 (13) | 0.0033 (8)   | 0.0010 (8)  | 0.0011 (10)  |
| C14 | 0.0090 (11) | 0.0184 (16) | 0.0119 (15) | 0.0034 (10)  | −0.0010 (10) | 0.0043 (12)  |
| C15 | 0.0123 (12) | 0.0229 (17) | 0.0119 (16) | −0.0001 (11) | 0.0002 (10) | 0.0026 (13)  |
| C16 | 0.0117 (12) | 0.0212 (17) | 0.0192 (17) | 0.0048 (11)  | 0.0016 (11) | 0.0052 (14)  |
| C17 | 0.0132 (12) | 0.0270 (18) | 0.0142 (17) | 0.0022 (12)  | 0.0023 (11) | 0.0053 (14)  |
| S1  | 0.0135 (3)  | 0.0140 (4)  | 0.0107 (4)  | −0.0017 (3)  | 0.0041 (3)  | −0.0009 (3)  |
| C21 | 0.0086 (11) | 0.0130 (14) | 0.0154 (16) | −0.0009 (10) | 0.0063 (10) | −0.0001 (12) |
| C22 | 0.0083 (11) | 0.0137 (15) | 0.0159 (16) | −0.0006 (10) | 0.0054 (10) | 0.0011 (12)  |
| C23 | 0.0112 (12) | 0.0189 (17) | 0.0234 (18) | −0.0029 (11) | 0.0063 (11) | −0.0030 (13) |
| C24 | 0.0203 (14) | 0.0123 (16) | 0.034 (2)   | −0.0031 (12) | 0.0143 (13) | −0.0012 (14) |
| C25 | 0.0180 (13) | 0.0178 (17) | 0.0227 (18) | −0.0003 (12) | 0.0107 (12) | 0.0065 (14)  |
| C26 | 0.0153 (13) | 0.0214 (17) | 0.0138 (16) | 0.0002 (11)  | 0.0081 (11) | 0.0026 (13)  |
| O31 | 0.0130 (9)  | 0.0117 (11) | 0.0176 (12) | −0.0015 (7)  | −0.0059 (8) | 0.0037 (9)   |
| C32 | 0.0099 (11) | 0.0162 (15) | 0.0084 (15) | 0.0028 (10)  | 0.0019 (10) | −0.0011 (12) |
| N33 | 0.0090 (9)  | 0.0074 (12) | 0.0105 (13) | 0.0005 (8)   | −0.0002 (8) | 0.0011 (9)   |
| C34 | 0.0123 (11) | 0.0102 (14) | 0.0107 (15) | 0.0035 (10)  | −0.0023 (10) | 0.0020 (11)  |
| C35 | 0.0189 (13) | 0.0135 (15) | 0.0211 (18) | −0.0005 (12) | −0.0055 (12) | 0.0023 (14)  |
| C36 | 0.0173 (13) | 0.0140 (15) | 0.0113 (16) | 0.0021 (11)  | −0.0008 (11) | 0.0007 (12)  |
| C37 | 0.0119 (12) | 0.0166 (16) | 0.0169 (17) | 0.0021 (11)  | 0.0013 (11) | 0.0001 (13)  |
| S2  | 0.0110 (3)  | 0.0106 (3)  | 0.0153 (4)  | 0.0014 (2)   | 0.0037 (2)  | −0.0013 (3)  |
| C41 | 0.0152 (12) | 0.0127 (15) | 0.0067 (14) | 0.0007 (10)  | 0.0036 (10) | −0.0012 (11) |
| C42 | 0.0128 (12) | 0.0085 (14) | 0.0105 (15) | 0.0012 (10)  | 0.0022 (10) | −0.0037 (11) |
| C43 | 0.0141 (12) | 0.0129 (15) | 0.0096 (15) | −0.0021 (10) | 0.0015 (10) | −0.0022 (11) |
| C44 | 0.0220 (14) | 0.0150 (15) | 0.0151 (17) | −0.0083 (12) | 0.0055 (12) | −0.0017 (13) |
| C45 | 0.0319 (16) | 0.0080 (14) | 0.0131 (16) | 0.0002 (12)  | 0.0049 (12) | 0.0004 (12)  |
| C46 | 0.0189 (13) | 0.0148 (16) | 0.0137 (16) | 0.0033 (11)  | 0.0033 (11) | 0.0003 (12)  |
### Geometric parameters (Å, °)

| Bond/Distance       | Length/Angle                  |
|---------------------|-------------------------------|
| Mo1—C1              | 2.024 (3)                     |
| Mo1—C2              | 2.059 (3)                     |
| Mo1—C3              | 1.953 (3)                     |
| Mo1—N13             | 2.236 (2)                     |
| Mo1—N33             | 2.203 (2)                     |
| Mo1—S1              | 2.5254 (8)                    |
| Mo1—S2              | 2.5297 (8)                    |
| C1—C2               | 1.314 (4)                     |
| C1—C10              | 1.483 (4)                     |
| C12—O11             | 1.364 (3)                     |
| C15—O11             | 1.453 (3)                     |
| C12—N13             | 1.289 (4)                     |
| C12—C22             | 1.459 (4)                     |
| N13—C14             | 1.515 (3)                     |
| C14—C17             | 1.505 (4)                     |
| C14—C16             | 1.525 (4)                     |
| C15—H151            | 0.99                          |
| C15—H152            | 0.99                          |
| C16—H161            | 0.98                          |
| C16—H162            | 0.98                          |
| C16—H163            | 0.98                          |
| N13—Mo1—N33         | 168.04 (8)                    |
| S1—Mo1—S2           | 79.54 (3)                     |
| C1—Mo1—S1           | 163.76 (8)                    |
| C2—Mo1—S1           | 156.87 (8)                    |
| C3—Mo1—S2           | 167.27 (9)                    |
| C3—Mo1—C1           | 107.43 (12)                   |
| C3—Mo1—C2           | 69.91 (12)                    |
| C3—Mo1—N33          | 94.51 (9)                     |
| H172—C17—H173       | 109.5                         |
| C21—S1—Mo1          | 101.22 (10)                   |
| C26—C21—C22         | 117.5 (3)                     |
| C26—C21—S1          | 119.5 (2)                     |
| C22—C21—S1          | 123.0 (2)                     |
| C22—C21—C1          | 120.0 (3)                     |
| C22—C21—C2          | 118.8 (3)                     |
| C21—C22             | 120.9 (3)                     |
| C21—C22             | 121.2 (3)                     |
C1—Mo1—N33 93.43 (9)  C24—C23—H23 119.4
C2—Mo1—N33 97.17 (9)  C22—C23—H23 119.4
C3—Mo1—N13 88.01 (9)  C23—C24—C25 119.2 (3)
C1—Mo1—N13 96.97 (9)  C23—C24—H24 120.4
C2—Mo1—N13 94.67 (9)  C25—C24—H24 120.4
C3—Mo1—S1 87.86 (8)  C26—C25—C24 120.7 (3)
N33—Mo1—S1 90.70 (6)  C26—C25—H25 119.6
N13—Mo1—S1 77.69 (6)  C24—C25—H25 119.6
C1—Mo1—S2 85.29 (9)  C25—C26—C21 121.3 (3)
C2—Mo1—S2 122.81 (9)  C25—C26—H26 119.3
N33—Mo1—S2 83.92 (6)  C21—C26—H26 119.3
N13—Mo1—S2 91.04 (6)  C32—O31—C35 107.1 (2)
C1—C10—H101 109.5  N33—C32—O31 116.3 (2)
C1—C10—H102 109.5  N33—C32—C42 131.4 (2)
H101—C10—H102 109.5  O31—C32—C42 112.3 (2)
C1—C10—H103 109.5  O31—C32—C34 107.1 (2)
H101—C10—H103 109.5  C32—O31—C35 107.1 (2)
C10—C1—C10 137.3 (3)  N33—C31—C35 112.5 (2)
C2—C1—C10 72.66 (18)  N33—C31—C36 112.5 (2)
C10—C1—Mo1 150.0 (2)  C36—C31—C35 109.0 (2)
N13—C1—Mo1 150.0 (2)  C36—C31—C36 109.0 (2)
C1—C2—C20 139.6 (3)  C34—C36—H361 109.5
C1—C2—Mo1 69.82 (18)  C34—C36—H362 109.5
C20—C2—Mo1 150.5 (2)  C34—C36—H363 109.5
C2—C20—H201 109.5  O31—C35—C36 112.3 (2)
C2—C20—H202 109.5  O31—C35—H351 107.1 (2)
H201—C20—H202 109.5  O31—C35—H352 107.1 (2)
C2—C20—H203 109.5  C36—C34—C35 109.0 (2)
C20—C20—H203 109.5  C36—C34—C37 109.0 (2)
H201—C20—H203 109.5  C34—C35—H351 112.3 (2)
H202—C20—H203 109.5  C34—C35—H352 112.3 (2)
Mo1—C3—O3 122.26 (18)  H351—C36—H361 109.5
C12—O11—C15 104.9 (2)  H352—C36—H362 109.5
N13—C12—O11 116.1 (3)  H361—C36—H362 109.5
N13—C12—C22 129.6 (2)  H362—C36—H363 109.5
O11—C12—C22 114.0 (2)  H363—C36—H364 109.5
C12—N13—C14 106.5 (2)  C34—C37—H371 109.5
C12—N13—Mo1 113.0 (3)  C34—C37—H372 109.5
C14—N13—Mo1 131.18 (17)  H371—C37—H372 109.5
C17—C14—N13 113.4 (2)  H371—C37—H372 109.5
C17—C14—C16 111.8 (3)  H372—C37—H373 109.5
N13—C14—C16 107.7 (2)  H372—C37—H373 109.5
C17—C14—C15 113.0 (3)  H372—C37—H373 109.5
N13—C14—C15 99.8 (2)  C41—S2—Mo1 105.32 (10)
C16—C14—C15 110.5 (2)  C46—C41—C42 117.3 (2)
O11—C15—C14 103.8 (2)  C46—C41—S2 118.1 (2)
O11—C15—H151 111.0  C42—C41—S2 124.6 (2)
C14—C15—H151 111.0  C43—C42—C41 119.6 (3)
O11—C15—H152 111.0  C43—C42—C32 116.8 (2)
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|----------|----------------------|----------|
| C14—C15—H152        | 111.0    | C41—C42—C32         | 123.6 (2)|
| H151—C15—H152       | 109.0    | C44—C43—C42         | 121.9 (3)|
| C14—C16—H161        | 109.5    | C44—C43—H43         | 119.1    |
| C14—C16—H162        | 109.5    | C42—C43—H43         | 119.1    |
| H161—C16—H162       | 109.5    | C43—C44—C45         | 118.8 (3)|
| C14—C16—H163        | 109.5    | C43—C44—H44         | 120.6    |
| H161—C16—H163       | 109.5    | C45—C44—H44         | 120.6    |
| C14—C17—H171        | 109.5    | C46—C45—H45         | 119.9    |
| C14—C17—H172        | 109.5    | C44—C45—H45         | 119.9    |
| H171—C17—H172       | 109.5    | C45—C46—C41         | 122.3 (3)|
| C14—C17—H173        | 109.5    | C45—C46—H46         | 118.9    |
| H171—C17—H173       | 109.5    | C41—C46—H46         | 118.9    |
| C1—C2—Mo1—C3        | 178.5 (2)| C22—C21—C26—C25    | −3.2 (4) |
| C10—C1—C2—C20       | 1.1 (6)  | S1—C21—C26—C25     | 178.4 (2)|
| Mo1—C1—C2—C20       | 179.2 (4)| C35—O31—C32—N33    | 7.8 (3)  |
| Mo1—C2—C1—C10       | −178.1 (3)| C35—O31—C32—C42    | −173.6 (2)|
| C15—O11—C12—N13     | −8.7 (3) | O31—C32—N33—C34    | 4.4 (3)  |
| C15—O11—C12—C22     | 177.1 (2)| C42—C32—N33—C34    | −173.8 (3)|
| O11—C12—N13—C14     | −11.2 (3)| O31—C32—N33—Mo1    | 175.82 (17)|
| C22—C12—N13—Mo1     | 162.0 (3)| C42—C32—N33—Mo1    | −2.4 (5) |
| O11—C12—N13—Mo1     | 171.36 (17)| C32—N33—C34—C36 | −132.2 (3)|
| C22—C12—N13—Mo1     | −15.5 (4)| Mo1—N33—C34—C36    | 56.4 (3) |
| C12—N13—C14—C17     | 145.1 (3)| C32—N33—C34—C37    | 102.6 (3)|
| Mo1—N13—C14—C17     | −37.8 (4)| Mo1—N33—C34—C37    | −68.8 (3)|
| C12—N13—C14—C16     | −90.7 (3)| C32—N33—C34—C35    | −13.7 (3)|
| Mo1—N13—C14—C16     | 86.5 (3) | Mo1—N33—C34—C35    | 174.92 (18)|
| C12—N13—C14—C15     | 24.7 (3) | C32—O31—C35—C34    | −16.0 (3)|
| Mo1—N13—C14—C15     | −158.15 (19)| N33—C34—C35—O31 | 17.6 (3) |
| C12—O11—C15—C14     | 24.1 (3) | C36—C34—C35—O31    | 137.4 (2)|
| C17—C14—C15—O11     | −149.7 (2)| C37—C34—C35—O31    | −97.9 (3)|
| N13—C14—C15—O11     | −29.0 (3)| Mo1—S2—C41—C46     | −144.6 (2)|
| C16—C14—C15—O11     | 84.3 (3) | Mo1—S2—C41—C42     | 36.7 (3) |
| Mo1—S1—C21—C26      | −138.2 (2)| C46—C41—C42—C43   | 1.8 (4)  |
| Mo1—S1—C21—C22      | 43.6 (2) | S2—C41—C42—C43     | −179.5 (2)|
| C26—C21—C22—C23     | 3.1 (4)  | C46—C41—C42—C32    | −174.7 (3)|
| S1—C21—C22—C23      | −178.6 (2)| S2—C41—C42—C32    | 4.0 (4)  |
| C26—C21—C22—C12     | −170.1 (2)| N33—C32—C42—C43   | 152.4 (3)|
| S1—C21—C22—C12      | 8.2 (4)  | O31—C32—C42—C43   | −25.9 (4)|
| N13—C12—C22—C23     | 153.7 (3)| N33—C32—C42—C41   | −31.0 (5)|
| O11—C12—C22—C23     | −33.0 (4)| O31—C32—C42—C41   | 150.7 (3)|
| N13—C12—C22—C21     | −33.0 (4)| C41—C42—C43—C44   | −0.7 (4) |
| O11—C12—C22—C21     | 140.3 (3)| C32—C42—C43—C44   | 176.1 (3)|
| C21—C22—C23—C24     | −0.1 (4) | C42—C43—C44—C45   | −1.3 (5) |
| C12—C22—C23—C24     | 173.2 (2)| C43—C44—C45—C46   | 2.1 (5)  |
| C22—C23—C24—C25     | −2.8 (4) | C44—C45—C46—C41   | −1.0 (5) |
| C23—C24—C25—C26     | 2.7 (4)  | C42—C41—C46—C45   | −1.0 (4) |
| Bond                   | Distance (Å) | Angle (°)  |
|-----------------------|--------------|------------|
| C24—C25—C26—C21      | 0.4 (4)      |            |
| S2—C41—C46—C45       | -179.8 (2)   |            |