Supporting Information

Activation and Photoinduced Release of Alkynes on a Biomimetic Tungsten Center: The Photochemical Behavior of the W–S-Phoz System

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Experimental

General Procedures. All manipulations were performed under an atmosphere of N₂ using standard Schlenk and glovebox techniques. All chemicals were purchased from commercial sources and were used without further purification if not stated otherwise. Solvents were dried via a Pure Solv Solvent Purification System. A desk light from DS-Produkte with a compact fluorescent light mimicking natural light (color temperature 6500 K; light output 1400 lumen; wattage: 27 W) was used as light source for preparative scale photochemical reactions. NMR spectra were measured on a Bruker Avance III 300 MHz spectrometer at 25 °C. 1H and 13C NMR spectroscopy chemical shifts are given in ppm. 1H spectra are referenced to residual protons in the solvent. Coupling constants J are listed in Hertz. The prefix b is used to identify broad signals. Solid state IR spectra were measured on a Bruker ALPHA-P Diamant ATR-FTIR spectrometer at a resolution of
Signal intensities were assigned according to their relative intensities as strong (s) or medium (m). Most medium and weak (w) resonances were omitted. Mass spectra were recorded with an Agilent Technologies 5975C inert XL MSD instrument using the direct insertion technique. Elemental analyses were performed by the Microanalytical Laboratory of the University of Vienna using a EuroVector EA3000.

Characterization of $[\text{W}_4\text{O}_4(\mu-\text{O})_6(\text{S-Phoz})_4]$ (5): $[\text{W}(\text{CO})(\text{C}_2\text{Me}_2)(\text{S-Phoz})_2]$ (1b) (104 mg, 0.15 mmol) was dissolved in 2 mL CH$_2$Cl$_2$ and a solution of 16 mg pyridine-\(\text{N}_2\text{O}\) (0.17 mmol) in 1 mL CH$_2$Cl$_2$ and molecular sieve was added. The flask was covered with aluminum foil and the reaction was stirred for 1h before a spatula tip of pyridine-\(\text{N}_2\text{O}\) was added. After another hour of stirring the color of the mixture turned from green to yellow. The aluminum foil was removed and the flask was stirred for another 24 h before it was dried in vacuo. The residue was taken up in 4 x 0.5 mL MeCN and filtered over Celite. The orange residue was eluted from Celite with CH$_2$Cl$_2$ and dried in vacuo. For the $^1$H NMR spectrum the residue was dissolved in the NMR solvent and filtered over Celite. Single crystals suitable for X-ray diffraction analysis were obtained from CH$_2$Cl$_2$/ heptane solutions at -35 °C. $^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta = 7.88$ (dd, $J=7.9$, 1.2, 4H, Ar-H), 7.49 (d, $J=7.4$, 4H, Ar-H), 7.32 (td, $J=7.7$, 1.4, 4H, Ar-H), 7.10 (t, $J=7.1$, 4H, Ar-H), 4.31 (s, 8H, CH$_2$), 1.71 (s, 12H, Me), 1.65 (s, 12H, Me). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) $\delta = 171.14$ (C$_q$), 147.08 (C$_q$), 132.92 (CH$_{arom}$), 131.97 (CH$_{arom}$), 130.64 (CH$_{arom}$), 128.95 (C$_q$), 124.91 (CH$_{arom}$), 81.33 (CH$_2$), 72.07 (C$_q$), 27.89 (Me), 27.56 (Me). IR (cm$^{-1}$): 1596 (C=N), 852 (W=O), 818 (W=O). El-MS: m/z 860.1 (M/2), 439.1 (M/2 – WO$_2$ – L).

Characterization of $[(\text{WO}(\mu-\text{O})(\text{S-Phoz})_2)]$ (6): In a Schlenk tube 100 mg of $[\text{WO}(\text{C}_2\text{H}_2)(\text{S-Phoz})_2]$ (2a) (0.16 mmol) were dissolved in 22 mL MeCN. The tube was equipped with a bubbler and the solution was irradiated with a day light lamp for approx. 3 h while it was heavily stirred. The solution was filtered and the solvent was removed in vacuo. It was redissolved in a mixture of 2 mL MeCN and 2 mL CH$_2$Cl$_2$. After evaporation of CH$_2$Cl$_2$ the solution was irradiated again with the day light lamp for 1.5 days until the formed precipitate was completely yellow. The mixture was stored in the fridge at 4 °C before it was filtered over Celite. The yellow residue was eluted from Celite with CH$_2$Cl$_2$ and dried in vacuo. Single crystals suitable for X-ray diffraction analysis were obtained from CH$_2$Cl$_2$/ toluene/ heptane solutions at -35 °C or toluene solutions at rt. $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 8.28$ (dd, $J=8.2$, 1.5, 2H, Ar-H), 7.82 ((dd, $J=8.1$, 1.2, 2H, Ar-H), 7.49 (ddd, $J=15.1$, 7.2, 1.3, 2H, Ar-H), 7.35 – 7.20 (m, 2H, Ar-H), 4.63 (d, $J=8.3$, 2H, CH$_2$), 4.46
(d, J=8.3, 2H, CH₂), 2.06 (s, 6H, Me), 1.96 (s, 6H, Me). IR (cm⁻¹): 1591 (C=N), 808 (W=O) 724 (µ-O). EI-MS: m/z 844.2 (M⁺), 828.2 (M – O), 422.1 (M/2).
$^1$H and $^{13}$C NMR spectra

$^1$H NMR (300 MHz, CD$_2$Cl$_2$) δ = 7.76 (dd, J = 8.0, 1.0, 1H), 7.65 (dd, J = 7.9, 1.3, 1H), 7.61 (dd, J = 7.9, 0.9, 1H), 7.43 (dd, J = 8.0, 1.4, 1H), 7.31 (td, J = 7.6, 1.5, 1H), 7.17 (ddd, J = 8.0, 7.2, 1.6, 1H), 7.07 (td, J = 7.9, 1.3, 1H), 6.89 (ddd, J = 8.3, 7.2, 1.3, 1H), 4.17 (d, J = 8.3, 1H), 4.04 – 3.88 (m, 3H), 2.90 (s, 3H), 2.46 (s, 3H), 1.87 (s, 3H), 1.41 (s, 3H), 0.77 (s, 3H), 0.58 (s, 3H).

The spectra show the assignments for the chemical shifts and coupling constants, indicating the resonance positions and multiplicities of the protons and carbons in the molecule.
$^1$H NMR (300 MHz, CD$_3$Cl$_2$) $\delta$ = 8.08 (dd, $J$ = 8.2, 1.1, 1H), 7.88 – 7.83 (m, 1H), 7.81 (dd, $J$ = 8.0, 1.2, 1H), 7.67 (d, $J$ = 6.4, 1H), 7.59 (d, $J$ = 8.0, 1H), 7.53 – 6.97 (m, 28H), 6.80 – 6.71 (m, 1H), 6.53 – 6.45 (m, 2H), 4.28 (dd, $J$ = 15.9, 8.3, 2H), 4.10 – 3.96 (m, 5H), 3.85 (d, $J$ = 8.3, 1H), 1.84 (s, 3H), 1.72 (s, 3H), 1.45 (s, 6H), 1.34 (s, 3H), 1.29 (s, 3H), 0.84 (4H, 0.76 (s, 3H).
2b
VT-NMR measurements

Figure S1. Variable temperature $^1$H-NMR of [WO$_2$(S-Phoz)$_2$] (4) in CD$_2$Cl$_2$. 
Figure S2. CH$_2$-region of VT $^1$H, $^1$H-COSY-NMR of [WO$_2$(S-Phoz)$_2$] (4) in CD$_2$Cl$_2$. Cross peaks of asymmetric S,N-trans are highlighted with boxes.

Figure S3. $^1$H NMR spectra in CD$_2$Cl$_2$ of the decomposition of [WO$_2$(S-Phoz)$_2$] (4) to [W$_4$O$_4$(μ-O)$_6$(S-Phoz)$_4$] (5) (light gray), [[WO(μ-O)(S-Phoz)]$_2$] (6) (white), HS-Phoz (dark gray) and (S-Phoz)$_2$ (black).
In-situ $^1$H NMR measurements

Measurements were performed on a Bruker Avance 200 MHz spectrometer with a Hamamatsu high pressure mercury lamp coupled to the probehead via a waveguide and quartz prism. The 362 nm emission band of the lamp was isolated by a set of glass filters. The sample was exposed to the UV-irradiation by using the internal lamp shutter with an opening time of 150 ms. Samples ($3.3 \cdot 10^{-3}$ mol/L) were prepared in CD$_2$Cl$_2$. The ratios of 2a-c to 3 were determined by integration of the oxazoline’s CH$_2$-moieties and normalization to 100%. The data points were fitted by a single exponential function which describes time-dependent concentration change in first order chemical reaction where $k$ is the rate constant of interest and $t$ is the irradiation time. $C$ and $C_0$ are NMR integrals at $t = t$ and $t = 0$ correspondingly.

$$C = C_0 e^{-kt}$$

**Figure S4.** In-situ $^1$H NMR measurements of [WO(C$_2$H$_2$)(S-Phoz)$_2$] (2a). Experimental data (right) and exponential fit (left).

**Figure S5.** In-situ $^1$H NMR measurements of [WO(C$_2$Me$_2$)(S-Phoz)$_2$] (2b). Experimental data (right) and exponential fit (left).
**Figure S6.** In-situ $^1$H NMR measurements of [WO(C$_2$Ph$_2$)(S-Phoz)$_2$] (2c). Experimental data (right) and exponential fit (left).

**Transient absorbance spectroscopy**

The experiments were performed with a LKS80 Laser Flash Photolysis Spectrometer (Applied Photophysics, UK). Samples were excited with the frequency tripled light from the Spitlight Compact 100 (InnoLas, Germany) solid-state Nd:YAG laser at 355 nm (pulse duration: 8 ns, energy: 10 mJ/pulse)

**Figure S7.** Time trace of the absorbance (525 nm) change recorded after the laser irradiation (355 nm, 8 ns, 10 mJ) of [WO(C$_2$H$_2$)(S-Phoz)$_2$] (2a)
Crystal structure determinations

**General.** X-ray data collection was performed with a Bruker AXS SMART APEX 2 CCD diffractometer using monochromated Mo-\(K_\alpha\) radiation (0.71073 Å) at 100 K. Semi-empirical from equivalents absorption corrections were made. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against \(F^2\) (SHELXL-2014/6).\(^2\) A weighting scheme of \(w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]\) where \(P = (F_o^2+2F_c^2)/3\) was used. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the phenyl rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl group. The H atoms of the CH\(_2\) groups were refined with a common isotropic displacement parameter and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. 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 rotation around the C–C bond, and C–H distances of 0.98Å. Further details are given in Tables S1-S2 and in the CIF files.

\([W(CO)(C_2Ph_2)(S-Phoz)_2] \cdot \text{heptane (1c')}\). The absolute configuration was established by anomalous dispersion effects in the diffraction measurements on the crystal. The heptane solvent molecules are disordered over several orientations in the large voids built by the complexes. Those which could be located in a difference Fourier map were refined with site occupation factors of 0.25. The C–C bonds were restrained to 1.53Å, their H atoms were included at calculated positions, and the same isotropic displacement parameters were used for these solvent molecules.
Stereoscopic ORTEP plots

Figure S8. Stereoscopic ORTEP plots of \([\text{W(CO)}(\text{C}_2\text{Me}_3)(\text{S-Phoz})_2] \) (1b) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity reasons.

Figure S9. Stereoscopic ORTEP plots of \([\text{W(CO)}(\text{C}_2\text{Ph}_2)(\text{S-Phoz})_2] \cdot \text{toluene} \) (1c) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms as well as the solvent molecule were omitted for clarity reasons.
Figure S10. Stereoscopic ORTEP	extsuperscript{3} plot of [W(CO)(C\textsubscript{2}Ph\textsubscript{2})(S-Phoz)\textsubscript{2}] · heptane (1c\textsuperscript{′}) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50\% probability level. The H atoms as well as the disordered solvent molecules were omitted for clarity reasons.

Figure S11. Stereoscopic ORTEP	extsuperscript{3} plot of the packing of [W(CO)(C\textsubscript{2}Ph\textsubscript{2})(S-Phoz)\textsubscript{2}] · heptane (1c\textsuperscript{′}). The atoms are drawn with arbitrary radii. The H atoms as well as the disordered solvent molecules were omitted.
**Figure S12.** Stereoscopic ORTEP plot of \([\text{WO(C}_2\text{Me}_2)(\text{S-Phoz})_2]\) (2b) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms and the dichloromethane solvate molecule were omitted for clarity reasons. The longer N–W contact \([\text{W1–N33} \; 2.4310(16)\text{Å} \; \text{vs.} \; \text{W1–N13} \; 2.2563(16)\text{Å}]\) is plotted with a dashed line.

**Figure S13.** Stereoscopic ORTEP plot of \([\text{WO(C}_2\text{Ph}_2)(\text{S-Phoz})_2]\) (2c) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms and the dichloromethane solvate molecule were omitted for clarity reasons. The longer N–W contact \([\text{W1–N33} \; 2.414(3)\text{Å} \; \text{vs.} \; \text{W1–N13} \; 2.260(3)\text{Å}]\) is plotted with a dashed line.
Figure S14. Stereoscopic ORTEP³ plot of [WO₂(S-Phoz)₂] (4) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity.
**Figure S15.** Stereoscopic ORTEP$^3$ plot of $[\text{W}_4\text{O}_4(\mu-\text{O})_6(\text{S-Phoz})_4]$ (5) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms and the atoms of the toluene solvent molecule were omitted for clarity reasons. The bonds to the W atoms having bond lengths larger than 2.0 Å were plotted with thinner lines.

**Figure S16.** Stereoscopic ORTEP$^3$ plot of $[\text{W}_4\text{O}_4(\mu-\text{O})_6(\text{S-Phoz})_4]$ (5') showing the atomic numbering scheme.
**Figure S17.** Mercury plot of \([W_4O_4(\mu-O)_6(S\text{-Phoz})_4]\) (5) depicting the \(W_4O_{10}\)-core and the observed W-O bond lengths [Å].

**Figure S15.** Stereoscopic ORTEP\(^3\) plot of \([WO(\mu-O)(S\text{-Phoz})_2]\) (6) showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.
### Crystal data and structure refinement

| Crystal data | 1b | 1c | 1c' | 2b | 2c |
|--------------|----|----|-----|----|----|
| **Identification code** | 1b | 1c | 1c' | 2b | 2c |
| **Empirical formula** | C₇H₆N₂O₂S₄W | C₇H₆N₂O₂S₄W | C₇H₆N₂O₂S₄W | C₇H₆N₂O₂S₄W | C₇H₆N₂O₂S₄W |
| **Formula weight** | 678.50 | 894.76 | 3511.11 | 751.41 | 875.55 |
| **Crystal description** | needle, dark orange | block, green | block, green | block, yellow | needle, yellow |
| **Crystal size [mm]** | 0.22 x 0.15 x 0.08 | 0.21 x 0.17 x 0.16 | 0.27 x 0.27 x 0.27 | 0.21 x 0.14 x 0.07 | 0.24 x 0.11 x 0.07 |
| **Space group** | P 2/c | P -1 | I 2 3 | monoclinic | P 2/c |
| **a [Å]** | 9.1325(3) Å | 10.9173(4) Å | 28.9358(13) Å | 18.253(3) Å | 8.5711(15) Å |
| **b [Å]** | 21.3487(7) Å | 11.9168(5) Å | 92.1885(17) Å | 11.2808(16) Å | 11.2524(19) Å |
| **c [Å]** | 13.2048(4) Å | 15.2395(6) Å | 99.3295(15) Å | 14.537(2) Å | 18.815(3) Å |
| **α [°]** | 98.7161(11)° | 98.8168(15)° | 98.9929(13) Å | 98.9929(13) Å | 96.305(3)° |
| **γ [°]** | 2544.80(14) Å | 1929.98(13) Å | 24227(3) Å | 29220(7) Å | 1730.6(5) Å |
| **Volume [Å³]** | 4 | 2 | 6 | 4 | 2 |
| **Calculated density [g/cm³]** | 1.771 Mg/m³ | 1.540 Mg/m³ | 1.444 Mg/m³ | 1.708 Mg/m³ | 1.680 Mg/m³ |
| **F(000)** | 1344 | 900 | 10644 | 1488 | 872 |
| **Max. and min. transmission** | 1.000 and 0.737 | 1.000 and 0.798 | 1.000 and 0.784 | 1.000 and 0.670 | 1.000 and 0.803 |
| **Unit cell volume** | 3.143 mm³ | 3.003 mm³ | 3.410 mm³ | 3.652 mm³ |
| **Reflections** | 163517 / 7389 | 48992 / 11265 | 61965 / 9747 | 109341 / 12866 | 25774 / 10046 |
| **Unique reflections** | 6580 with I > 2σ(I) | 10604 with I > 2σ(I) | 9196 with I > 2σ(I) | 1126 with I > 2σ(l) | 8892 with I > 2σ(l) |
| **R(int), R(sigma)** | 0.0185, 0.0252 | 0.0319, 0.0225 | 0.0522, 0.0361 | 0.0440, 0.0302 | 0.0279, 0.0471 |
| **Completeness to θmax** | 99.6% | 99.9% | 99.8% | 99.9% | 99.7% |

### Data collection

| Radiation source | fine-focus sealed tube | fine-focus sealed tube | fine-focus sealed tube | Incoatec micro-focus sealed tube | Incoatec micro-focus sealed tube |
|------------------|------------------------|------------------------|------------------------|-------------------------------|-------------------------------|
| Monochromator    | graphite               | graphite               | graphite               | monochromator                | monochromator                |
| θ range for data collection | 2.45 to 30.00° | 2.35 to 30.00° | 2.23 to 28.00° | 2.14 to 35.00° | 1.11 to 30.00° |
| Reflections collected / unique | 2n(l) | 2n(l) | 2n(l) | 2n(l) | 2n(l) |
| R(int), R(sigma) | 0.0185, 0.0252 | 0.0319, 0.0225 | 0.0522, 0.0361 | 0.0440, 0.0302 | 0.0279, 0.0471 |
| Completeness to θmax | 99.6% | 99.9% | 99.8% | 99.9% | 99.7% |

### Refinement

| Data / parameters / restraints | 7389 / 332 / 0 | 11265 / 485 / 0 | 9747 / 483 / 36 | 12866 / 352 / 0 | 10046 / 439 / 0 |
| Goodness-of-fit on F² | 1.018 | 1.050 | 1.058 | 1.075 | 1.084 |
| Final R indices | R1 = 0.0173, Rw2 = 0.0391 | R1 = 0.0219, Rw2 = 0.0553 | R1 = 0.0212, Rw2 = 0.0586 | R1 = 0.0254, Rw2 = 0.0545 | R1 = 0.0364, Rw2 = 0.0515 |
| R indices (all data) | R1 = 0.0220, Rw2 = 0.0407 | R1 = 0.0246, Rw2 = 0.0575 | R1 = 0.0250, Rw2 = 0.0605 | R1 = 0.0332, Rw2 = 0.0576 | R1 = 0.0437, Rw2 = 0.0959 |
| Absolute structure parameter | | | -0.212(1) | | |
| Weighting scheme | | | | | |
| parameters a, b | | | | | |
| Largest Δ/σ in last cycle | 0.002 | 0.003 | 0.002 | 0.001 | 0.002 |
| Largest difference peak and hole | 1.214 and -3.131e Å³ | 3.377 and -1.955e Å³ | 0.760 and -0.528e Å³ | 2.146 and -1.643e Å³ | 3.123 and -2.298e Å³ |

**Table S1.** Crystal data and structure refinement for [W(CO)(C₂Me₂)(S-Phoz)] (1b), [W(CO)(C₂Ph₂)(S-Phoz)] · toluene (1c), [W(CO)(C₂Ph₂)(S-Phoz)] · heptane (1c'), [WO(C₂Me₂)(S-Phoz)] · dichloromethane (2b), and [WO(C₂Ph₂)(S-Phoz)] · dichloromethane (2c)
Table S2. Crystal data and structure refinement for, \([\text{WO}_2(\text{S-Phoz})_2]\) (4) and \([\text{W}_4\text{O}_8(\mu-\text{O})_6(\text{S-Phoz})_4]\) · toluene (5), \([\text{W}_4\text{O}_8(\mu-\text{O})_6(\text{S-Phoz})_4]\) · toluene (5') and [[WO(\mu-\text{O})(\text{S-Phoz})]_2] (6).

| Crystal data                  |                        |                        |                        |                        |
|------------------------------|------------------------|------------------------|------------------------|------------------------|
| Identification code          | code                   | code                   | code                   | code                   |
| Empirical formula            | \(\text{C}_2\text{H}_2\text{N}_2\text{O}_4\text{S}_4\text{W}\) | \(\text{C}_2\text{H}_2\text{N}_2\text{O}_4\text{S}_4\text{W}\) | \(\text{C}_2\text{H}_2\text{N}_2\text{O}_4\text{S}_4\text{W}\) | \(\text{C}_2\text{H}_2\text{N}_2\text{O}_4\text{S}_4\text{W}\) |
| Formula weight               | 628.40                 | 1904.77                | 1904.77                | 1904.77                |
| Crystal description          | block, yellow          | block, orange          | needle, yellow         | block, yellow          |
| Crystal size [mm]            | 0.24 × 0.09 × 0.07     | 0.23 × 0.19 × 0.18     | 0.14 × 0.03 × 0.03     | 0.21 × 0.17 × 0.14     |
| Crystal system               | monoclinic             | monoclinic             | monoclinic/c           | monoclinic/c           |
| Space group                  | \(P \, 2_1/n\)         | \(C \, 2/c\)           | \(C \, 2/c\)           | \(C \, 2/c\)           |
| a                            | 10.2425(6)Å            | 19.7559(5)Å            | 21.0287(14)Å           | 13.7474(6)Å            |
| b                            | 15.9011(11)Å           | 12.3410(3)Å            | 10.4050(7)Å            | 13.5041(5)Å            |
| c                            | 12.9751(7)Å            | 24.9965(7)Å            | 27.2306(18)Å           | 14.1710(6)Å            |
| \(\beta\)                   | 94.937(3)^a            | 93.1530(10)^a          | 96.3476(18)^a          | 109.6576(12)^a         |
| \(\alpha\)                  | 90.3788°               | 90.319°                | 90.4054°               | 90.319°                |
| \(\gamma\)                  | 99.9%                  | 99.9%                  | 99.9%                  | 99.9%                  |
| Volume                       | 2237.8(2)Å³            | 6085.1(3)Å³            | 5921.6(7)Å³            | 2477.47(18)Å³          |
| Z                            | 4                      | 4                      | 4                      | 4                      |
| Calculated density           | 1.865Mg/m³             | 2.079Mg/m³             | 2.137Mg/m³             | 2.263Mg/m³             |
| F(000)                       | 1232                   | 3648                   | 3648                   | 1592                   |
| Linear absorption coefficient \(\mu\) | 5.381mm⁻¹              | 7.741mm⁻¹              | 7.955mm⁻¹              | 9.488mm⁻¹              |
| Max. and min. transmission   | 1.000 and 0.438         | 0.746 and 0.468        | 1.000 and 0.658        | 0.748 and 0.411        |
| Unit cell determination      | 2.65° < \(\theta\) < 35.61° | 2.50° < \(\theta\) < 35.20° | 2.59° < \(\theta\) < 30.73° | 3.15° < \(\theta\) < 40.76° |
| Used reflections             | 9895                   | 9723                   | 9230                   | 9966                   |

Data collection

| Radiation source            | Incoatec microfocus     | Incoatec microfocus     | Incoatec microfocus     | Incoatec microfocus     |
|                            | sealed tube             | sealed tube             | sealed tube             | sealed tube             |
|                            | monolayer               | monolayer               | monolayer               | monolayer               |
| \(\theta\) range for data | 1.98 to 35.00°          | 2.58 to 35.00°          | 2.59 to 26.00°          | 2.18 to 35.00°          |
| collection                 |                        |                        |                        |                        |
| Reflections collected / unique | 34861 / 9843            | 38503 / 13368           | 32417 / 5824            | 16739 / 5466            |
| Significant unique          | 7626 with \(I > 2\sigma(I)\) | 11896 with \(I > 2\sigma(I)\) | 4923 with \(I > 2\sigma(I)\) | 4716 with \(I > 2\sigma(I)\) |
| reflections                |                        |                        |                        |                        |
| R(int), R(sigma)            | 0.0572, 0.0574          | 0.0295, 0.0376          | 0.0606, 0.0551          | 0.0238, 0.0336          |
| Completeness to \(\theta_{max}\) | 99.9%                    | 99.9%                    | 99.9%                    | 99.8%                    |

Refinement

| Data / parameters / restraints | 9843 / 292 / 0 | 13368 / 395 / 0 | 5824 / 395 / 0 | 5466 / 160 / 0 |
| Goodness-of-fit on \(F^2\)  | 1.068            | 1.041            | 1.036            | 1.052            |
| R indices                    | 1.0309, 0.0235, 0.0580 | 0.0235, 0.0498, 0.0288, 0.0264 | 0.0304, 0.0572, 0.0512 | 0.0203, 0.0457, 0.0483 |
| I \(> 2\sigma(I)\)           | R1 = 0.0508, wR2 = 0.0642 | R1 = 0.0101, wR2 = 0.0512 | R1 = 0.0101, wR2 = 0.0512 | R1 = 0.0268, wR2 = 0.0483 |
| R indices (all data)         | 0.0057, 1.1552, 0.0166, 2.8834 | 0.0124, 3.0407, 0.0133, 3.2694 |
| Absolute structure parameter | -                | -                | -                | -                |
| Weighting scheme parameters | 0.001            | 0.003            | 0.003            | 0.003            |
| a, b in last cycle           | 1.949 and -2.089eÅ²  | 2.985 and -2.023eÅ² | 1.557 and -1.464eÅ² | 2.725 and -1.360eÅ² |
| Largest difference peak and hole | 1868881            | 1868882          | 1868883          | 1868884          |

References

[1] a) L. M. Peschel, F. Belaj, N. C. Mösch-Zanetti, *Angew. Chem. Int. Ed.* 2015, 54, 13018; b) L. M. Peschel, J. A. Schachner, C. H. Sala, F. Belaj, N. C. Mösch-Zanetti, *Z. Anorg. Allg. Chem.* 2013, 639, 1559.
[2] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, 64, 112.
[3] C. K. Johnson, ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA (1965).