Supporting Information

Dibismuthanes in Catalysis: From Synthesis and Characterization to Redox Behavior towards Oxidative Cleavage of 1,2-Diols

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1. General considerations

Experimental methods

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under dry argon in flame-dried glassware. Anhydrous n-pentane, THF, Et₂O and toluene were distilled from appropriate drying agents and were transferred under argon.

Flash chromatography: Merck silica gel 60 (40-63 µm). Preparative TLC plates: PLC Silica gel 60 F₂₅₄, 1 mm, 20x20 cm (Sigma-Aldrich). ESI-MS: ESQ 3000 (Bruker). High-resolution mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan). NMR spectra were recorded using 300 MHz Bruker Avance III, 400 MHz Bruker Avance III HD and 500 MHz Bruker Avance III NMR spectrometers. ¹H NMR spectra (300.13 MHz, 400.2 MHz, 500.1 Hz) were referenced to the residual protons of the deuterated solvent, and are reported to tetramethylsilane (δ TMS = 0 ppm), chloroform-d (δTMS= 7.26 ppm) or acetonitrile-d₃ (δTMS= 1.94ppm). ¹³C{¹H} NMR spectra (75.47 MHz, 101 MHz, 125 MHz) were referenced internally to the D-coupled ¹³C resonances of the NMR solvent and are reported to tetramethylsilane (δTMS= 0 ppm) and chloroform-d (δTMS= 77.16ppm). Chemical shifts (δ) are given in ppm, relative to deuterated solvent residual peak, and coupling constants (J) provided in Hz. C, H, Bi, Cl elemental analyses were performed by the Microanalytical Laboratory Kolbe.
2. Synthesis of Ligands 3 and 4

2.1 Synthesis of 4,6-dibromo-10,11-dihydrodibenzo[b,f]oxepine (3)

To a flame dried Schlenk-flask charged with a stir bar was added 10,11-dihydrodibenzo[b,f]oxepine\(^{[1,2]}\) (3.1) (585 mg, 2.98 mmol, 1.0 equiv.), anhydrous Et\(_2\)O (28 mL), anhydrous TMEDA (1.3 mL, 8.6 mmol, 2.9 equiv.) and dropwise a solution of 1.4 M s-BuLi (6.2 mL, 8.64 mmol, 2.9 equiv.) at −78 °C. The mixture was warmed to 23 °C and left to stir for 18 h. The solution was cooled to −78 °C, followed by a slow addition of Br\(_2\) (0.50 mL, 9.83 mmol, 3.3 equiv.) in pentane (6.5 mL) and allowed to stir for another 18 h at 23 °C. After completion, a saturated aqueous solution of Na\(_2\)S\(_2\)O\(_3\) was added, followed by Et\(_2\)O and the layers were separated. The aqueous layer was washed with Et\(_2\)O (3 × 20 mL) and the combined organics were washed with Na\(_2\)S\(_2\)O\(_3\), dried over MgSO\(_4\), filtered and concentrated under reduced pressure. Purification via flash chromatography (SiO\(_2\), 100% hexane) yielded 4,6-dibromo-10,11-dihydrodibenzo[b,f]oxepine (3) as a white solid (510 mg, 48% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.47 (dd, \(J = 7.9, 1.7\) Hz, 2H), 7.05 (dd, \(J = 7.6, 1.7\) Hz, 2H), 6.89 (t, \(J = 7.7\) Hz, 2H), 3.14 (s, 4H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): δ 152.7, 133.5, 132.0, 129.4, 124.7, 115.1, 32.1.

HRMS (ESI): calc’d for C\(_{14}\)H\(_{10}\)O\(_1\)Br\(_2\) [M]\(^+\) 351.909315; found 351.909350.
2.2 Synthesis of 2,2'-oxybis(iodobenzene) (4)

To a flame dried Schlenk-flask charged with a stir bar was added diphenylether (4.1) (1 g, 5.8 mmol, 1 equiv.), anhydrous THF (12 mL) and the solution was cooled to –78 °C. Then, anhydrous TMEDA (1.93 mL, 12.9 mmol, 2.2 equiv.) and a solution of 2.6 M n-BuLi (4.97 mL, 12.9 mmol, 2.9 equiv.) were added dropwise. The mixture was warmed to 23 °C and left to stir for 18 h. The solution was cooled to –78 °C, followed by a slow addition of I₂ (3.4 g, 13.5 mmol, 2.3 equiv.) and allowed to stir for another 18 h at 23 °C. After completion, a saturated aqueous solution of Na₂S₂O₃ was added, followed by Et₂O and the layers were separated. The aqueous layer was washed with Et₂O (3 × 10 mL) and the combined organics were washed with Na₂S₂O₃, dried over MgSO₄, filtered and concentrated under reduced pressure. Purification via flash chromatography (SiO₂, 100% hexane) yielded 2,2'-oxybis(iodobenzene) (4) as a white solid (1.047 g, 56% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.88 (dd, J = 7.9, 1.6 Hz, 2H), 7.28 (ddd, J = 8.2, 7.3, 1.5 Hz, 2H), 6.89 (td, J = 7.6, 1.4 Hz, 2H), 6.78 (dd, J = 8.2, 1.4 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃): δ 156.0, 140.1, 129.6, 125.5, 118.7, 88.4.

HRMS (ESI): calc’d for C₁₂H₈O₁I₂Na₁ [M+Na]⁺ 444.855679; found 444.856070.
3. Synthesis of Dibismuthanes 5-8

3.1 Synthesis of 4,6-bis(diphenylbismuthanyl)dibenzo[\textit{b,d}]furan (5)

4,6-dibromodibenzofuran\textsuperscript{[3]} (1) (150 mg, 0.46 mmol) was placed in a flame-dried Schlenk-flask under Ar atmosphere and dissolved in 6.5 mL of anhydrous THF. The solution was cooled to \(-78\) °C and a solution of 2.6 M \textit{n}-BuLi in hexane (0.35 mL, 0.92 mmol, 2.0 equiv.) was added dropwise. The mixture was warmed to 23 °C and left to stir for 45 min. Then, the mixture was cooled again to \(-78\) °C and a solution of \(\text{ZnCl}_2\) in anhydrous THF was added (0.92 mmol, 4.5 mL, 2.0 equiv.). The mixture was warmed to 23 °C and left to stir for 45 min. After this, \(\text{Ph}_2\text{BiOTs}\)\textsuperscript{[4]} (491.8 mg, 0.92 mmol, 2.0 equiv.) was added in one portion at \(-10\) °C, followed by the addition of additional 3 mL of anhydrous THF and the reaction was left to stir for 1.5 h at this temperature. The solution was quenched with a saturated aqueous solution of \(\text{NaHCO}_3\) and diluted with \(\text{Et}_2\text{O}\), whereupon it was extracted twice with \(\text{Et}_2\text{O}\) (2 \(\times\) 8 mL). The combined organic phases were dried over \(\text{MgSO}_4\), filtered and concentrated under reduced pressure (not to dryness!).\textsuperscript{[\textit{a}]}

The crude reaction mixture was then purified by flash chromatography (SiO\textsubscript{2}, 20:1 hexane:EtOAc). The obtained solid was washed further with cold pentane (2 \(\times\) 5 mL) to yield the desired complex 5 as an off-white solid (173 mg, 42\% yield).

\textbf{\textsuperscript{1}H NMR} (300 MHz, CDCl\textsubscript{3}): \(\delta 7.94\) (dd, \(J = 7.6, 1.3\) Hz, 2H [H\textsubscript{4}]), 7.77 (dt, \(J = 5.9, 1.6\) Hz, 8H [H\textsubscript{8,12}]), 7.68 (dd, \(J = 7.2, 1.2\) Hz, 2H, [H\textsubscript{2}]), 7.32 (m, \(J = 8.0, 3.4\) Hz, 14H [H\textsubscript{3,9,10,11}]).

\textbf{\textsuperscript{13}C NMR} (75 MHz, CDCl\textsubscript{3}): \(\delta 170.7\) [C\textsubscript{q}], 160.0 [C\textsubscript{q}], 137.9 [C\textsubscript{8}], 136.0 [C\textsubscript{2}], 130.5 [C\textsubscript{9}], 127.8 [C\textsubscript{1}], 125.5 [C\textsubscript{3}], 123.6 [C\textsubscript{1}], 120.7 [C\textsubscript{4}].\textsuperscript{[b]}

\textbf{HRMS (ESI)}: calc’d for \(\text{C}_{36}\text{H}_{27}\text{O}_{1}\text{Bi}_2\) [M+H]\textsuperscript{+} 893.166410; found 893.166160.

\textbf{EA}: \(\text{C}_{36}\text{H}_{27}\text{O}_{1}\text{Bi}_2\cdot\text{H}_2\text{O}\), calc’d C 47.49, H 3.10, Bi 45.90 %, exp. C 47.66, H 3.05, Bi 46.05 %.
X-ray quality crystals were obtained from slow evaporation of a solution of complex 5 in CH$_2$Cl$_2$:hexane (1:5) at 23 °C.

[a]Note: To avoid dismutation, which results in lower yields, it is advised to not to reach dryness.

[b]Note: One quartenary carbon signal was not observed in the $^{13}$C NMR spectra. To avoid a misassignment, the observable quaternary carbons were assigned as Cq.
3.2 Synthesis of (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(diphenylbismuthane) (6)

4,5-dibromo-9,9-dimethyl-9H-xanthene\textsuperscript{[5]} (2) (555 mg, 1.5 mmol) was placed in a flame-dried Schlenk-flask under Ar atmosphere and dissolved in 25 mL of anhydrous THF. The solution was cooled to −78 °C and a solution of 2.6 M \textit{n}-BuLi in hexane (0.28 mL, 3 mmol, 2.0 equiv.) was added dropwise. The mixture was warmed to 23 °C and left to stir for 45 min. After this time, the mixture was cooled again to −78 °C and a solution of ZnCl\textsubscript{2} in anhydrous THF was added (3.0 mmol, 15 mL, 2.0 equiv.). The mixture was warmed to 23 °C and left to stir for 45 min. Then, Ph\textsubscript{2}BiOTs\textsuperscript{[4]} (1.6 g, 3.0 mmol, 2.0 equiv.) was added in one portion at −10 °C, followed by the addition of additional 5 mL of anhydrous THF and the reaction was left to stir for 1.5 h at this temperature. The solution was quenched with a saturated aqueous solution of NaHCO\textsubscript{3} and diluted with Et\textsubscript{2}O, whereupon it was extracted twice with Et\textsubscript{2}O (2 × 25 mL). The combined organic phases were dried over MgSO\textsubscript{4}, filtered and concentrated under reduced pressure (not to dryness)! The obtained solid was washed further with cold pentane (2 × 5 mL) to yield the desired complex 6 as an off-white solid (750 mg, 53% yield).

\textbf{1H NMR} (300 MHz, CDCl\textsubscript{3}): δ 7.66 (dd, \textit{J} = 7.7, 1.6 Hz, 8H [H\textsubscript{10,14}]), 7.47 (dd, \textit{J} = 7.2, 1.5 Hz, 2H [H\textsubscript{6}]), 7.42 (dd, \textit{J} = 7.7, 1.5 Hz, 2H [H\textsubscript{4}]), 7.37 – 7.26 (m, 12H [H\textsubscript{11,12,13}]), 7.05 (dd, \textit{J} = 7.7, 7.2 Hz, 2H [H\textsubscript{5}]), 1.67 (s, 6H [H\textsubscript{1}]).

\textbf{13C NMR} (75 MHz, CDCl\textsubscript{3}): δ 155.5 [C\textsubscript{q}], 152.6 [C\textsubscript{q}], 137.8 [C\textsubscript{10}], 136.7 [C\textsubscript{6}], 130.4 [C\textsubscript{11}], 130.0 [C\textsubscript{3}], 127.6 [C\textsubscript{12}], 126.6 [C\textsubscript{5}], 126.3 [C\textsubscript{4}], 35.2 [C\textsubscript{2}], 32.5 [C\textsubscript{1}].\textsuperscript{[b]}

\textbf{HRMS (ESI)}: calc. for C\textsubscript{39}H\textsubscript{33}Bi\textsubscript{2}O\textsubscript{1} [M+H]\textsuperscript{+} 935.2133; found 935.2131.

\textbf{EA}: C\textsubscript{39}H\textsubscript{32}Bi\textsubscript{2}O·0.5H\textsubscript{2}O, calc’d C 49.64, H 3.53, Bi 44.29 %; exp. C 49.76, H 3.51, Bi 44.44 %.
X-ray quality crystals were obtained from a phase transfer diffusion (5:1) of pentane into a concentrated solution of complex 6 in CH$_2$Cl$_2$ at +5 °C.

[a] Note: To avoid dismutation, which results in lower yields, it is advised to not to reach dryness.[4]

[b] Note: One quartenary carbon signal was not observed in the $^{13}$C NMR spectra. To avoid a misassignment, the observable quaternary carbons were assigned as Cq.
3.3 Synthesis of 4,6-bis(diphenylbismuthanyl)-10,11-dihydridibenzo[b,f]oxepine (7)

4,6-dibromo-10,11-dihydridibenzo-oxepine (3) (200 mg, 0.56 mmol) was placed in a flame-dried Schlenk-flask under Ar atmosphere and dissolved in 9 mL of anhydrous THF. The solution was cooled to −78 °C and a solution of 2.6 M n-BuLi in hexane (0.43 mL, 1.1 mmol, 2.0 equiv.) was added dropwise. The mixture was stirred at 23 °C for 45 min. After this time, the mixture was cooled again to −78 °C and a solution of ZnCl₂ in anhydrous THF was added (1.1 mmol, 6 mL, 2 equiv.). The mixture was warmed to 23 °C and left to stir for 45 min. Then, Ph₂BiOTs[4] (603.7 mg, 1.1 mmol, 2.0 equiv.) was added in one portion at −10 °C, followed by the addition of additional 4 mL of anhydrous THF and the reaction was left to stir for 1.5 h at this temperature. The reaction mixture was quenched with a saturated aqueous solution of NaHCO₃ and diluted with Et₂O, whereupon it was extracted twice with Et₂O (2 × 8 mL). The combined organic phases were dried over MgSO₄, filtered and concentrated under reduced pressure (not to dryness!)[a]. The crude reaction mixture was then purified by flash chromatography (SiO₂, 20:1 hexane:EtOAc). The obtained solid was washed further with cold pentane (2 × 5 mL) to yield the desired complex 7 as an off-white solid (234 mg, 45% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.64 – 7.59 (m, 8H [H₉,₁₃]), 7.53 (dd, J = 7.2, 1.7 Hz, 2H [H₅]), 7.36 – 7.26 (m, 12H [H₁₀,₁₁,₁₂]), 7.08 (dd, J = 7.4, 1.7 Hz, 2H [H₃]), 6.92 (t, J = 7.3 Hz, 2H [H₄]), 3.13 (s, 4H [H₁]).

¹³C NMR (75 MHz, CDCl₃): δ 158.9 [C₉], 157.3 [C₈], 138.2 [C₉], 137.7 [C₅], 132.0 [C₂], 131.4 [C₃], 130.8 [C₁₀], 128.0 [C₁₁], 126.9 [C₄], 34.5 [C₁].[b]

HRMS (ESI): calc’d for C₃₈H₃₀Bi₂O₁Na₁ [M+Na]⁺ 943.17965; found 943.179980.

EA: C₃₈H₃₀Bi₂O·0.5H₂O, calc’d C 49.10, H 3.36, Bi 44.96 %; exp. C 49.30, H 3.27, Bi 45.12 %.
X-ray quality crystals were obtained from slow evaporation of a solution of complex 7 in CH$_2$Cl$_2$:hexane (1:5) at 23°C.

[a] Note: To avoid dismutation, which results in lower yields, it is advised to not to reach dryness.[4]

[b] Note: One quartenary carbon signal was not observed in the $^{13}$C NMR spectra. To avoid a misassignment, the observable quaternary carbons were assigned as Cq.
3.4 Synthesis of (oxybis(2,1-phenylene))bis(diphenylbismuthane) (8)

A flame-dried Schlenk-flask was charged with activated magnesium turnings (41.4 mg, 1.7 mmol, 4.0 equiv.) and anhydrous THF (0.5 mL) under Ar atmosphere, followed by addition of 1,2-dibromoethane (38.6 μL, 1.05 equiv.) and 10 mg (0.0237 mmol) of 2,2'-oxybis(iodobenzene) (4). This mixture was gently heated with a heat gun (70 °C) and a solution of the remaining 2,2'-oxybis(iodobenzene) (4) (170 mg, 0.4028 mmol) in anhydrous THF (6.2 mL) was slowly added. The mixture was placed in an oil bath and heated at 70 °C for 3 h. Then, the solution was cooled to room temperature, additional 15 mL of anhydrous THF were added and the mixture was cooled to −10 °C. Finally, Ph₂BiOTs[4] (455.8 mg, 0.85 mmol, 2 equiv.) was added in one portion and the solution was left to stir for 1.5 h at −10 °C. The mixture was quenched with a saturated aqueous solution of NaHCO₃ and diluted with Et₂O, whereupon it was extracted twice with Et₂O (2 × 10 mL). The combined organic phases were dried over MgSO₄, filtered and concentrated under reduced pressure (not to dryness!). The crude reaction mixture was then purified by flash chromatography (SiO₂, 20:1 hexane:EtOAc). The obtained solid was washed further with cold pentane (2 × 5 mL) to yield the desired complex 8 as an off-white solid (104 mg, 33% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.68 – 7.61 (m, 10H, [H₅,8,12]), 7.38 – 7.28 (m, 12H, [H₉,10,11]), 7.23 (ddd, J = 8.1, 7.2, 1.7 Hz, 2H [H₃]), 7.04 (td, J = 7.3, 1.1 Hz, 2H (H₄)), 6.93 (dd, J = 8.1, 1.1 Hz, 2H (H₂)).

¹³C NMR (101 MHz, CDCl₃): δ 159.6 [C₄], 155.4 [C₁], 138.9 [C₅], 137.9 [C₈], 130.4 [C₉], 129.6 [C₃], 127.6 [C₁₀], 126.5 [C₄], 117.4 [C₂].[b]

HRMS (ESI): calc’d for C₃₆H₂₈O₁Bi₂Na₁ [M+Na]⁺ 917.16400; found 917.164080.

EA: C₃₆H₂₈Bi₂O, calc’d C 48.34, H 3.16, Bi 46.72 %; exp. C 48.24, H 3.35, Bi 46.61 %.

X-ray quality crystals were obtained a phase transfer diffusion (5:1) of pentane into a concentrated solution of complex 8 in Et₂O at 23 °C.
[a] Note: To avoid dismutation, which results in lower yields, it is advised to not to reach dryness.[4]

[b] Note: One quartenary carbon signal was not observed in the $^{13}$C NMR spectra. To avoid a misassignment, the observable quaternary carbons were assigned as Cq.
4. Synthesis of Pentavalent Dibismuth Compounds 9-12

General Synthesis

In a flame-dried Schlenk-flask under Ar atmosphere, the corresponding dibismuthane (1.0 equiv.) was dissolved in anhydrous CH₂Cl₂ (6 mL) and SO₂Cl₂ (3.5 equiv.) was added. After 5 min, the solvent was evaporated. The crude was washed with Et₂O (2 × 10 mL), affording the corresponding pentavalent dibismuth 9-12 as yellow solids.

**4,6-bis(dichlorodiphenyl-\(\lambda^5\)-bismuthanyl)dibenzo[\(b,d\)]furan (9)**

Yield: 201 mg (96%).

**\(^1\)H NMR** (400 MHz, CDCl₃): δ 8.50 – 8.45 (m, 8H [H₈,1₂]), 8.15 (dd, \(J = 7.6, 1.1 \text{ Hz}, 2\)H [H₄]), 8.07 (dd, \(J = 7.9, 1.1 \text{ Hz}, 2\)H [H₂]), 7.66 – 7.60 (m, 8H [H₉,1₁]), 7.56 (t, \(J = 7.7 \text{ Hz}, 2\)H [H₃]), 7.53 – 7.47 (m, 4H [H₁₀]).

**\(^{13}\)C NMR** (101 MHz, CDCl₃): δ 154.9 [C₆], 154.6 [C₉], 141.9 [C₇], 134.3 [C₈], 132.4 [C₂], 131.9 [C₉], 131.6 [C₁₀], 126.9 [C₁], 125.8 [C₃], 124.0 [C₄].

**HRMS (ESI)**: calc’d for C₃₆H₂₆Bi₂Cl₄O₁Na₁ [M+Na]⁺ 1055.02376; found 1055.02316.
**EA**: $\text{C}_{36}\text{H}_{26}\text{Bi}_2\text{Cl}_4\text{O}_1\cdot\text{H}_2\text{O}$, calc’d C 41.09, H 2.68, Bi 39.72, Cl 13.47%; exp. C 40.89, H 2.47, Bi 39.39, Cl 13.34 %.

**X-ray** quality crystals were obtained by vapour diffusion of a solution of complex 9 in CH$_2$Cl$_2$:pentane (1:5).

[b]Note: To avoid a misassignment, the observable quaternary carbons were assigned as Cq.
(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(dichlorodiphenyl-\(\lambda^5\)-bismuthane) (10)

Yield: 194 mg (94%).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.15 (d, \(J = 7.7\) Hz, 8H \([H_{10,14}]\)), 7.94 (d, \(J = 8.0\) Hz, 2H \([H_6]\)), 7.59 (d, \(J = 7.6\) Hz, 2H \([H_4]\)), 7.40 (dd, \(J = 11.7, 7.1\) Hz, 12H \([H_{11,12,13}]\)), 7.27 (t, \(J = 7.3\) Hz, 2H \([H_5]\)), 1.75 (s, 6H \([H_1]\)).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 159.3 \([C_q]\), 150.1 \([C_q]\), 134.8 \([C_3]\), 134.0 \([C_{10}]\), 132.5 \([C_6]\), 131.4 \([C_{11}]\), 130.7 \([C_{12}]\), 128.1 \([C_4]\), 126.2 \([C_5]\), 36.9\([C_2]\), 30.8\([C_1]^{[b]}\).

HRMS (ESI): calc’d for C\(_{39}\)H\(_{32}\)Bi\(_2\)Cl\(_3\)O\(_1\) [M-Cl]\(^+\) 1039.1121; found 1039.1117.

EA: C\(_{39}\)H\(_{32}\)Bi\(_2\)Cl\(_4\)O\(_1\), calc’d C 43.52, H 3.00, Bi 38.83, Cl 13.17 %; exp. C 43.35, H 3.05, Bi 38.54, Cl 13.02 %.

X-ray quality crystals were obtained from slow evaporation of a solution of complex 10 in CH\(_2\)Cl\(_2\):hexane (1:5).

\(^{[b]}\)Note: One quartenary carbon signal was not observed in the \(^{13}\)C NMR spectra. To avoid a misassignment, the observable quartenary carbons were assigned as C\(_q\).
4,6-bis(dichlorodiphenyl-$\lambda^5$-bismuthanyl)-10,11-dihydrodibenzo[b,f]oxepine (11)

Yield: 210 mg (97%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.23 – 8.18 (m, 8H, [H$_{9,13}$]), 7.98 (dd, $J = 7.8, 1.6$ Hz, 2H [H$_5$]), 7.57 – 7.51 (m, 8H [H$_{10,12}$]), 7.48 – 7.43 (m, 4H [H$_{11}$]), 7.28 – 7.25 (m, 2H [H$_3$]), 7.22 – 7.17 (m, 2H [H$_4$]), 3.48 – 3.05 (m, 4H [H$_1$]).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 155.4 [C$_q$], 153.1 [C$_q$], 152.8 [C$_q$], 136.0 [C$_2$], 134.1 [C$_9$], 133.7 [C$_3$], 132.0 [C$_{10}$], 131.9 [C$_5$], 131.2 [C$_{11}$], 124.6 [C$_4$], 36.8 [C$_1$].$^{[b]}$

HRMS (ESI): calc’d for C$_{38}$H$_{30}$Bi$_2$Cl$_4$O$_1$Na$_1$ [M+Na]$^+$ 1083.05506; found 1083.056120.

EA: C$_{38}$H$_{30}$Bi$_2$Cl$_4$O$_1$, calc’d C 42.94, H 2.83, Bi 39.31, Cl 13.36 %; exp. C 42.96, H 2.85, Bi 39.34, Cl 13.35%.

X-ray quality crystals were obtained from liquid transfer diffusion of a mixture of C$_6$D$_6$:pentane (1:1) at 23 °C.

$^{[b]}$Note: To avoid a misassignment, the observable quaternary carbons were assigned as C$_q$. 

S17
Oxybis(2,1-phenylene))bis(dichlorodiphenyl-κ₅-bismuthane) (12)

**Yield:** 195 mg (93%).

**¹H NMR** (400 MHz, CDCl₃): δ 8.51 – 8.45 (m, 8H [H₈,₁₂]), 7.85 (dd, J = 7.9, 1.5 Hz, 2H [H₅]), 7.64 – 7.58 (m, 10H [H₃,₉,₁₁]), 7.49 – 7.44 (m, 4H [H₁₀]), 7.44 – 7.40 (m, 2H [H₂]), 7.37 – 7.32 (m, 2H [H₄]).

**¹³C NMR** (101 MHz, CDCl₃): δ 155.9 [C₉], 154.1 [C₉], 153.6 [C₈], 134.4 [C₈], 132.84 [C₈], 132.2 [C₉+C₅], 131.5 [C₁₀], 127.4 [C₄], 123.2 [C₃].

**HRMS (ESI):** calc’d for C₃₆H₂₈Cl₃Bi₂O₁ [M-Cl]+ 999.08079; found 999.07967.

**EA:** C₃₆H₂₈Bi₂Cl₄O₁·H₂O, calc’d C 41.01, H 2.87, Bi 39.64, Cl 13.45 %; exp. C 40.90, H 3.03, Bi 39.53, Cl 13.41 %

**X-ray** quality crystals were obtained from slow evaporation of a solution of complex 12 in CH₂Cl₂:hexane (1:5).

[b]Note: To avoid a misassignment, the observable quaternary carbons were assigned as Cq.
5. Low temperature and VT NMR analysis

5.1. Pentavalent Bi–(V) 10

$^1$H NMR of 10 (400 MHz in CD$_2$Cl$_2$) at 23 °C

$^1$H NMR of 10 (400 MHz in CD$_2$Cl$_2$) at -90 °C
VT $^1$H NMR of 10 (500 MHz in CD$_2$Cl$_2$) from 23 °C (bottom) to -90 °C (top)

Zoom area: 10.00 – 6.50 ppm
5.2. Pentavalent Bi–(V) 11

$^1$H NMR of 11 (500 MHz in CD$_2$Cl$_2$) at 23 °C

$^1$H NMR of 11 (500 MHz in CD$_2$Cl$_2$) at -90 °C
VT $^1$H NMR of 11 (500 MHz in CD$_2$Cl$_2$) from 23 °C (bottom) to -90 °C (top)

Zoom area: 10.00 – 6.50 ppm
6. Stoichiometric experiments of 9-12 for the oxidative cleavage of 1,2-diphenylethane-1,2-diol (13)

![Chemical structure of 13](image)

**Bi (1 or 0.5 equiv.)**
NBS (1.2 equiv.), K$_2$CO$_3$ (5 equiv.)
CD$_3$CN, 23 °C, 30 min

![Chemical structure of 14](image)

| Entry | Bismuth (V) reagent | Yield (%)$^b$ |
|-------|---------------------|---------------|
| 1     | Ph$_3$BiCl$_2$ (1 equiv.) | 90            |
| 2     | 9 (0.5 equiv.) | 90            |
| 3     | 10 (0.5 equiv.) | 89            |
| 4     | 11 (0.5 equiv.) | 93            |
| 5     | 12 (0.5 equiv.) | 92            |

$^a$ Reaction conditions: 13 (0.12 mmol), Bi-(V) reagent (1 or 0.5 equiv.) NBS (1.2 equiv.), K$_2$CO$_3$ (5 equiv.) in 1.2 mL of CD$_3$CN [0.1 M] at 23 °C for 30 min. $^b$ Yields were determined by $^1$H NMR using mesitylene as internal standard.
7. Kinetic experiments of 5-8 and BiPh₃ for Bi-catalyzed oxidative cleavage of 1,2-diphenylethane-1,2-diol (13)
Barton´s proposed mechanism

Barton and co-workers proposed a mechanism for the Bi-catalyzed oxidative cleavage of 1,2-diols based on NMR spectroscopy and experimental evidences. In the first step, the glycol reacts with NBS to form a hypobromite species, which acts as an oxidant of BiPh₃ to form a pentavalent Bi-alcoxy intermediate. The last step is a base-induced reductive elimination with cleavage of the C-C bond to the carbonyl derivatives and regenerating triphenylbismuth.

Barton's proposed mechanism (NBS-BiPh₃-K₂CO₃ system)
8. Scope of Bi-catalyzed oxidative cleavage of 1,2-diols

General procedure for Bi-catalyzed the oxidative cleavage of 1,2-diols

In a culture tube the corresponding 1,2-diol (0.12 mmol), K$_2$CO$_3$ (83 mg, 5.0 equiv.), dibismuthane 8 (2.1 mg, 2 mol%) and mesitylene (16.7 μL, 1.0 equiv.) were dissolved in 0.6 mL CD$_3$CN and stirred for 2 min. After that, a solution of NBS (25.6 mg, 1.2 equiv.) in 0.6 mL of CD$_3$CN was added dropwise and the reaction was left at 23 °C for the desired time (see Table 2 in the manuscript). An aliquot was taken and $^1$H NMR was recorded to determine the NMR yield. The sample was returned to the reaction crude and solvent was evaporated. The reaction crude was purified via flash chromatography (SiO$_2$, 8:2 pentane:Et$_2$O) to afford the corresponding carbonyl compounds.

Benzaldehyde (14) (Table 2, entry 1)

Yield: 22.5 mg (88%). Colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$): δ 10.03 (s, 1H), 7.91 – 7.86 (m, 2H), 7.68 – 7.60 (m, 1H), 7.57 – 7.50 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 192.3, 136.4, 134.4, 129.7, 129.0.

Spectroscopic data are in agreement with the reported values in the literature.$^{[7]}$
Benzophenone (16) (Table 2, entry 2)

Yield: 29.7 mg (68%). White solid.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.84 – 7.78 (m, 4H), 7.59 (ddt, $J$ = 8.4, 6.6, 1.4 Hz, 2H), 7.52 – 7.45 (m, 4H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 196.69, 137.59, 132.36, 130.02, 128.24.

Spectroscopic data are in agreement with the reported values in the literature.$^8$

Nonanal (18) (Table 2, entry 3)

Yield: 11.3 mg (66%). Colorless oil.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.76 (t, $J$ = 1.9 Hz, 1H), 2.41 (td, $J$ = 7.4, 1.9 Hz, 2H), 1.63 (dd, $J$ = 9.4, 5.3 Hz, 2H), 1.36 – 1.21 (m, 10H), 0.92 – 0.84 (m, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 202.91, 43.90, 31.77, 29.29, 29.16, 29.07, 22.64, 22.61, 22.08, 14.05.

Spectroscopic data are in agreement with the reported values in the literature.$^9$
Benzaldehyde (14) (Table 2, entry 4)

\[
\text{14}
\]

**Yield:** 11.3 mg (66%). Colorless oil.

2-((1S,3S)-3-acetyl-2,2-dimethylcyclobutyl)acetaldehyde (21) (Table 2, entry 5)

\[
\text{21}
\]

**Yield:** 19 mg (94%). Yellowish oil.

**\(^1\)H NMR** (300 MHz, CDCl\(_3\)):\( \delta 9.74\) (t, \(J = 1.5\) Hz, 1H), 2.92 (dd, \(J = 9.9, 7.8\) Hz, 1H), 2.51 – 2.36 (m, 3H), 2.04 (s, 3H), 2.01 – 1.92 (m, 2H), 1.34 (s, 3H), 0.84 (s, 3H).

**\(^{13}\)C NMR** (75 MHz, CDCl\(_3\)):\( \delta 207.31, 201.33, 54.34, 45.11, 43.26, 35.78, 30.34, 30.13, 22.82, 17.63.\)

\([\alpha]_D^{20}\) (CH\(_2\)Cl\(_2\)): +61° (Lit. +40°).\([^{10}\])

Spectroscopic data are in agreement with the reported values in the literature.\([^{11}\])
9. References

[1] H. Yueh, A. Voevodin and A. B. Beeler, J. Flow Chem. 2015, 5, 155–159.
[2] B. A. Hess, A. S. Bailey, B. Bartusek and V. Boekelheide, J. Am. Chem. Soc. 1969, 91, 1665–1672.
[3] A. R. Davalos, E. Sylvester and S. T. Diver, Organometallics 2019, 38, 2338–2346.
[4] T. Louis-Goff, A. L. Rheingold and J. Hyvl, Organometallics 2020, 39, 778–782.
[5] A. Buhling, P. C. J. Kamer and P. W. N. M. van Leeuwen, Organometallics 1997, 16, 3027–3037.
[6] D. H. R. Barton, J.-P. Finet, W. B. Motherwell and C. Pichon, Tetrahedron 1986, 42, 5627–5636.
[7] E. Prathibha, R. Rangasamy, A. Sridhar and K. Lakshmi, ChemistrySelect 2020, 5, 988–993.
[8] Z. Shen, Z. Zhao, Y.-L. Ren, W. Liu, X. Tian, X. Zheng and B. Zhao, ChemistrySelect 2020, 5, 14288–14291.
[9] S. Wertz and A. Studer, Adv. Synth. Catal. 2011, 353, 69–72.
[10] H. E. Eschinazi, J. Am. Chem. Soc. 1959, 81, 2905–2906.
[11] A. V. Iosub, S. Moravcik, C.-J. Wallentin and J. Bergman, Org. Lett. 2019, 21, 7804–7808.
10. NMR spectra

$^1$H NMR (300 MHz, CDCl$_3$) of 3

$^{13}$C NMR (75 MHz, CDCl$_3$) of 3
$^1$H NMR (300 MHz, CDCl$_3$) of 4

$^{13}$C NMR (75 MHz, CDCl$_3$) of
$^1$H NMR (300 MHz, CDCl$_3$) of 5

$^{13}$C NMR (75 MHz, CDCl$_3$) of 5
$^1$H NMR (300 MHz, CDCl$_3$) of 6

$^{13}$C NMR (75 MHz, CDCl$_3$) of 6
$^{1}H$ NMR (300 MHz, CDCl$_3$) of 7

$^{13}C$ NMR (75 MHz, CDCl$_3$) of 7
$^1$H NMR (400 MHz, CDCl$_3$) of 8

$^{13}$C NMR (101 MHz, CDCl$_3$) of 8
$^1$H NMR (400 MHz, CDCl$_3$) of 9

$^{13}$C NMR (101 MHz, CDCl$_3$) of 9
$^1$H NMR (300 MHz, CDCl$_3$) of 10

$^{13}$C NMR (75 MHz, CDCl$_3$) of 10
$^1$H NMR (400 MHz, CDCl$_3$) of 11

$^{13}$C NMR (101 MHz, CDCl$_3$) of 11
**S39**

**1H NMR (400 MHz, CDCl₃) of 12**

![1H NMR spectrum of 12](image)

**13C NMR (101 MHz, CDCl₃) of 12**

![13C NMR spectrum of 12](image)
$^1$H NMR (300 MHz, CDCl$_3$) of 14

$^{13}$C NMR (75 MHz, CDCl$_3$) of 14
$^1$H NMR (300 MHz, CDCl$_3$) of 16

$^{13}$C NMR (75 MHz, CDCl$_3$) of 16
$^1$H NMR (300 MHz, CDCl$_3$) of 18

$^{13}$C NMR (75 MHz, CDCl$_3$) of 18
$^1$H NMR (300 MHz, CDCl$_3$) of 21

$^{13}$C NMR (75 MHz, CDCl$_3$) of 21
11. Xray single crystal analysis

Single crystal structure analysis of 5 (13712)

Figure 1. The molecular structure of complex 5. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of complex 5: C₃₆H₂₆Bi₂O₄, $M_r = 892.53$ g mol⁻¹, colourless plate, crystal size 0.16 x 0.05 x 0.02 mm³, orthorhombic, $P2_12_12_1$ [19], $a = 6.1284(3)$ Å, $b = 13.2853(8)$ Å, $c = 34.731(3)$ Å, $V = 2827.7(3)$ Å³, $T = 100(2)$ K, $Z = 4$, $D_{calc} = 2.096$ g·cm⁻³, $\lambda = 0.71073$ Å, $\mu(Mo-K\alpha) = 12.457$ mm⁻¹, Gaussian absorption correction ($T_{min} = 0.17161$, $T_{max} = 0.77837$), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, 2.802 < θ < 30.508°, 38138 measured reflections, 8618 independent reflections, 7693 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0522$. The structure was solved by SHELXS and refined by full-matrix least-squares (SHELXL) against $F^2$ to $R_1 = 0.0287$ [$I > 2\sigma(I)$], $wR_2 = 0.0604$, 352 parameters. Absolute structure parameter Flack (x) = -0.044(6)
**Figure 2.** Crystal faces and unit cell determination of complex 5.

### INTENSITY STATISTICS FOR DATASET

| Resolution | #Data | #Theory | %Complete | Redundancy | Mean I | Mean I/s | Rmerge | Rsigma |
|------------|-------|---------|-----------|------------|--------|---------|--------|--------|
| Inf - 2.60 | 174   | 182     | 95.6      | 5.57       | 131.10 | 41.53   | 0.0417 | 0.0194 |
| 2.60 - 1.73| 420   | 420     | 100.0     | 6.09       | 106.45 | 41.07   | 0.0370 | 0.0200 |
| 1.73 - 1.37| 587   | 587     | 100.0     | 6.00       | 68.90  | 34.90   | 0.0386 | 0.0220 |
| 1.37 - 1.19| 584   | 584     | 100.0     | 5.73       | 51.66  | 31.40   | 0.0430 | 0.0249 |
| 1.19 - 1.08| 610   | 610     | 100.0     | 5.29       | 42.94  | 26.93   | 0.0453 | 0.0286 |
| 1.08 - 1.00| 599   | 599     | 100.0     | 4.91       | 35.62  | 22.89   | 0.0499 | 0.0332 |
| 1.00 - 0.95| 502   | 502     | 100.0     | 4.69       | 29.04  | 20.79   | 0.0540 | 0.0382 |
| 0.95 - 0.90| 604   | 604     | 100.0     | 4.41       | 28.21  | 19.38   | 0.0561 | 0.0419 |
| 0.90 - 0.86| 587   | 587     | 100.0     | 4.14       | 19.86  | 15.36   | 0.0672 | 0.0529 |
| 0.86 - 0.83| 553   | 553     | 100.0     | 4.08       | 20.22  | 15.00   | 0.0737 | 0.0550 |
| 0.83 - 0.80| 595   | 595     | 100.0     | 3.82       | 15.55  | 12.04   | 0.0853 | 0.0690 |
| 0.80 - 0.77| 672   | 672     | 100.0     | 3.65       | 15.49  | 11.15   | 0.0899 | 0.0736 |
| 0.77 - 0.75| 564   | 564     | 100.0     | 3.56       | 12.98  | 9.92    | 0.1066 | 0.0866 |
| 0.75 - 0.73| 589   | 589     | 100.0     | 3.37       | 12.18  | 8.91    | 0.1102 | 0.0960 |
| 0.73 - 0.71| 671   | 673     | 99.7      | 3.21       | 10.65  | 7.79    | 0.1377 | 0.1149 |
| 0.71 - 0.69| 715   | 718     | 99.6      | 3.09       | 9.17   | 6.50    | 0.1570 | 0.1393 |
| 0.69 - 0.68| 398   | 400     | 99.5      | 3.02       | 8.15   | 5.77    | 0.1671 | 0.1620 |
| 0.68 - 0.66| 901   | 905     | 99.6      | 2.96       | 7.78   | 5.24    | 0.1880 | 0.1790 |
| 0.66 - 0.65| 489   | 494     | 99.0      | 2.84       | 6.96   | 4.47    | 0.2065 | 0.2190 |
| 0.65 - 0.64| 516   | 522     | 98.9      | 2.70       | 5.69   | 3.45    | 0.2487 | 0.2950 |
| 0.64 - 0.63| 262   | 276     | 94.9      | 2.55       | 5.92   | 3.29    | 0.2413 | 0.3034 |
| 0.73 - 0.63| 3952  | 3988    | 99.1      | 2.95       | 8.06   | 5.50    | 0.1763 | 0.1757 |
| Inf - 0.63 | 11592 | 11636   | 99.6      | 4.02       | 26.44  | 15.54   | 0.0575 | 0.0498 |

A resolution cut off (SHEL 99 0.7) was applied to suppress poorly measured intensities at higher diffraction angles. Complete .cif-data of the compound are available under the CCDC number CCDC-2063973.
Table 1. Crystal data and structure refinement.

| Property                                      | Value                          |
|-----------------------------------------------|--------------------------------|
| Identification code                          | 13712                          |
| Empirical formula                            | $\text{C}_{36}\text{H}_{26}\text{Bi}_2\text{O}$ |
| Color                                         | colourless                     |
| Formula weight                                | 892.53 g · mol$^{-1}$          |
| Temperature                                   | 100(2) K                       |
| Wavelength                                    | 0.71073 Å                      |
| Crystal system                                | ORTHORHOMBIC                   |
| Space group                                   | $P2_12_12_1$ (No. 19)          |
| Unit cell dimensions                          | $a = 6.1284(3)$ Å, $\alpha = 90^\circ$. |
|                                               | $b = 13.2853(8)$ Å, $\beta = 90^\circ$. |
|                                               | $c = 34.731(3)$ Å, $\gamma = 90^\circ$. |
| Volume                                        | 2827.7(3) Å$^3$                |
| Z                                             | 4                              |
| Density (calculated)                          | 2.096 Mg · m$^{-3}$            |
| Absorption coefficient                        | 12.457 mm$^{-1}$               |
| F(000)                                        | 1664 e                         |
| Crystal size                                  | 0.16 x 0.05 x 0.02 mm$^3$      |
| $\theta$ range for data collection           | 2.802 to 30.508°.              |
| Index ranges                                  | $-8 \leq h \leq 8, -18 \leq k \leq 18, -45 \leq l \leq 49$ |
| Reflections collected                         | 38138                          |
| Independent reflections                       | 8618 [R$_{int}$ = 0.0522]      |
| Reflections with I>2$\sigma$(I)              | 7693                           |
| Completeness to $\theta = 25.242^\circ$      | 99.8 %                         |
| Absorption correction                         | Gaussian                       |
| Max. and min. transmission                    | 0.78 and 0.17                  |
| Refinement method                             | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters                | 8618 / 0 / 352                 |
| Goodness-of-fit on F$^2$                      | 1.069                          |
| Final R indices [I>2$\sigma$(I)]             | $R_1 = 0.0287$, $wR^2 = 0.0571$ |
| R indices (all data)                          | $R_1 = 0.0374$, $wR^2 = 0.0604$ |
| Absolute structure parameter                  | $-0.044(6)$                    |
| Largest diff. peak and hole                   | 1.2 and $-1.9$ e · Å$^{-3}$    |
Table 2. Bond lengths [Å] and angles [°].

|                  | Bond Lengths [Å] |                  | Bond Angles [°] |
|------------------|------------------|------------------|-----------------|
| Bi(1)-C(2)       | 2.262(7)         | Bi(1)-C(13)      | 2.244(6)        |
| Bi(1)-C(19)      | 2.253(7)         | Bi(1)-C(11)      | 2.252(7)        |
| Bi(2)-C(25)      | 2.243(7)         | Bi(2)-C(31)      | 2.248(7)        |
| O(1)-C(1)        | 1.397(8)         | O(1)-C(12)       | 1.387(8)        |
| C(1)-C(2)        | 1.374(9)         | C(1)-C(6)        | 1.392(10)       |
| C(2)-C(3)        | 1.387(10)        | C(3)-C(4)        | 1.403(10)       |
| C(4)-C(5)        | 1.397(10)        | C(5)-C(6)        | 1.394(10)       |
| C(6)-C(7)        | 1.456(9)         | C(7)-C(8)        | 1.403(9)        |
| C(7)-C(12)       | 1.392(9)         | C(8)-C(9)        | 1.392(10)       |
| C(9)-C(10)       | 1.385(10)        | C(10)-C(11)      | 1.410(9)        |
| C(11)-C(12)      | 1.383(9)         | C(13)-C(14)      | 1.397(9)        |
| C(13)-C(18)      | 1.389(9)         | C(14)-C(15)      | 1.393(10)       |
| C(15)-C(16)      | 1.397(10)        | C(16)-C(17)      | 1.391(10)       |
| C(17)-C(18)      | 1.381(10)        | C(19)-C(20)      | 1.392(9)        |
| C(19)-C(24)      | 1.396(11)        | C(20)-C(21)      | 1.392(9)        |
| C(21)-C(22)      | 1.365(10)        | C(22)-C(23)      | 1.383(12)       |
| C(23)-C(24)      | 1.393(12)        | C(25)-C(26)      | 1.400(9)        |
| C(25)-C(30)      | 1.378(9)         | C(26)-C(27)      | 1.379(10)       |
| C(27)-C(28)      | 1.369(12)        | C(28)-C(29)      | 1.384(11)       |
| C(29)-C(30)      | 1.405(10)        | C(31)-C(32)      | 1.391(10)       |
| C(31)-C(36)      | 1.393(9)         | C(32)-C(33)      | 1.397(10)       |
| C(33)-C(34)      | 1.382(9)         | C(34)-C(35)      | 1.393(9)        |
| C(35)-C(36)      | 1.394(10)        |                  |                 |
|                  |                  | C(13)-Bi(1)-C(2) | 93.7(2)         |
|                  |                  | C(19)-Bi(1)-C(2) | 96.3(3)         |
|                  |                  | C(25)-Bi(2)-C(31)| 96.4(2)         |
|                  |                  | C(12)-O(1)-C(1)  | 105.4(5)        |
|                  |                  | C(2)-C(1)-C(6)   | 125.6(6)        |
|                  |                  | C(1)-C(2)-Bi(1)  | 121.0(5)        |
|                  |                  | C(3)-C(2)-Bi(1)  | 123.6(5)        |
|                  |                  | C(5)-C(4)-C(3)   | 121.3(6)        |
|                  |                  | C(1)-C(6)-C(5)   | 118.1(7)        |
|                  |                  | C(5)-C(6)-C(7)   | 135.9(7)        |
|                  |                  | C(13)-Bi(1)-C(19)| 93.8(2)         |
|                  |                  | C(25)-Bi(2)-C(11)| 95.8(2)         |
|                  |                  | C(31)-Bi(2)-C(11)| 94.0(2)         |
|                  |                  | C(2)-C(1)-C(1)   | 123.2(6)        |
|                  |                  | C(6)-C(1)-O(1)   | 111.2(6)        |
|                  |                  | C(1)-C(2)-C(3)   | 115.4(7)        |
|                  |                  | C(2)-C(3)-C(4)   | 121.4(7)        |
|                  |                  | C(6)-C(5)-C(4)   | 118.1(7)        |
|                  |                  | C(1)-C(6)-C(7)   | 106.0(6)        |
|                  |                  | C(8)-C(7)-C(6)   | 135.8(7)        |
| Bond                        | Angle (°)       | Bond                        | Angle (°)       |
|-----------------------------|-----------------|-----------------------------|-----------------|
| C(12)-C(7)-C(6)             | 105.7(6)        | C(12)-C(7)-C(8)             | 118.4(6)        |
| C(9)-C(8)-C(7)              | 117.5(7)        | C(10)-C(9)-C(8)             | 122.3(7)        |
| C(9)-C(10)-C(11)            | 121.6(7)        | C(10)-C(11)-Bi(2)           | 127.9(5)        |
| C(12)-C(11)-Bi(2)           | 117.6(5)        | C(12)-C(11)-C(10)           | 114.4(7)        |
| O(1)-C(12)-C(7)             | 111.7(6)        | C(11)-C(12)-O(1)            | 122.6(6)        |
| C(11)-C(12)-C(7)            | 125.7(6)        | C(14)-C(13)-Bi(1)           | 122.5(5)        |
| C(18)-C(13)-Bi(1)           | 118.8(5)        | C(18)-C(13)-C(14)           | 118.7(6)        |
| C(15)-C(14)-C(13)           | 120.5(6)        | C(14)-C(15)-C(16)           | 119.8(7)        |
| C(17)-C(16)-C(15)           | 119.8(7)        | C(18)-C(17)-C(16)           | 119.9(7)        |
| C(17)-C(18)-C(13)           | 121.3(7)        | C(20)-C(19)-Bi(1)           | 124.0(5)        |
| C(20)-C(19)-C(24)           | 118.0(7)        | C(24)-C(19)-Bi(1)           | 117.1(5)        |
| C(19)-C(20)-C(21)           | 120.8(7)        | C(22)-C(21)-C(20)           | 120.6(7)        |
| C(21)-C(22)-C(23)           | 119.8(7)        | C(22)-C(23)-C(24)           | 120.1(8)        |
| C(23)-C(24)-C(19)           | 120.7(7)        | C(26)-C(25)-Bi(2)           | 116.6(5)        |
| C(30)-C(25)-Bi(2)           | 124.2(5)        | C(30)-C(25)-C(26)           | 119.0(7)        |
| C(27)-C(26)-C(25)           | 120.4(7)        | C(28)-C(27)-C(26)           | 120.4(7)        |
| C(27)-C(28)-C(29)           | 120.4(7)        | C(28)-C(29)-C(30)           | 119.5(7)        |
| C(25)-C(30)-C(29)           | 120.3(7)        | C(32)-C(31)-Bi(2)           | 118.4(5)        |
| C(32)-C(31)-C(36)           | 119.2(6)        | C(36)-C(31)-Bi(2)           | 122.3(5)        |
| C(31)-C(32)-C(33)           | 120.2(6)        | C(34)-C(33)-C(32)           | 120.7(7)        |
| C(33)-C(34)-C(35)           | 119.1(6)        | C(34)-C(35)-C(36)           | 120.5(6)        |
| C(31)-C(36)-C(35)           | 120.2(7)        |                             |                 |
Single crystal structure analysis of 6 (13015)

Figure 3. The molecular structure of complex 6. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of complex 6: C_{39}H_{32}Bi_{2}O, \( M_r = 934.60 \) g mol\(^{-1}\), colourless prism, crystal size 0.035 x 0.031 x 0.021 mm\(^3\), orthorhombic, \( F_{dd2} \) [43], \( a = 37.8761(11) \) Å, \( b = 51.1850(17) \) Å, \( c = 6.6097(2) \) Å, \( V = 12814.1(7) \) Å\(^3\), \( T = 100(2) \) K, \( Z = 16 \), \( D_{calc} = 1.938 \) g·cm\(^{-3}\), \( \lambda = 0.71073 \) Å, \( \mu(Mo-K\alpha) = 11.000 \) mm\(^{-1}\), Gaussian absorption correction (\( T_{min} = 0.72004 \), \( T_{max} = 0.85446 \)), Bruker-AXS Mach3 diffractometer with APEX-II detector and \( \mu S \) microfocus Mo-anode X-ray source, 1.338 < \( \theta \) < 32.028°, 112958 measured reflections, 11150 independent reflections, 9565 reflections with \( I > 2\sigma(I) \), \( R_{int} = 0.0665 \). The structure was solved by SHELXT and refined by full-matrix least-squares (SHELXL) against \( F^2 \) to \( R_1 = 0.0288 \) \( [I > 2\sigma(I)] \), \( wR_2 = 0.0410 \), 381 parameters. Absolute structure parameter Flack (x) = -0.013(4)
**Figure 4.** Crystal faces and unit cell determination of complex 6.

| Resolution | #Data | #Theory | %Complete | Redundancy | Mean I | Mean I/s | Rmerge | Rsigma |
|------------|-------|---------|-----------|------------|--------|---------|--------|--------|
| Inf - 2.66 | 200   | 201     | 99.5      | 16.96      | 95.19  | 68.76   | 0.0220 | 0.0116 |
| 2.66 - 1.75 | 463   | 463     | 100.0     | 18.49      | 70.61  | 65.58   | 0.0274 | 0.0125 |
| 1.75 - 1.38 | 671   | 671     | 100.0     | 18.31      | 45.20  | 52.21   | 0.0388 | 0.0156 |
| 1.38 - 1.20 | 695   | 695     | 100.0     | 18.26      | 37.69  | 45.16   | 0.0481 | 0.0180 |
| 1.20 - 1.09 | 645   | 645     | 100.0     | 16.62      | 27.11  | 34.02   | 0.0651 | 0.0239 |
| 1.09 - 1.01 | 703   | 703     | 100.0     | 12.42      | 25.28  | 25.97   | 0.0736 | 0.0309 |
| 1.01 - 0.95 | 656   | 656     | 100.0     | 10.20      | 25.28  | 25.97   | 0.0885 | 0.0399 |
| 0.95 - 0.90 | 714   | 714     | 100.0     | 8.84       | 17.50  | 16.32   | 0.1038 | 0.0517 |
| 0.90 - 0.86 | 682   | 682     | 100.0     | 7.95       | 14.48  | 13.41   | 0.1218 | 0.0650 |
| 0.86 - 0.83 | 592   | 592     | 100.0     | 7.70       | 12.60  | 11.82   | 0.1369 | 0.0759 |
| 0.83 - 0.80 | 703   | 703     | 100.0     | 7.15       | 12.03  | 10.28   | 0.1521 | 0.0841 |
| 0.80 - 0.78 | 541   | 541     | 100.0     | 7.03       | 10.33  | 8.97    | 0.1652 | 0.0981 |
| 0.78 - 0.75 | 897   | 897     | 100.0     | 6.82       | 9.33   | 8.03    | 0.1877 | 0.1123 |
| 0.75 - 0.73 | 664   | 664     | 100.0     | 6.61       | 7.82   | 6.62    | 0.2204 | 0.1371 |
| 0.73 - 0.71 | 783   | 784     | 99.9      | 6.26       | 7.07   | 5.81    | 0.2493 | 0.1573 |
| 0.71 - 0.70 | 438   | 438     | 100.0     | 6.16       | 6.44   | 5.20    | 0.2553 | 0.1765 |
| 0.70 - 0.68 | 875   | 876     | 99.9      | 6.04       | 5.64   | 4.60    | 0.2969 | 0.2071 |
| 0.68 - 0.67 | 476   | 479     | 99.4      | 5.84       | 5.22   | 4.11    | 0.3323 | 0.2332 |
| 0.67 - 0.66 | 484   | 492     | 98.4      | 5.71       | 4.70   | 3.69    | 0.3623 | 0.2616 |
| 0.66 - 0.64 | 1164  | 1194    | 97.5      | 4.90       | 3.96   | 2.87    | 0.3944 | 0.3500 |
| 0.64 - 0.63 | 144   | 145     | 31.6      | 0.57       | 2.74   | 1.14    | 0.4023 | 1.0221 |
| 0.73 - 0.63 | 4364  | 4719    | 92.5      | 5.22       | 5.28   | 4.15    | 0.3079 | 0.2421 |
| Inf - 0.63  | 13190 | 13546   | 97.4      | 9.10       | 18.07  | 17.77   | 0.0694 | 0.0565 |

Complete .cif-data of the compound are available under the CCDC number **CCDC-2063975**.
Table 3. Crystal data and structure refinement.

| Property                          | Value                           |
|-----------------------------------|---------------------------------|
| Identification code               | 13015                           |
| Empirical formula                 | C_{39}H_{32}Bi_{2}O              |
| Color                             | colourless                      |
| Formula weight                    | 934.60 g · mol\(^{-1}\)         |
| Temperature                       | 100(2) K                        |
| Wavelength                        | 0.71073 Å                       |
| Crystal system                    | ORTHORHOMBIC                    |
| Space group                       | Fdd2, (No. 43)                  |
| Unit cell dimensions              |                                 |
| a                                 | 37.8761(11) Å                   |
| \(\alpha\)                        | 90°                             |
| b                                 | 51.1850(17) Å                   |
| \(\beta\)                        | 90°                             |
| c                                 | 6.6097(2) Å                     |
| \(\gamma\)                       | 90°                             |
| Volume                            | 12814.1(7) Å\(^3\)             |
| Z                                 | 16                              |
| Density (calculated)              | 1.938 Mg · m\(^{-3}\)          |
| Absorption coefficient            | 11.000 mm\(^{-1}\)             |
| F(000)                            | 7040 e                          |
| Crystal size                      | 0.035 x 0.031 x 0.021 mm\(^3\) |
| \(\theta\) range for data collection | 1.338 to 32.028°.              |
| Index ranges                      | -56 \leq h \leq 56, -76 \leq k \leq 76, -9 \leq l \leq 9 |
| Reflections collected             | 112958                          |
| Independent reflections           | 11150 \( [R_{int} = 0.0665 \] ) |
| Reflections with I>2\(\sigma\)(I) | 9565                            |
| Completeness to \(\theta = 25.242°\) | 100.0 %                        |
| Absorption correction             | Gaussian                        |
| Max. and min. transmission        | 0.85 and 0.72                   |
| Refinement method                 | Full-matrix least-squares on F\(^2\) |
| Data / restraints / parameters     | 11150 / 1 / 381                 |
| Goodness-of-fit on F\(^2\)        | 1.046                           |
| Final R indices [I>2\(\sigma\)(I)] | \( R_i = 0.0288 \) \quad \text{w}R^2 = 0.0415 |
| R indices (all data)              | \( R_i = 0.0410 \) \quad \text{w}R^2 = 0.0437 |
| Absolute structure parameter      | -0.013(4)                       |
| Largest diff. peak and hole       | 0.9 and -1.3 e · Å\(^{-3}\)    |
| Bond                  | Length [Å] | Bond                  | Length [Å] |
|-----------------------|------------|-----------------------|------------|
| Bi(1)-C(2)            | 2.268(6)   | Bi(1)-C(16)           | 2.246(5)   |
| Bi(1)-C(22)           | 2.262(5)   | Bi(2)-C(12)           | 2.255(5)   |
| Bi(2)-C(28)           | 2.242(5)   | Bi(2)-C(34)           | 2.252(5)   |
| O(1)-C(1)             | 1.387(6)   | O(1)-C(13)            | 1.391(6)   |
| C(1)-C(2)             | 1.399(7)   | C(1)-C(6)             | 1.400(7)   |
| C(2)-C(3)             | 1.369(8)   | C(3)-C(4)             | 1.391(8)   |
| C(4)-C(5)             | 1.391(8)   | C(5)-C(6)             | 1.396(8)   |
| C(6)-C(7)             | 1.522(7)   | C(7)-C(8)             | 1.523(7)   |
| C(7)-C(14)            | 1.541(8)   | C(7)-C(15)            | 1.530(8)   |
| C(8)-C(9)             | 1.403(7)   | C(8)-C(13)            | 1.390(7)   |
| C(9)-C(10)            | 1.392(8)   | C(10)-C(11)           | 1.389(8)   |
| C(11)-C(12)           | 1.400(7)   | C(12)-C(13)           | 1.394(7)   |
| C(16)-C(17)           | 1.383(8)   | C(16)-C(21)           | 1.392(7)   |
| C(17)-C(18)           | 1.399(8)   | C(18)-C(19)           | 1.375(7)   |
| C(19)-C(20)           | 1.392(8)   | C(20)-C(21)           | 1.391(7)   |
| C(22)-C(23)           | 1.394(8)   | C(22)-C(27)           | 1.395(7)   |
| C(23)-C(24)           | 1.379(8)   | C(24)-C(25)           | 1.394(8)   |
| C(25)-C(26)           | 1.381(8)   | C(26)-C(27)           | 1.391(8)   |
| C(28)-C(29)           | 1.399(8)   | C(28)-C(33)           | 1.400(7)   |
| C(29)-C(30)           | 1.383(8)   | C(30)-C(31)           | 1.395(8)   |
| C(31)-C(32)           | 1.382(8)   | C(32)-C(33)           | 1.388(7)   |
| C(34)-C(35)           | 1.396(7)   | C(34)-C(39)           | 1.392(8)   |
| C(35)-C(36)           | 1.387(8)   | C(36)-C(37)           | 1.387(9)   |
| C(37)-C(38)           | 1.388(8)   | C(38)-C(39)           | 1.370(8)   |
| C(16)-Bi(1)-C(2)      | 96.16(19)  | C(16)-Bi(1)-C(22)     | 93.82(18)  |
| C(22)-Bi(1)-C(2)      | 93.60(19)  | C(28)-Bi(2)-C(12)     | 90.36(19)  |
| C(28)-Bi(2)-C(34)     | 93.06(19)  | C(34)-Bi(2)-C(12)     | 94.8(2)    |
| C(1)-O(1)-C(13)       | 116.5(4)   | O(1)-C(1)-C(2)        | 116.8(5)   |
| O(1)-C(1)-C(6)        | 120.4(5)   | C(2)-C(1)-C(6)        | 122.8(5)   |
| C(1)-C(2)-Bi(1)       | 119.9(4)   | C(3)-C(2)-Bi(1)       | 121.5(4)   |
| C(3)-C(2)-C(1)        | 118.6(5)   | C(2)-C(3)-C(4)        | 120.5(5)   |
| C(3)-C(4)-C(5)        | 120.3(5)   | C(4)-C(5)-C(6)        | 120.9(5)   |
| C(1)-C(6)-C(7)        | 119.7(5)   | C(5)-C(6)-C(1)        | 116.9(5)   |
| Bond         | Distance (Å) | Bond         | Distance (Å) |
|--------------|--------------|--------------|--------------|
| C(5)-C(6)-C(7) | 123.4(5)     | C(6)-C(7)-C(8) | 107.4(4)     |
| C(6)-C(7)-C(14) | 108.0(4)    | C(6)-C(7)-C(15) | 112.0(5)     |
| C(8)-C(7)-C(14) | 108.0(5)    | C(8)-C(7)-C(15) | 112.0(5)     |
| C(15)-C(7)-C(14) | 109.2(4)   | C(9)-C(8)-C(7) | 123.3(5)     |
| C(13)-C(8)-C(7) | 119.7(5)    | C(13)-C(8)-C(9) | 116.9(5)     |
| C(10)-C(9)-C(8) | 121.3(5)    | C(11)-C(10)-C(9) | 119.5(5)    |
| C(10)-C(11)-C(12) | 121.6(5)  | C(11)-C(12)-Bi(2) | 123.2(4) |
| C(13)-C(12)-Bi(2) | 120.0(4)   | C(13)-C(12)-C(11) | 116.7(5)    |
| O(1)-C(13)-C(12) | 115.2(4)   | C(8)-C(13)-O(1) | 120.7(4)     |
| C(8)-C(13)-C(12) | 124.1(5)    | C(17)-C(16)-Bi(1) | 117.7(4)    |
| C(17)-C(16)-C(21) | 119.0(5)   | C(21)-C(16)-Bi(1) | 123.0(4)    |
| C(16)-C(17)-C(18) | 121.1(5)    | C(19)-C(18)-C(17) | 119.7(6)    |
| C(18)-C(19)-C(20) | 119.8(5)    | C(21)-C(20)-C(19) | 120.4(5)    |
| C(20)-C(21)-C(16) | 120.1(5)    | C(23)-C(22)-Bi(1) | 119.6(4)    |
| C(23)-C(22)-C(27) | 118.3(5)    | C(27)-C(22)-Bi(1) | 121.9(4)    |
| C(24)-C(23)-C(22) | 121.6(6)    | C(23)-C(24)-C(25) | 119.7(6)    |
| C(26)-C(25)-C(24) | 119.4(5)    | C(25)-C(26)-C(27) | 120.8(5)    |
| C(26)-C(27)-C(22) | 120.2(5)    | C(29)-C(28)-Bi(2) | 119.0(4)    |
| C(29)-C(28)-C(33) | 118.0(5)    | C(33)-C(28)-Bi(2) | 122.9(4)    |
| C(30)-C(29)-C(28) | 121.3(5)    | C(29)-C(30)-C(31) | 119.7(5)    |
| C(32)-C(31)-C(30) | 119.8(5)    | C(31)-C(32)-C(33) | 120.4(5)    |
| C(32)-C(33)-C(28) | 120.7(5)    | C(35)-C(34)-Bi(2) | 118.7(4)    |
| C(39)-C(34)-Bi(2) | 122.9(4)    | C(39)-C(34)-C(35) | 118.4(5)    |
| C(36)-C(35)-C(34) | 120.9(6)    | C(35)-C(36)-C(37) | 120.1(5)    |
| C(36)-C(37)-C(38) | 118.7(5)    | C(39)-C(38)-C(37) | 121.5(6)    |
| C(38)-C(39)-C(34) | 120.4(5)    |               |              |
Single crystal structure analysis of 7 (13364)

Figure 5. The molecular structure of complex 7. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of complex 7: C_{38}H_{30}Bi_{12}O, $M_r = 920.58$ g mol$^{-1}$, colourless prism, crystal size 0.07 x 0.05 x 0.04 mm$^3$, triclinic, $P-1$ [2], $a = 10.6951(17)$ Å, $b = 10.8286(12)$ Å, $c = 13.7009(8)$ Å, $\alpha = 83.462(6)$ °, $\beta = 88.592(9)$ °, $\gamma = 79.178(12)$ °, $V = 1548.4(3)$ Å$^3$, $T = 100(2)$ K, $Z = 2$, $D_{calc} = 1.975$ g·cm$^{-3}$, $\lambda = 0.71073$ Å, $\mu$(Mo-K$\alpha$) = 11.378 mm$^{-1}$, Gaussian absorption correction ($T_{min} = 0.47746$, $T_{max} = 0.68309$), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, $2.768 < \theta < 33.080$°, 47337 measured reflections, 11728 independent reflections, 8776 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0502$. The structure was solved by SHELXT and refined by full-matrix least-squares (SHELXL) against $F^2$ to $R_I = 0.0314 [I > 2\sigma(I)]$, $wR_2 = 0.0553$, 370 parameters.
**Figure 6.** Crystal faces and unit cell determination of complex 7.

### INTENSITY STATISTICS FOR DATASET

| Resolution | #Data | #Theory | %Complete | Redundancy | Mean I | Mean I/s | Rmerge | Rsigma |
|------------|-------|---------|-----------|------------|--------|----------|--------|--------|
| Inf - 2.60 | 176   | 184     | 95.7      | 8.72       | 140.68 | 63.91    | 0.0360 | 0.0124 |
| 2.60 - 1.75| 419   | 419     | 100.0     | 6.29       | 102.07 | 46.48    | 0.0312 | 0.0163 |
| 1.75 - 1.40| 584   | 584     | 100.0     | 5.68       | 73.63  | 38.69    | 0.0337 | 0.0190 |
| 1.40 - 1.22| 597   | 597     | 100.0     | 5.35       | 51.08  | 31.55    | 0.0365 | 0.0224 |
| 1.22 - 1.11| 591   | 591     | 100.0     | 5.04       | 43.27  | 27.54    | 0.0371 | 0.0252 |
| 1.11 - 1.03| 595   | 595     | 100.0     | 4.85       | 36.74  | 24.02    | 0.0396 | 0.0288 |
| 1.03 - 0.97| 564   | 564     | 100.0     | 4.55       | 29.10  | 20.28    | 0.0455 | 0.0338 |
| 0.97 - 0.92| 628   | 628     | 100.0     | 4.44       | 26.32  | 18.54    | 0.0491 | 0.0380 |
| 0.92 - 0.88| 599   | 599     | 100.0     | 4.23       | 23.14  | 16.89    | 0.0563 | 0.0436 |
| 0.88 - 0.84| 710   | 710     | 100.0     | 3.94       | 18.12  | 13.57    | 0.0673 | 0.0534 |
| 0.84 - 0.82| 412   | 412     | 100.0     | 3.81       | 17.62  | 12.66    | 0.0667 | 0.0575 |
| 0.82 - 0.79| 707   | 707     | 100.0     | 3.72       | 13.90  | 10.81    | 0.0828 | 0.0697 |
| 0.79 - 0.77| 504   | 504     | 100.0     | 3.48       | 13.18  | 9.90     | 0.0883 | 0.0779 |
| 0.77 - 0.75| 590   | 590     | 100.0     | 3.42       | 11.46  | 8.66     | 0.1088 | 0.0905 |
| 0.75 - 0.73| 663   | 663     | 100.0     | 3.26       | 11.17  | 7.89     | 0.1150 | 0.0996 |
| 0.73 - 0.71| 717   | 717     | 100.0     | 3.10       | 9.60   | 6.91     | 0.1343 | 0.1220 |
| 0.71 - 0.70| 403   | 403     | 100.0     | 3.08       | 9.82   | 6.74     | 0.1283 | 0.1272 |
| 0.70 - 0.68| 834   | 834     | 100.0     | 2.94       | 7.09   | 4.87     | 0.1727 | 0.1846 |
| 0.68 - 0.67| 483   | 483     | 100.0     | 2.84       | 6.68   | 4.24     | 0.2018 | 0.2225 |
| 0.67 - 0.66| 488   | 488     | 100.0     | 2.78       | 6.32   | 3.84     | 0.2072 | 0.2548 |
| 0.66 - 0.65| 464   | 482     | 96.3      | 2.60       | 5.41   | 3.03     | 0.2528 | 0.3300 |
| 0.75 - 0.65| 4052  | 4070    | 99.6      | 2.96       | 8.14   | 5.50     | 0.1557 | 0.1669 |
| Inf - 0.65 | 11728 | 11754   | 99.8      | 4.03       | 26.57  | 16.27    | 0.0489 | 0.0449 |

Complete .cif-data of the compound are available under the CCDC number **CCDC-2063978**.
Table 5. Crystal data and structure refinement.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | 13364                                      |
| Empirical formula                             | C_{38}H_{30}Bi_{2}O                       |
| Color                                         | colourless                                 |
| Formula weight                                | 920.58 g·mol⁻¹                            |
| Temperature                                   | 100(2) K                                   |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system                                | TRICLINIC                                  |
| Space group                                   | P-1, (No. 2)                               |
| Unit cell dimensions                          | a = 10.6951(17) Å  \( \alpha = 83.462(6)° \) |
|                                             | b = 10.8286(12) Å  \( \beta = 88.592(9)° \) |
|                                             | c = 13.7009(8) Å  \( \gamma = 79.178(12)° \) |
| Volume                                        | 1548.4(3) Å⁻³                              |
| Z                                             | 2                                          |
| Density (calculated)                          | 1.975 Mg·m⁻³                               |
| Absorption coefficient                        | 11.378 mm⁻¹                                |
| F(000)                                        | 864 e                                      |
| Crystal size                                  | 0.07 x 0.05 x 0.04 mm³                    |
| \( \theta \) range for data collection       | 2.768 to 33.080°                           |
| Index ranges                                  | \(-16 \leq h \leq 16, \ -16 \leq k \leq 16, \ -21 \leq l \leq 21\) |
| Reflections collected                         | 47337                                      |
| Independent reflections                       | 11728 [\( R_{int} = 0.0502 \)]           |
| Reflections with \( I > 2 \sigma(I) \)       | 8776                                       |
| Completeness to \( \theta = 25.242° \)       | 99.9 %                                     |
| Absorption correction                         | Gaussian                                   |
| Max. and min. transmission                    | 0.68309 and 0.47746                        |
| Refinement method                             | Full-matrix least-squares on \( F^2 \)    |
| Data / restraints / parameters                 | 11728 / 0 / 370                            |
| Goodness-of-fit on \( F^2 \)                  | 1.011                                      |
| Final R indices [\( I > 2 \sigma(I) \)]       | \( R_I = 0.0314 \)  \( wR^2 = 0.0553 \)    |
| R indices (all data)                          | \( R_I = 0.0555 \)  \( wR^2 = 0.0613 \)    |
| Extinction coefficient                        | n/a                                        |
| Largest diff. peak and hole                   | 1.339 and -1.781 e·Å⁻³                     |
Table 6. Bond lengths [Å] and angles [°].

| Bond                  | Length [Å] | Bond                  | Length [Å] |
|-----------------------|------------|-----------------------|------------|
| Bi(2)-C(27)           | 2.259(4)   | Bi(2)-C(33)           | 2.262(3)   |
| Bi(2)-C(11)           | 2.252(3)   | Bi(1)-C(21)           | 2.247(4)   |
| Bi(1)-C(1)            | 2.251(3)   | Bi(1)-C(15)           | 2.255(3)   |
| O(1)-C(10)            | 1.413(4)   | O(1)-C(6)             | 1.415(4)   |
| C(21)-C(26)           | 1.393(5)   | C(21)-C(22)           | 1.397(5)   |
| C(27)-C(28)           | 1.394(5)   | C(27)-C(32)           | 1.386(5)   |
| C(10)-C(9)            | 1.405(5)   | C(10)-C(11)           | 1.404(5)   |
| C(30)-H(30)           | 0.9500     | C(30)-C(29)           | 1.388(6)   |
| C(30)-C(31)           | 1.378(6)   | C(1)-C(6)             | 1.390(5)   |
| C(1)-C(2)             | 1.403(5)   | C(33)-C(34)           | 1.390(5)   |
| C(33)-C(38)           | 1.400(5)   | C(12)-H(12)           | 0.9500     |
| C(12)-C(11)           | 1.387(5)   | C(12)-C(13)           | 1.397(5)   |
| C(34)-H(34)           | 0.9500     | C(34)-C(35)           | 1.393(5)   |
| C(9)-C(8)             | 1.523(5)   | C(9)-C(14)            | 1.394(5)   |
| C(28)-H(28)           | 0.9500     | C(28)-C(29)           | 1.395(6)   |
| C(13)-H(13)           | 0.9500     | C(13)-C(14)           | 1.373(5)   |
| C(26)-H(26)           | 0.9500     | C(26)-C(25)           | 1.387(6)   |
| C(6)-C(5)             | 1.393(5)   | C(2)-H(2)             | 0.9500     |
| C(2)-C(3)             | 1.383(5)   | C(22)-H(22)           | 0.9500     |
| C(22)-C(23)           | 1.387(6)   | C(29)-H(29)           | 0.9500     |
| C(15)-C(20)           | 1.396(5)   | C(15)-C(16)           | 1.388(5)   |
| C(7)-H(7A)            | 0.9900     | C(7)-H(7B)            | 0.9900     |
| C(7)-C(8)             | 1.529(6)   | C(7)-C(5)             | 1.496(5)   |
| C(31)-H(31)           | 0.9500     | C(31)-C(32)           | 1.384(5)   |
| C(20)-H(20)           | 0.9500     | C(20)-C(19)           | 1.396(5)   |
| C(19)-H(19)           | 0.9500     | C(19)-C(18)           | 1.379(6)   |
| C(32)-H(32)           | 0.9500     | C(16)-H(16)           | 0.9500     |
| C(16)-C(17)           | 1.392(5)   | C(38)-H(38)           | 0.9500     |
| C(38)-C(37)           | 1.385(5)   | C(8)-H(8A)            | 0.9900     |
| C(8)-H(8B)            | 0.9900     | C(5)-C(4)             | 1.395(5)   |
| C(35)-H(35)           | 0.9500     | C(35)-C(36)           | 1.386(5)   |
| C(14)-H(14)           | 0.9500     | C(25)-H(25)           | 0.9500     |
| C(25)-C(24)           | 1.392(6)   | C(36)-H(36)           | 0.9500     |
| C(36)-C(37)           | 1.381(6)   | C(17)-H(17)           | 0.9500     |
| Bond                        | Distance     | Bond                        | Distance     |
|-----------------------------|--------------|-----------------------------|--------------|
| C(17)-C(18)                 | 1.396(6)     | C(23)-H(23)                 | 0.9500       |
| C(23)-C(24)                 | 1.383(7)     | C(37)-H(37)                 | 0.9500       |
| C(18)-H(18)                 | 0.9500       | C(3)-H(3)                   | 0.9500       |
| C(3)-C(4)                   | 1.389(5)     | C(24)-H(24)                 | 0.9500       |
| C(4)-H(4)                   | 0.9500       |                             |              |
| C(27)-Bi(2)-C(33)           | 94.34(12)    | C(11)-Bi(2)-C(27)           | 92.72(12)    |
| C(11)-Bi(2)-C(33)           | 93.21(12)    | C(21)-Bi(1)-C(1)            | 97.62(12)    |
| C(21)-Bi(1)-C(15)           | 94.52(13)    | C(1)-Bi(1)-C(15)            | 92.32(12)    |
| C(10)-O(1)-C(6)             | 118.8(3)     | C(26)-C(21)-Bi(1)           | 122.8(3)     |
| C(26)-C(21)-C(22)           | 118.9(4)     | C(22)-C(21)-Bi(1)           | 118.4(3)     |
| C(28)-C(27)-Bi(2)           | 118.8(3)     | C(32)-C(27)-Bi(2)           | 123.0(3)     |
| C(32)-C(27)-C(28)           | 118.2(3)     | C(9)-C(10)-O(1)             | 125.0(3)     |
| C(11)-C(10)-O(1)            | 114.0(3)     | C(11)-C(10)-C(9)            | 121.0(3)     |
| C(29)-C(30)-H(30)           | 120.2        | C(31)-C(30)-H(30)           | 120.2        |
| C(31)-C(30)-C(29)           | 119.6(4)     | C(6)-C(1)-Bi(1)             | 121.3(2)     |
| C(6)-C(1)-C(2)              | 117.6(3)     | C(2)-C(1)-Bi(1)             | 120.5(2)     |
| C(34)-C(33)-Bi(2)           | 122.9(2)     | C(34)-C(33)-C(38)           | 118.2(3)     |
| C(38)-C(33)-Bi(2)           | 118.7(3)     | C(11)-C(12)-H(12)           | 119.8        |
| C(11)-C(12)-C(13)           | 120.4(3)     | C(13)-C(12)-H(12)           | 119.8        |
| C(33)-C(34)-H(34)           | 119.6        | C(33)-C(34)-C(35)           | 120.9(3)     |
| C(35)-C(34)-H(34)           | 119.6        | C(10)-C(9)-C(8)             | 126.3(3)     |
| C(14)-C(9)-C(10)            | 117.1(3)     | C(14)-C(9)-C(8)             | 116.4(3)     |
| C(10)-C(11)-Bi(2)           | 118.8(2)     | C(12)-C(11)-Bi(2)           | 121.8(3)     |
| C(12)-C(11)-C(10)           | 119.3(3)     | C(27)-C(28)-H(28)           | 119.5        |
| C(27)-C(28)-C(29)           | 121.0(4)     | C(29)-C(28)-H(28)           | 119.5        |
| C(12)-C(13)-H(13)           | 120.4        | C(14)-C(13)-C(12)           | 119.1(3)     |
| C(14)-C(13)-H(13)           | 120.4        | C(21)-C(26)-H(26)           | 119.8        |
| C(25)-C(26)-C(21)           | 120.4(4)     | C(25)-C(26)-H(26)           | 119.8        |
| C(1)-C(6)-O(1)              | 118.6(3)     | C(1)-C(6)-C(5)              | 122.6(3)     |
| C(5)-C(6)-O(1)              | 118.7(3)     | C(1)-C(2)-H(2)              | 119.6        |
| C(3)-C(2)-C(1)              | 120.7(3)     | C(3)-C(2)-H(2)              | 119.6        |
| C(21)-C(22)-H(22)           | 119.7        | C(23)-C(22)-C(21)           | 120.6(4)     |
| C(23)-C(22)-H(22)           | 119.7        | C(30)-C(29)-C(28)           | 119.6(4)     |
| C(30)-C(29)-H(29)           | 120.2        | C(28)-C(29)-H(29)           | 120.2        |
| C(20)-C(15)-Bi(1)           | 118.5(3)     | C(16)-C(15)-Bi(1)           | 122.3(3)     |
| Bond                        | Distance (Å) | Bond                        | Distance (Å) |
|-----------------------------|--------------|-----------------------------|--------------|
| C(16)-C(15)-C(20)          | 119.2(3)     | H(7A)-C(7)-H(7B)           | 108.3        |
| C(8)-C(7)-H(7A)            | 109.9        | C(8)-C(7)-H(7B)            | 109.9        |
| C(5)-C(7)-H(7A)            | 109.9        | C(5)-C(7)-H(7B)            | 109.9        |
| C(5)-C(7)-C(8)             | 108.8(3)     | C(30)-C(31)-H(31)          | 119.7        |
| C(30)-C(31)-C(32)          | 120.5(4)     | C(32)-C(31)-H(31)          | 119.7        |
| C(15)-C(20)-H(20)          | 119.9        | C(15)-C(20)-C(19)          | 120.3(4)     |
| C(19)-C(20)-H(20)          | 119.9        | C(20)-C(19)-H(19)          | 119.8        |
| C(18)-C(19)-C(20)          | 120.4(4)     | C(18)-C(19)-H(19)          | 119.8        |
| C(27)-C(32)-H(32)          | 119.5        | C(31)-C(32)-C(27)          | 121.0(4)     |
| C(31)-C(32)-H(32)          | 119.5        | C(15)-C(16)-H(16)          | 119.8        |
| C(15)-C(16)-C(17)          | 120.3(4)     | C(17)-C(16)-H(16)          | 119.8        |
| C(33)-C(38)-H(38)          | 119.5        | C(37)-C(38)-C(33)          | 120.9(3)     |
| C(37)-C(38)-H(38)          | 119.5        | C(9)-C(8)-C(7)             | 115.0(3)     |
| C(9)-C(8)-H(8A)            | 108.5        | C(9)-C(8)-H(8B)            | 108.5        |
| C(7)-C(8)-H(8A)            | 108.5        | C(7)-C(8)-H(8B)            | 108.5        |
| H(8A)-C(8)-H(8B)           | 107.5        | C(6)-C(5)-C(7)             | 119.5(3)     |
| C(6)-C(5)-C(4)             | 118.1(3)     | C(4)-C(5)-C(7)             | 122.1(3)     |
| C(34)-C(35)-H(35)          | 120.0        | C(36)-C(35)-C(34)          | 120.1(4)     |
| C(36)-C(35)-H(35)          | 120.0        | C(9)-C(14)-H(14)           | 118.6        |
| C(13)-C(14)-C(9)           | 122.7(3)     | C(13)-C(14)-H(14)          | 118.6        |
| C(26)-C(25)-H(25)          | 119.8        | C(26)-C(25)-C(24)          | 120.3(4)     |
| C(24)-C(25)-H(25)          | 119.8        | C(35)-C(36)-H(36)          | 120.1        |
| C(37)-C(36)-C(35)          | 119.7(3)     | C(37)-C(36)-H(36)          | 120.1        |
| C(16)-C(17)-H(17)          | 119.9        | C(16)-C(17)-C(18)          | 120.3(4)     |
| C(18)-C(17)-H(17)          | 119.9        | C(22)-C(23)-H(23)          | 119.9        |
| C(24)-C(23)-C(22)          | 120.2(4)     | C(24)-C(23)-H(23)          | 119.9        |
| C(38)-C(37)-H(37)          | 119.9        | C(36)-C(37)-C(38)          | 120.2(3)     |
| C(36)-C(37)-H(37)          | 119.9        | C(19)-C(18)-C(17)          | 119.5(4)     |
| C(19)-C(18)-H(18)          | 120.2        | C(17)-C(18)-H(18)          | 120.2        |
| C(2)-C(3)-H(3)             | 119.8        | C(2)-C(3)-C(4)             | 120.4(3)     |
| C(4)-C(3)-H(3)             | 119.8        | C(25)-C(24)-H(24)          | 120.2        |
| C(23)-C(24)-C(25)          | 119.6(4)     | C(23)-C(24)-H(24)          | 120.2        |
| C(5)-C(4)-H(4)             | 119.8        | C(3)-C(4)-C(5)             | 120.4(3)     |
| C(3)-C(4)-H(4)             | 119.8        |                             |              |
Single crystal structure analysis of 8 (13443)

Figure 7. The molecular structure of complex 8. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of complex 8: C\textsubscript{36}H\textsubscript{28}Bi\textsubscript{2}O, \( M_r = 894.54 \) g mol\(^{-1}\), colourless needle, crystal size 0.056 x 0.041 x 0.020 mm\(^3\), monoclinic, \( P2_1/c \) [14], \( a = 11.0777(7) \) Å, \( b = 17.8599(11) \) Å, \( c = 15.0585(9) \) Å, \( \beta = 92.997(2) ^\circ \), \( V = 2975.2(3) \) Å\(^3\), \( T = 100(2) \) K, \( Z = 4 \), \( D_{calc} = 1.997 \) g·cm\(^{-3}\), \( \lambda = 0.71073 \) Å, \( \mu(Mo-K_{\alpha}) = 11.840 \) mm\(^{-1}\), Gaussian absorption correction (\( T_{\text{min}} = 0.60899, T_{\text{max}} = 0.85677 \)), Bruker-AXS Mach3 diffractometer with APEX-II detector and \( \mu \)S microfocus Mo-anode X-ray source, 1.770 < \( \theta < 34.337 \) °, 116047 measured reflections, 12473 independent reflections, 10883 reflections with \( I > 2\sigma(I) \), \( R_{int} = 0.0363 \). The structure was solved by \textit{SHELXT} and refined by full-matrix least-squares (\textit{SHELXL}) against \( F^2 \) to \( R_l = 0.0187 \) [\( I > 2\sigma(I) \)], \( wR_2 = 0.0330 \), 352 parameters.
**Figure 8.** Crystal faces and unit cell determination of complex 8.

| Resolution | #Data | #Theory | %Complete | Redundancy Mean | I Mean | I/s | Rmerge | Rsigma |
|------------|-------|---------|-----------|----------------|--------|-----|--------|--------|
| Inf - 2.62 | 193   | 193     | 100.0     | 16.66          | 105.31 | 100.95 | 0.0218 | 0.0077 |
| 2.62 - 1.73| 465   | 465     | 100.0     | 18.07          | 77.19  | 95.92 | 0.0213 | 0.0078 |
| 1.73 - 1.36| 659   | 659     | 100.0     | 18.21          | 56.68  | 85.70 | 0.0239 | 0.0084 |
| 1.36 - 1.19| 637   | 637     | 100.0     | 17.89          | 40.21  | 73.92 | 0.0290 | 0.0095 |
| 1.19 - 1.08| 644   | 644     | 100.0     | 16.19          | 34.66  | 63.67 | 0.0328 | 0.0110 |
| 1.08 - 1.00| 659   | 659     | 100.0     | 12.04          | 30.16  | 50.59 | 0.0367 | 0.0144 |
| 1.00 - 0.94| 643   | 643     | 100.0     | 9.96           | 24.96  | 41.52 | 0.0403 | 0.0173 |
| 0.94 - 0.89| 700   | 700     | 100.0     | 8.42           | 22.48  | 34.84 | 0.0441 | 0.0206 |
| 0.89 - 0.85| 654   | 654     | 100.0     | 7.81           | 18.60  | 29.75 | 0.0501 | 0.0243 |
| 0.85 - 0.82| 606   | 606     | 100.0     | 7.49           | 18.04  | 27.34 | 0.0527 | 0.0262 |
| 0.82 - 0.79| 676   | 676     | 100.0     | 7.22           | 14.37  | 23.26 | 0.0635 | 0.0317 |
| 0.79 - 0.77| 526   | 526     | 100.0     | 6.93           | 14.23  | 21.71 | 0.0608 | 0.0330 |
| 0.77 - 0.74| 882   | 882     | 100.0     | 6.73           | 13.25  | 19.76 | 0.0695 | 0.0367 |
| 0.74 - 0.72| 680   | 680     | 100.0     | 6.25           | 12.03  | 17.70 | 0.0789 | 0.0427 |
| 0.72 - 0.71| 354   | 354     | 100.0     | 6.39           | 12.06  | 17.95 | 0.0819 | 0.0426 |
| 0.71 - 0.69| 773   | 773     | 100.0     | 6.05           | 9.64   | 14.48 | 0.0936 | 0.0526 |
| 0.69 - 0.67| 914   | 914     | 100.0     | 5.83           | 9.13   | 13.50 | 0.1011 | 0.0579 |
| 0.67 - 0.66| 488   | 488     | 100.0     | 5.68           | 8.11   | 11.88 | 0.1123 | 0.0651 |
| 0.66 - 0.65| 509   | 509     | 100.0     | 5.49           | 7.47   | 11.07 | 0.1194 | 0.0728 |
| 0.65 - 0.64| 555   | 555     | 100.0     | 5.38           | 8.04   | 11.27 | 0.1236 | 0.0705 |
| 0.64 - 0.63| 601   | 601     | 100.0     | 5.13           | 7.03   | 9.96  | 0.1317 | 0.0819 |
| 0.73 - 0.63| 4559  | 4559    | 100.0     | 5.74           | 8.91   | 13.13 | 0.1027 | 0.0599 |
| Inf - 0.63 | 12818 | 12818   | 100.0     | 9.20           | 22.61  | 34.27 | 0.0359 | 0.0217 |

Complete .cif-data of the compound are available under the CCDC number **CCDC-2063976**.
Table 7. Crystal data and structure refinement.

| Property                        | Value                           |
|---------------------------------|---------------------------------|
| Identification code             | 13443                           |
| Empirical formula               | C$_{36}$H$_{28}$Bi$_2$O         |
| Color                           | colourless                      |
| Formula weight                  | 894.54 g · mol$^{-1}$           |
| Temperature                     | 100(2) K                        |
| Wavelength                      | 0.71073 Å                       |
| Crystal system                  | MONOCLINIC                      |
| Space group                     | $P2_1/c$, (No. 14)              |
| Unit cell dimensions            | $a = 11.0777(7)$ Å, $\alpha = 90^\circ$, $b = 17.8599(11)$ Å, $\beta = 92.997(2)^\circ$, $c = 15.0585(9)$ Å, $\gamma = 90^\circ$. |
| Volume                          | 2975.2(3) Å$^3$                 |
| Z                               | 4                               |
| Density (calculated)            | 1.997 Mg · m$^{-3}$             |
| Absorption coefficient          | 11.840 mm$^{-1}$                |
| F(000)                          | 1672 e                          |
| Crystal size                    | 0.056 x 0.041 x 0.020 mm$^3$    |
| $\theta$ range for data collection | 1.770 to 34.337°.            |
| Index ranges                    | $-17 \leq h \leq 17$, $-28 \leq k \leq 28$, $-23 \leq l \leq 23$ |
| Reflections collected           | 116047                          |
| Independent reflections         | 12473 [$R_{int}$ = 0.0363]      |
| Reflections with I>2$\sigma$(I) | 10883                           |
| Completeness to $\theta = 25.242^\circ$ | 100.0 %                      |
| Absorption correction           | Gaussian                        |
| Max. and min. transmission      | 0.86 and 0.61                   |
| Refinement method               | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters  | 12473 / 0 / 352                 |
| Goodness-of-fit on $F^2$        | 1.038                           |
| Final R indices [I>2$\sigma$(I)] | $R_1 = 0.0187$, $wR^2 = 0.0330$ |
| R indices (all data)            | $R_1 = 0.0262$, $wR^2 = 0.0344$ |
| Largest diff. peak and hole     | 1.9 and -1.2 e · Å$^{-3}$      |
Table 8. Bond lengths [Å] and angles [°].

| Bond                  | Length  | Bond                  | Length  |
|-----------------------|---------|-----------------------|---------|
| Bi(1)-C(1)            | 2.2624(17) | Bi(1)-C(13)         | 2.2494(19) |
| Bi(1)-C(19)           | 2.2605(18) | Bi(2)-C(7)           | 2.2426(18) |
| Bi(2)-C(25)           | 2.2491(18) | Bi(2)-C(31)         | 2.2525(19) |
| O(1)-C(2)             | 1.400(2)  | O(1)-C(8)            | 1.397(2)  |
| C(1)-C(2)             | 1.384(3)  | C(1)-C(6)            | 1.399(2)  |
| C(2)-C(3)             | 1.394(3)  | C(3)-C(4)            | 1.393(3)  |
| C(4)-C(5)             | 1.388(3)  | C(5)-C(6)            | 1.391(3)  |
| C(7)-C(8)             | 1.389(3)  | C(7)-C(12)           | 1.400(3)  |
| C(8)-C(9)             | 1.392(3)  | C(9)-C(10)           | 1.390(3)  |
| C(10)-C(11)           | 1.387(3)  | C(11)-C(12)          | 1.388(3)  |
| C(13)-C(14)           | 1.397(3)  | C(13)-C(18)          | 1.394(2)  |
| C(14)-C(15)           | 1.395(3)  | C(15)-C(16)          | 1.391(3)  |
| C(16)-C(17)           | 1.386(3)  | C(17)-C(18)          | 1.390(3)  |
| C(19)-C(20)           | 1.392(3)  | C(19)-C(24)          | 1.390(3)  |
| C(20)-C(21)           | 1.393(3)  | C(21)-C(22)          | 1.387(3)  |
| C(22)-C(23)           | 1.385(3)  | C(23)-C(24)          | 1.395(3)  |
| C(25)-C(26)           | 1.390(3)  | C(25)-C(30)          | 1.395(3)  |
| C(26)-C(27)           | 1.395(3)  | C(27)-C(28)          | 1.386(3)  |
| C(28)-C(29)           | 1.380(3)  | C(29)-C(30)          | 1.385(3)  |
| C(31)-C(32)           | 1.395(3)  | C(31)-C(36)          | 1.395(3)  |
| C(32)-C(33)           | 1.395(3)  | C(33)-C(34)          | 1.388(3)  |
| C(34)-C(35)           | 1.384(4)  | C(35)-C(36)          | 1.394(3)  |
| C(13)-Bi(1)-C(1)      | 97.61(6)  | C(13)-Bi(1)-C(19)   | 92.20(7)  |
| C(19)-Bi(1)-C(1)      | 92.13(6)  | C(7)-Bi(2)-C(25)    | 94.66(7)  |
| C(7)-Bi(2)-C(31)      | 97.14(7)  | C(25)-Bi(2)-C(31)   | 91.50(7)  |
| C(8)-O(1)-C(2)        | 118.78(14)| C(2)-C(1)-Bi(1)     | 118.57(12)|
| C(2)-C(1)-C(6)        | 117.86(16)| C(6)-C(1)-Bi(1)     | 122.94(13)|
| C(1)-C(2)-O(1)        | 117.03(16)| C(1)-C(2)-C(3)      | 122.08(17)|
| C(3)-C(2)-O(1)        | 120.75(16)| C(4)-C(3)-C(2)      | 118.99(18)|
| C(5)-C(4)-C(3)        | 120.12(18)| C(4)-C(5)-C(6)      | 119.83(18)|
| C(5)-C(6)-C(1)        | 121.13(18)| C(8)-C(7)-Bi(2)     | 117.52(13)|
| C(8)-C(7)-C(12)       | 118.09(17)| C(12)-C(7)-Bi(2)    | 124.06(13)|
| C(7)-C(8)-O(1)        | 116.54(16)| C(9)-C(8)-O(1)      | 121.33(17)|
| Bond          | Angle [°] (measured) |
|--------------|---------------------|
| C(9)-C(8)-C(7)| 122.10(17)          |
| C(11)-C(10)-C(9)| 120.53(19)          |
| C(11)-C(12)-C(7)| 120.59(18)          |
| C(18)-C(13)-Bi(1)| 116.99(14)          |
| C(15)-C(14)-C(13)| 120.28(17)          |
| C(17)-C(16)-C(15)| 119.39(19)          |
| C(17)-C(18)-C(13)| 120.66(18)          |
| C(24)-C(19)-Bi(1)| 118.65(14)          |
| C(19)-C(20)-C(21)| 120.44(17)          |
| C(23)-C(22)-C(21)| 119.47(18)          |
| C(19)-C(24)-C(23)| 120.57(19)          |
| C(26)-C(25)-C(30)| 118.84(18)          |
| C(25)-C(26)-C(27)| 120.39(19)          |
| C(29)-C(28)-C(27)| 120.43(19)          |
| C(29)-C(30)-C(25)| 120.9(2)            |
| C(32)-C(31)-C(36)| 118.90(18)          |
| C(31)-C(32)-C(33)| 120.53(19)          |
| C(35)-C(34)-C(33)| 120.2(2)            |
| C(35)-C(36)-C(31)| 120.6(2)            |
| C(8)-C(9)-C(10)| 118.84(19)          |
| C(10)-C(11)-C(12)| 119.85(18)          |
| C(14)-C(13)-Bi(1)| 124.02(13)          |
| C(18)-C(13)-C(14)| 118.83(18)          |
| C(16)-C(15)-C(14)| 120.39(19)          |
| C(16)-C(17)-C(18)| 120.45(18)          |
| C(20)-C(19)-Bi(1)| 122.43(13)          |
| C(24)-C(19)-C(20)| 118.92(17)          |
| C(22)-C(21)-C(20)| 120.38(18)          |
| C(22)-C(23)-C(24)| 120.22(18)          |
| C(26)-C(25)-Bi(2)| 123.91(14)          |
| C(30)-C(25)-Bi(2)| 117.20(14)          |
| C(30)-C(26)-C(27)| 119.7(2)            |
| C(28)-C(27)-C(26)| 119.6(2)            |
| C(32)-C(31)-Bi(2)| 123.08(14)          |
| C(36)-C(31)-Bi(2)| 117.84(14)          |
| C(34)-C(33)-C(32)| 119.8(2)            |
| C(34)-C(35)-C(36)| 119.9(2)            |
Single crystal structure analysis of 9 (13680)

Figure 9. The molecular structure of complex 9. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of complex 9: C_{36}H_{26}Bi_{2}Cl_{4}O, M_r = 1034.33 g mol\(^{-1}\), colourless plate, crystal size 0.062 x 0.035 x 0.011 mm\(^3\), triclinic, P-1 [2], a = 9.0281(4) Å, b = 12.1880(5) Å, c = 15.1195(6) Å, α = 101.289(2) °, β = 90.246(2) °, γ = 95.156(2) ° V = 1624.47(12) Å\(^3\), T = 100(2) K, Z = 2, D_{calc} = 2.115 g·cm\(^{-3}\), λ = 0.71073 Å, μ(Mo-Kα) = 11.176 mm\(^{-1}\), Gaussian absorption correction (T_{min} = 0.62769, T_{max} = 0.89794), Bruker-AXS Mach3 diffractometer with APEX-II detector and μS microfocus Mo-anode X-ray source, 1.374 < θ < 35.077 °, 65647 measured reflections, 14207 independent reflections, 11437 reflections with I > 2σ(I), R_{int} = 0.0403. The structure was solved by SHELXT and refined by full-matrix least-squares (SHELXL) against F\(^2\) to R_f = 0.0262 [I > 2σ(I)], wR_2 = 0.0566, 388 parameters.
Figure 10. Crystal faces and unit cell determination of complex 9.

| Resolution | #Data | #Theory | %Complete | Redundancy | Mean I | Mean I/s | Rmerge | Rsigma |
|------------|-------|---------|-----------|------------|--------|----------|--------|--------|
| Inf - 2.62 | 193   | 193     | 100.0     | 16.66      | 105.31 | 100.95   | 0.0218 | 0.0077 |
| 2.62 - 1.73| 465   | 465     | 100.0     | 18.07      | 77.19  | 95.92    | 0.0213 | 0.0078 |
| 1.73 - 1.36| 659   | 659     | 100.0     | 18.21      | 56.68  | 85.70    | 0.0239 | 0.0084 |
| 1.36 - 1.19| 637   | 637     | 100.0     | 17.89      | 40.21  | 73.92    | 0.0290 | 0.0095 |
| 1.19 - 1.08| 644   | 644     | 100.0     | 16.19      | 34.66  | 63.67    | 0.0328 | 0.0110 |
| 1.08 - 1.00| 659   | 659     | 100.0     | 12.04      | 30.16  | 50.59    | 0.0367 | 0.0144 |
| 1.00 - 0.94| 643   | 643     | 100.0     | 9.96       | 24.96  | 41.52    | 0.0403 | 0.0173 |
| 0.94 - 0.89| 700   | 700     | 100.0     | 8.42       | 22.48  | 34.84    | 0.0441 | 0.0206 |
| 0.89 - 0.85| 654   | 654     | 100.0     | 7.81       | 18.60  | 29.75    | 0.0501 | 0.0243 |
| 0.85 - 0.82| 606   | 606     | 100.0     | 7.49       | 18.04  | 27.34    | 0.0527 | 0.0262 |
| 0.82 - 0.79| 676   | 676     | 100.0     | 7.22       | 14.37  | 23.26    | 0.0635 | 0.0317 |
| 0.79 - 0.77| 526   | 526     | 100.0     | 6.93       | 14.23  | 21.71    | 0.0608 | 0.0330 |
| 0.77 - 0.74| 882   | 882     | 100.0     | 6.73       | 13.25  | 19.76    | 0.0695 | 0.0367 |
| 0.74 - 0.72| 680   | 680     | 100.0     | 6.25       | 12.03  | 17.70    | 0.0789 | 0.0427 |
| 0.72 - 0.71| 354   | 354     | 100.0     | 6.39       | 12.06  | 17.95    | 0.0819 | 0.0426 |
| 0.71 - 0.69| 773   | 773     | 100.0     | 6.05       | 9.64   | 14.48    | 0.0936 | 0.0526 |
| 0.69 - 0.67| 914   | 914     | 100.0     | 5.83       | 9.13   | 13.50    | 0.1011 | 0.0579 |
| 0.67 - 0.66| 488   | 488     | 100.0     | 5.68       | 8.11   | 11.88    | 0.1123 | 0.0651 |
| 0.66 - 0.65| 509   | 509     | 100.0     | 5.49       | 7.47   | 11.07    | 0.1194 | 0.0728 |
| 0.65 - 0.64| 555   | 555     | 100.0     | 5.38       | 8.04   | 11.27    | 0.1236 | 0.0705 |
| 0.64 - 0.63| 601   | 601     | 100.0     | 5.13       | 7.03   | 9.96     | 0.1317 | 0.0819 |
| 0.73 - 0.63| 4559  | 4559    | 100.0     | 5.74       | 8.91   | 13.13    | 0.1027 | 0.0599 |
| Inf - 0.63 | 12818 | 12818   | 100.0     | 9.20       | 22.61  | 34.27    | 0.0359 | 0.0217 |

Complete .cif-data of the compound are available under the CCDC number **CCDC-2063977**.
### Table 9. Crystal data and structure refinement.

| Identification code | 13680          |
|---------------------|----------------|
| Empirical formula   | C$_{36}$H$_{26}$Bi$_2$Cl$_4$O |
| Color               | colourless     |
| Formula weight      | 1034.33 g · mol$^{-1}$ |
| Temperature         | 100(2) K       |
| Wavelength          | 0.71073 Å      |
| Crystal system      | TRICLINIC      |
| Space group         | P-1, (No. 2)   |
| Unit cell dimensions| $a = 9.0281(4)$ Å, $a = 101.289(2)^\circ$. |
|                      | $b = 12.1880(5)$ Å, $\beta = 90.246(2)^\circ$. |
|                      | $c = 15.1195(6)$ Å, $\gamma = 95.156(2)^\circ$. |
| Volume              | 1624.47(12) Å$^3$ |
| Z                   | 2              |
| Density (calculated)| 2.115 Mg · m$^{-3}$ |
| Absorption coefficient | 11.176 mm$^{-1}$ |
| F(000)              | 968 e          |
| Crystal size        | 0.062 x 0.035 x 0.011 mm$^3$ |
| $\theta$ range for data collection | 1.374 to 35.077°. |
| Index ranges        | -14 $\leq h \leq$ 14, -19 $\leq k \leq$ 19, -24 $\leq l \leq$ 24 |
| Reflections collected| 65647          |
| Independent reflections | 14207 [R$\text{int} = 0.0403$] |
| Reflections with I>2$\sigma$(I) | 11437          |
| Completeness to $\theta = 25.242^\circ$ | 100.0 %       |
| Absorption correction | Gaussian       |
| Max. and min. transmission | 0.90 and 0.63 |
| Refinement method   | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 14207 / 0 / 388 |
| Goodness-of-fit on F$^2$ | 1.046          |
| Final R indices [I>2$\sigma$(I)] | R$_{I}$ = 0.0262, wR$^2$ = 0.0527 |
| R indices (all data) | R$_{I}$ = 0.0408, wR$^2$ = 0.0566 |
| Largest diff. peak and hole | 2.0 and -1.4 e · Å$^{-3}$ |
Table 10. Bond lengths [Å] and angles [°].

| Bond                  | Length/Angle   |
|-----------------------|---------------|
| Bi(1)-Cl(1)           | 2.5816(6)     |
| Bi(1)-C(2)            | 2.184(2)      |
| Bi(1)-C(19)           | 2.213(2)      |
| Bi(1)-Cl(4)           | 2.5769(6)     |
| Bi(1)-C(25)           | 2.197(3)      |
| O(1)-C(1)             | 1.381(3)      |
| C(1)-C(2)             | 1.375(3)      |
| C(2)-C(3)             | 1.395(4)      |
| C(4)-C(5)             | 1.375(4)      |
| C(6)-C(7)             | 1.441(4)      |
| C(7)-C(12)            | 1.396(3)      |
| C(9)-C(10)            | 1.393(4)      |
| C(11)-C(12)           | 1.379(4)      |
| C(13)-C(18)           | 1.383(4)      |
| C(15)-C(16)           | 1.376(4)      |
| C(17)-C(18)           | 1.392(4)      |
| C(19)-C(24)           | 1.380(4)      |
| C(21)-C(22)           | 1.364(4)      |
| C(23)-C(24)           | 1.387(4)      |
| C(25)-C(30)           | 1.393(4)      |
| C(27)-C(28)           | 1.371(5)      |
| C(29)-C(30)           | 1.383(4)      |
| C(31)-C(36)           | 1.383(3)      |
| C(33)-C(34)           | 1.372(4)      |
| C(35)-C(36)           | 1.390(4)      |
| Cl(1)-Bi(1)-Cl(2)     | 177.46(2)     |
| C(2)-Bi(1)-C(13)      | 130.24(9)     |
| C(13)-Bi(1)-Cl(1)     | 89.26(7)      |
| C(19)-Bi(1)-Cl(1)     | 116.51(8)     |
| Cl(3)-Bi(2)-Cl(4)     | 92.41(7)      |
| C(11)-Bi(2)-Cl(4)     | 112.86(9)     |
| C(11)-Bi(2)-C(31)     | 93.52(7)      |
Single crystal structure analysis of 10 (13220)

Figure 11. The molecular structure of complex 10. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of complex 10: C_{39.50} H_{33} Bi_2 Cl_5 O, M_r = 1118.87 g mol\(^{-1}\), colourless prism, crystal size 0.052 x 0.026 x 0.021 mm\(^3\), monoclinic, \(P2_1/c\) [14], \(a = 12.3959(6)\) \(\text{Å}\), \(b = 13.9993(6)\) \(\text{Å}\), \(c = 21.7582(10)\) \(\text{Å}\), \(\beta = 100.772(2)\) °, \(V = 3709.3(3)\) \(\text{Å}^3\), \(T = 100(2)\) K, \(Z = 4\), \(D_{\text{calc}} = 2.004\) g·cm\(^{-3}\), \(\lambda = 0.71073\) Å, \(\mu(\text{Mo-K\(\alpha\)}) = 9.867\) mm\(^{-1}\), Gaussian absorption correction \((T_{\text{min}} = 0.67911, T_{\text{max}} = 0.83591)\), Bruker-AXS Mach3 diffractometer with APEX-II detector and \(\mu\)S microfocus Mo-anode X-ray source, \(1.672 < \theta < 27.499\) °, 144619 measured reflections, 8521 independent reflections, 7847 reflections with \(I > 2\sigma(I)\), \(R_{\text{int}} = 0.0334\). The structure was solved by \textit{SHELXT} and refined by full-matrix least-squares (\textit{SHELXL}) against \(F^2\) to \(R_I = 0.0160\) \([I > 2\sigma(I)]\), \(wR_2 = 0.0323\), 492 parameters.
The structure contains a rotational disorder of 60:40 and 60:40 at phenyl ligands of Bi1. Disordered atoms have been partially refined isotropically. Additionally a solute molecule (DCM) is disordered about a crystallographic special position (inversion center) with 50:50 occupancy and the bond situation has been described using FREE instruction. The high residual electron density (highest peak: 2.45 at 0.66 Å from Bi1 and deepest hole: -3.00 at 0.72 Å from Bi1) could possibly be caused by anharmonic displacement of the Bi atom.

Complete .cif-data of the compound are available under the CCDC number CCDC-2063980.
Table 11. Crystal data and structure refinement.

| Description                                      | Value                        |
|--------------------------------------------------|------------------------------|
| Identification code                              | 13220                        |
| Empirical formula                                | C_{39.50}H_{33}Bi_{2}Cl_{5}O |
| Color                                            | colourless                   |
| Formula weight                                   | 1118.87 g · mol^{-1}         |
| Temperature                                      | 100(2) K                     |
| Wavelength                                       | 0.71073 Å                    |
| Crystal system                                   | MONOCLINIC                   |
| Space group                                      | P2_1/c, (No. 14)             |
| Unit cell dimensions                             | a = 12.3959(6) Å             |
|                                                   | α = 90°                      |
|                                                   | b = 13.9993(6) Å             |
|                                                   | β = 100.772(2)°              |
|                                                   | c = 21.7582(10) Å            |
|                                                   | γ = 90°                      |
| Volume                                           | 3709.3(3) Å³                |
| Z                                                | 4                            |
| Density (calculated)                             | 2.004 Mg · m⁻³               |
| Absorption coefficient                           | 9.867 mm⁻¹                   |
| F(000)                                           | 2116 e                       |
| Crystal size                                     | 0.052 x 0.026 x 0.021 mm³    |
| θ range for data collection                      | 1.672 to 27.499°             |
| Index ranges                                     | -16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -28 ≤ l ≤ 28 |
| Reflections collected                            | 144619                       |
| Independent reflections                          | 8521 [R_{int} = 0.0334]      |
| Reflections with I>2σ(I)                          | 7847                         |
| Completeness to θ = 25.242°                     | 100.0 %                      |
| Absorption correction                            | Gaussian                     |
| Max. and min. transmission                       | 0.84 and 0.68                |
| Refinement method                                | Full-matrix least-squares on F² |
| Data / restraints / parameters                    | 8521 / 0 / 492               |
| Goodness-of-fit on F²                             | 1.043                        |
| Final R indices [I>2σ(I)]                        | R₁ = 0.0160, wR² = 0.0323    |
| R indices (all data)                             | R₁ = 0.0196, wR² = 0.0339    |
| Largest diff. peak and hole                       | 2.5 and -3.0 e · Å⁻³         |
Table 12. Bond lengths [Å] and angles [°].

| Bond                  | Length  | Bond                  | Length  |
|-----------------------|---------|-----------------------|---------|
| Bi(1)-Cl(3)           | 2.5828(7)| Bi(1)-Cl(4)           | 2.5825(7)|
| Bi(1)-C(12)           | 2.190(2) | Bi(1)-C(28)           | 2.214(3) |
| Bi(1)-C(34A)          | 2.189(5) | Bi(1)-C(34B)          | 2.258(10)|
| Bi(2)-Cl(1)           | 2.5977(6)| Bi(2)-Cl(2)           | 2.5702(7)|
| Bi(2)-C(2)            | 2.212(3) | Bi(2)-C(16)           | 2.223(2) |
| Bi(2)-C(22)           | 2.212(2) | O(1)-C(1)             | 1.391(3) |
| O(1)-C(13)            | 1.391(3) | C(1)-C(2)             | 1.388(4) |
| C(1)-C(6)             | 1.402(4) | C(2)-C(3)             | 1.394(3) |
| C(3)-C(4)             | 1.381(4) | C(4)-C(5)             | 1.386(4) |
| C(5)-C(6)             | 1.392(4) | C(6)-C(7)             | 1.521(4) |
| C(7)-C(8)             | 1.527(4) | C(7)-C(14)            | 1.541(4) |
| C(7)-C(15)            | 1.397(4) | O(1)-C(9)             | 1.389(4) |
| C(10)-C(11)           | 1.386(4) | C(9)-C(10)            | 1.388(4) |
| C(12)-C(13)           | 1.384(4) | C(11)-C(12)           | 1.388(4) |
| C(16)-C(21)           | 1.381(4) | C(15)-C(16)           | 1.380(4) |
| C(18)-C(19)           | 1.384(4) | C(17)-C(18)           | 1.391(4) |
| C(20)-C(21)           | 1.393(4) | C(19)-C(20)           | 1.385(4) |
| C(22)-C(27)           | 1.391(4) | C(22)-C(23)           | 1.379(4) |
| C(24)-C(25)           | 1.381(5) | C(23)-C(24)           | 1.394(4) |
| C(26)-C(27)           | 1.395(4) | C(25)-C(26)           | 1.377(5) |
| C(28)-C(29B)          | 1.391(14)| C(28)-C(33)           | 1.379(4) |
| (29A)-C(30A)          | 1.377(11)| C(29B)-C(30B)         | 1.402(17)|
| C(30A)-C(31)          | 1.367(8) | C(30B)-C(31)          | 1.472(11)|
| C(31)-C(32)           | 1.365(4) | C(32)-C(33)           | 1.384(4) |
| C(34A)-C(35A)         | 1.377(8) | C(34A)-C(39A)         | 1.389(7) |
| C(34B)-C(35B)         | 1.364(13)| C(34B)-C(39B)         | 1.375(13)|
| C(35A)-C(36A)         | 1.391(6) | C(35B)-C(36B)         | 1.439(15)|
| C(36A)-C(37A)         | 1.398(8) | C(36B)-C(37B)         | 1.367(14)|
| C(37A)-C(38A)         | 1.376(8) | C(37B)-C(38B)         | 1.353(15)|
| C(38A)-C(39A)         | 1.398(7) | C(38B)-C(39B)         | 1.386(13)|
| Cl(5A)-C(99)          | 1.155(8) | Cl(5A)-C(99)          | 1.769(7) |
| Cl(5B)-C(99)*         | 2.256(7) | Cl(5B)-C(99)          | 1.750(8) |
| C(99)-H(99A)          | 0.92(8)  | C(99)-H(99B)          | 0.96(9)  |
| Bond / Angle | Value (°) |
|--------------|----------|
| Cl(4)-Bi(1)-Cl(3) | 172.07(2) |
| C(12)-Bi(1)-Cl(4) | 85.19(7) |
| C(12)-Bi(1)-C(34B) | 129.8(3) |
| C(28)-Bi(1)-Cl(4) | 93.43(7) |
| C(34A)-Bi(1)-Cl(3) | 90.43(15) |
| C(34A)-Bi(1)-C(12) | 137.74(16) |
| C(34B)-Bi(1)-Cl(3) | 100.0(2) |
| Cl(2)-Bi(2)-Cl(1) | 176.01(2) |
| C(2)-Bi(2)-C(22) | 89.03(7) |
| C(2)-Bi(2)-C(22) | 102.11(9) |
| C(16)-Bi(2)-Cl(2) | 92.14(7) |
| C(22)-Bi(2)-Cl(2) | 92.19(7) |
| C(13)-O(1)-C(1) | 113.94(19) |
| C(2)-C(1)-O(1) | 120.3(2) |
| C(1)-C(2)-Bi(2) | 128.98(18) |
| C(3)-C(2)-Bi(2) | 110.27(18) |
| C(3)-C(4)-C(5) | 119.8(2) |
| C(1)-C(6)-C(7) | 117.7(2) |
| C(5)-C(6)-C(7) | 123.4(2) |
| C(6)-C(7)-C(14) | 109.1(2) |
| C(8)-C(7)-C(14) | 109.1(2) |
| C(15)-C(7)-C(14) | 108.7(2) |
| C(9)-C(8)-C(13) | 118.4(2) |
| C(10)-C(9)-C(8) | 121.5(2) |
| C(10)-C(11)-C(12) | 119.1(3) |
| C(13)-C(12)-Bi(1) | 124.27(19) |
| C(13)-C(12)-Bi(1) | 121.2(19) |
| C(12)-C(13)-C(8) | 120.6(2) |
| C(12)-C(13)-C(8) | 119.8(2) |
| C(17)-C(16)-C(21) | 123.2(2) |
| C(16)-C(17)-C(18) | 117.4(3) |
| C(18)-C(19)-C(20) | 120.4(3) |
| C(16)-C(21)-C(20) | 118.2(3) |
| C(23)-C(22)-C(27) | 121.2(2) |
| C(22)-C(23)-C(24) | 119.2(3) |
| C(26)-C(25)-C(24) | 120.6(3) |
| Bond                        | Distance (Å) | Bond                        | Distance (Å) |
|-----------------------------|--------------|-----------------------------|--------------|
| C(22)-C(27)-C(26)          | 118.9(3)     | C(29A)-C(28)-Bi(1)          | 121.5(4)     |
| C(29B)-C(28)-Bi(1)         | 114.9(6)     | C(33)-C(28)-Bi(1)           | 119.6(2)     |
| C(33)-C(28)-C(29A)         | 117.8(4)     | C(33)-C(28)-C(29B)          | 123.8(6)     |
| C(28)-C(29A)-H(29A)        | 119.2        | C(30A)-C(29A)-C(28)         | 121.6(7)     |
| C(28)-C(29B)-C(30B)        | 113.4(10)    | C(31)-C(30A)-C(29A)         | 118.2(6)     |
| C(29B)-C(30B)-C(31)        | 122.6(9)     | C(32)-C(31)-C(30A)          | 120.1(4)     |
| C(32)-C(31)-C(30B)         | 115.6(5)     | C(31)-C(32)-C(33)           | 120.4(3)     |
| C(28)-C(33)-C(32)          | 119.5(3)     | C(35A)-C(34A)-Bi(1)         | 117.6(4)     |
| C(35A)-C(34A)-C(39A)       | 122.4(4)     | C(39A)-C(34A)-Bi(1)         | 119.0(4)     |
| C(35B)-C(34B)-Bi(1)        | 111.0(7)     | C(35B)-C(34B)-C(39B)        | 124.9(9)     |
| C(39B)-C(34B)-Bi(1)        | 123.1(7)     | C(34A)-C(35A)-C(36A)        | 118.4(5)     |
| C(34B)-C(35B)-C(36B)       | 117.3(10)    | C(35A)-C(36A)-C(37A)        | 120.1(5)     |
| C(37B)-C(36B)-C(35B)       | 117.3(10)    | C(38A)-C(37A)-C(36A)        | 120.6(5)     |
| C(38B)-C(37B)-C(36B)       | 123.1(11)    | C(37A)-C(38A)-C(39A)        | 119.9(5)     |
| C(37B)-C(38B)-C(39B)       | 121.1(10)    | C(34A)-C(39A)-C(38A)        | 118.6(5)     |
| C(34B)-C(39B)-C(38B)       | 116.2(10)    | C(99)-Cl(5A)-C(99)*         | 78.0(5)      |
| C(99)-Cl(5B)-C(99)*        | 54.9(4)      | Cl(5A)-C(99)-Cl(5A)*       | 102.0(5)     |
| Cl(5B)-C(99)-Cl(5A)*       | 112.6(4)     | Cl(5B)-C(99)-H(99A)         | 109(5)       |
| Cl(5B)-C(99)-H(99B)        | 111(5)       | H(99A)-C(99)-H(99B)         | 110(7)       |

Symmetry transformations used to generate equivalent atoms: * -x+2,-y+2,-z+1
Single crystal structure analysis of 11 (13708)

Figure 13. The molecular structure of complex 11. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of complex 11: C_{44}H_{36}Bi_{2}Cl_{4}O, \( M_r = 1140.49 \) g mol\(^{-1}\), yellow prism, crystal size 0.15 x 0.13 x 0.07 mm\(^3\), triclinic, \( P-1 \) [2], \( a = 12.0198(3) \) Å, \( b = 12.1771(7) \) Å, \( c = 15.7796(11) \) Å, \( \alpha = 96.190(5) \) °, \( \beta = 103.900(4) \) °, \( \gamma = 114.199(3) \) °, \( V = 1988.7(2) \) Å\(^3\), \( T = 100(2) \) K, \( Z = 2 \), \( D_{calc} = 1.905 \) g·cm\(^{-3}\), \( \lambda = 0.71073 \) Å, \( \mu(Mo-K\alpha) = 9.139 \) mm\(^{-1}\), Gaussian absorption correction (\( T_{min} = 0.30255 \), \( T_{max} = 0.59321 \)), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, \( 2.716 < \theta < 30.508 \) °, 75349 measured reflections, 12134 independent reflections, 10803 reflections with \( I > 2\sigma(I) \), \( R_{int} = 0.0444 \). The structure was solved by \textit{SHELXS} and refined by full-matrix least-squares (\textit{SHELXL}) against \( F^2 \) to \( R_f = 0.0210 \) [\( I > 2\sigma(I) \)], \( wR_2 = 0.0436 \), 460 parameters.
**Figure 14.** Crystal faces and unit cell determination of complex 11.

**INTENSITY STATISTICS FOR DATASET**

| Resolution | #Data | #Theory | %Complete | Redundancy | Mean I | Mean I/s | Rmerge | Rsigma |
|------------|-------|---------|-----------|------------|--------|---------|--------|--------|
| Inf - 2.32 | 326   | 335     | 97.3      | 132.92     | 52.70  | 0.0448  | 0.0163 |
| 2.32 - 1.56| 763   | 763     | 100.0     | 95.60      | 47.40  | 0.0342  | 0.0166 |
| 1.56 - 1.24| 1082  | 1082    | 100.0     | 62.64      | 39.99  | 0.0341  | 0.0181 |
| 1.24 - 1.08| 1130  | 1130    | 100.0     | 47.51      | 36.25  | 0.0368  | 0.0201 |
| 1.08 - 0.98| 1126  | 1126    | 100.0     | 36.41      | 30.62  | 0.0417  | 0.0228 |
| 0.98 - 0.91| 1098  | 1098    | 100.0     | 28.86      | 27.10  | 0.0457  | 0.0263 |
| 0.91 - 0.86| 1011  | 1011    | 100.0     | 24.12      | 23.50  | 0.0506  | 0.0300 |
| 0.86 - 0.81| 1279  | 1279    | 100.0     | 20.66      | 20.40  | 0.0557  | 0.0344 |
| 0.81 - 0.78| 947   | 947     | 100.0     | 18.15      | 18.56  | 0.0619  | 0.0389 |
| 0.78 - 0.75| 1091  | 1091    | 100.0     | 15.08      | 15.78  | 0.0735  | 0.0454 |
| 0.75 - 0.72| 1289  | 1289    | 100.0     | 14.01      | 14.83  | 0.0794  | 0.0509 |
| 0.72 - 0.70| 992   | 992     | 100.0     | 11.26      | 12.27  | 0.0925  | 0.0623 |
| 0.70 - 0.68| 1115  | 1115    | 100.0     | 10.57      | 11.32  | 0.1002  | 0.0688 |
| 0.68 - 0.66| 1225  | 1225    | 100.0     | 9.44       | 9.44   | 0.1237  | 0.0863 |
| 0.66 - 0.64| 1423  | 1423    | 100.0     | 8.63       | 8.63   | 0.1461  | 0.1079 |
| 0.64 - 0.62| 729   | 729     | 100.0     | 7.55       | 7.95   | 0.1461  | 0.1176 |
| 0.62 - 0.60| 842   | 842     | 100.0     | 7.00       | 6.68   | 0.1665  | 0.1369 |
| 0.60 - 0.59| 1796  | 1796    | 100.0     | 5.60       | 4.96   | 0.2054  | 0.1933 |
| 0.59 - 0.58| 1020  | 1020    | 100.0     | 4.73       | 3.67   | 0.2448  | 0.2715 |
| 0.58 - 0.57| 1426  | 1474    | 96.7      | 4.54       | 3.11   | 0.2664  | 0.3321 |
| 0.57 - 0.55| 8461  | 8509    | 99.4      | 6.39       | 6.03   | 0.1755  | 0.1652 |
| 0.55 - 0.54| 21718 | 21767   | 99.7      | 22.57      | 17.57  | 0.0540  | 0.0416 |

A resolution cut off (SHEL 99 0.7) was applied to suppress poorly measured intensities at higher diffraction angles.

Complete .cif-data of the compound are available under the CCDC number **CCDC-2063974**.
Table 13. Crystal data and structure refinement.

| Property                              | Value                        |
|---------------------------------------|------------------------------|
| Identification code                   | 13708                        |
| Empirical formula                     | C₄₄H₃₆Bi₂Cl₄O               |
| Color                                 | yellow                       |
| Formula weight                        | 1140.49 g · mol⁻¹            |
| Temperature                           | 100(2) K                     |
| Wavelength                            | 0.71073 Å                    |
| Crystal system                        | TRICLINIC                    |
| Space group                           | P-1, (No. 2)                 |
| Unit cell dimensions                  | a = 12.0198(3) Å, α = 96.190(5)° |
|                                      | b = 12.1771(7) Å, β = 103.900(4)° |
|                                      | c = 15.7796(11) Å, γ = 114.199(3)° |
| Volume                                | 1988.7(2) Å³                 |
| Z                                     | 2                            |
| Density (calculated)                  | 1.905 Mg · m⁻³               |
| Absorption coefficient                | 9.139 mm⁻¹                   |
| F(000)                                | 1084 e                       |
| Crystal size                          | 0.15 x 0.13 x 0.07 mm³       |
| θ range for data collection           | 2.716 to 30.508°             |
| Index ranges                          | -17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -22 ≤ l ≤ 22 |
| Reflections collected                 | 75349                        |
| Independent reflections               | 12134 [R₁ = 0.0444]          |
| Reflections with I > 2σ(I)            | 10803                        |
| Completeness to θ = 25.242°          | 99.9 %                       |
| Absorption correction                 | Gaussian                     |
| Max. and min. transmission            | 0.59 and 0.30                |
| Refinement method                     | Full-matrix least-squares on F² |
| Data / restraints / parameters        | 12134 / 0 / 460              |
| Goodness-of-fit on F²                 | 1.072                        |
| Final R indices [I > 2σ(I)]           | R₁ = 0.0210, wR² = 0.0436    |
| R indices (all data)                  | R₁ = 0.0270, wR² = 0.0457    |
| Largest diff. peak and hole           | 1.0 and -1.8 e · Å⁻³         |
Table 14. Bond lengths [Å] and angles [°].

| Bond Lengths/Molecular Angles | Value 1 | Value 2 |
|-------------------------------|---------|---------|
| Bi(1)-Cl(1)                  | 2.5972(6) | Bi(1)-Cl(2)  | 2.5962(6) |
| Bi(1)-C(2)                   | 2.192(2)  | Bi(1)-C(15)  | 2.200(2)  |
| Bi(1)-Cl(3)                  | 2.5881(7) | Bi(2)-Cl(3)  | 2.5881(7) |
| Bi(2)-C(13)                  | 2.218(3)  | Bi(2)-C(13)  | 2.218(3)  |
| Bi(2)-C(15)                  | 2.200(2)  | Bi(2)-C(33)  | 2.206(3)  |
| C(1)-C(2)                    | 1.386(3)  | C(1)-C(6)    | 1.400(3)  |
| C(2)-C(3)                    | 1.386(3)  | C(10)-C(14)  | 1.379(3)  |
| C(3)-C(4)                    | 1.392(4)  | C(5)-C(6)    | 1.391(4)  |
| C(4)-C(5)                    | 1.380(4)  | C(7)-C(8)    | 1.537(5)  |
| C(6)-C(7)                    | 1.502(4)  | C(9)-C(10)   | 1.397(4)  |
| C(8)-C(9)                    | 1.499(4)  | C(11)-C(12)  | 1.376(4)  |
| C(11)-C(12)                  | 1.383(4)  | C(12)-C(13)  | 1.387(4)  |
| C(12)-C(13)                  | 1.387(3)  | C(15)-C(16)  | 1.388(3)  |
| C(13)-C(14)                  | 1.392(3)  | C(16)-C(17)  | 1.392(4)  |
| C(14)-C(15)                  | 1.386(3)  | C(18)-C(19)  | 1.384(4)  |
| C(15)-C(16)                  | 1.386(3)  | C(19)-C(20)  | 1.376(4)  |
| C(16)-C(17)                  | 1.386(3)  | C(21)-C(22)  | 1.376(4)  |
| C(17)-C(18)                  | 1.388(4)  | C(22)-C(23)  | 1.391(4)  |
| C(18)-C(19)                  | 1.388(4)  | C(23)-C(24)  | 1.373(5)  |
| C(19)-C(20)                  | 1.389(4)  | C(24)-C(25)  | 1.373(5)  |
| C(20)-C(21)                  | 1.373(4)  | C(25)-C(26)  | 1.377(5)  |
| C(21)-C(22)                  | 1.373(4)  | C(26)-C(27)  | 1.395(4)  |
| C(22)-C(23)                  | 1.373(4)  | C(27)-C(28)  | 1.377(5)  |
| C(23)-C(24)                  | 1.375(5)  | C(28)-C(29)  | 1.395(4)  |
| C(24)-C(25)                  | 1.375(5)  | C(29)-C(30)  | 1.376(7)  |
| C(25)-C(30)                  | 1.391(5)  | C(30)-C(31)  | 1.372(4)  |
| C(30)-C(31)                  | 1.391(5)  | C(33)-C(34)  | 1.372(4)  |
| C(31)-C(32)                  | 1.389(4)  | (34)-C(35)   | 1.387(5)  |
| C(32)-C(33)                  | 1.389(4)  | C(36)-C(37)  | 1.382(5)  |
| C(33)-C(36)                  | 1.384(5)  | C(37)-C(38)  | 1.381(5)  |
| C(34)-C(35)                  | 1.394(4)  | C(51)-C(52)  | 1.371(5)  |
| C(35)-C(51)*                 | 1.364(5)  | C(52)-C(53)  | 1.371(5)  |
| C(51)-C(53)                  | 1.372(5)  | C(61)-C(62)** | 1.388(5) |
| C(52)-C(61)**                | 1.377(5)  | C(62)-C(63)  | 1.377(5)  |

Cl(2)-Bi(1)-Cl(1)  170.725(19)  C(2)-Bi(1)-Cl(1)  88.91(7)  
C(2)-Bi(1)-Cl(2)  85.48(7)  C(2)-Bi(1)-C(15)  119.38(9)  
C(2)-Bi(1)-C(21)  127.71(9)  C(15)-Bi(1)-Cl(1)  88.26(6)  
C(15)-Bi(1)-Cl(2)  88.06(6)  C(15)-Bi(1)-C(21)  112.80(9)  

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| Bond          | Distance (Å) |
|---------------|--------------|
| C(21)-Bi(1)-Cl(1) | 96.08(7)     |
| Cl(4)-Bi(2)-Cl(3)   | 175.59(2)    |
| C(13)-Bi(2)-Cl(4)   | 89.29(7)     |
| C(27)-Bi(2)-Cl(4)   | 91.67(9)     |
| C(33)-Bi(2)-Cl(3)   | 87.62(7)     |
| C(33)-Bi(2)-C(13)   | 110.94(10)   |
| C(14)-O(1)-C(1)     | 127.87(19)   |
| O(1)-C(1)-C(6)      | 126.8(2)     |
| C(1)-C(2)-Bi(1)     | 116.30(17)   |
| C(3)-C(2)-C(1)      | 122.6(2)     |
| C(5)-C(4)-C(3)      | 119.4(2)     |
| C(1)-C(6)-C(7)      | 121.7(2)     |
| C(5)-C(6)-C(7)      | 120.5(2)     |
| C(9)-C(8)-C(7)      | 109.6(2)     |
| C(10)-C(9)-C(14)    | 117.3(2)     |
| C(11)-C(10)-C(9)    | 122.8(3)     |
| C(11)-C(12)-C(13)   | 118.9(3)     |
| C(12)-C(13)-C(14)   | 121.7(2)     |
| O(1)-C(14)-C(9)     | 125.4(2)     |
| C(13)-C(14)-C(9)    | 119.3(2)     |
| C(20)-C(15)-Bi(1)   | 116.02(17)   |
| C(15)-C(16)-C(17)   | 118.0(3)     |
| C(19)-C(18)-C(17)   | 120.4(3)     |
| C(15)-C(20)-C(19)   | 118.6(2)     |
| C(26)-C(21)-Bi(1)   | 119.80(18)   |
| C(21)-C(22)-C(23)   | 118.7(3)     |
| C(25)-C(24)-C(23)   | 119.9(3)     |
| C(21)-C(26)-C(25)   | 118.1(3)     |
| C(28)-C(27)-C(32)   | 123.0(3)     |
| C(27)-C(28)-C(29)   | 118.0(3)     |
| C(31)-C(30)-C(29)   | 120.2(3)     |
| C(27)-C(32)-C(31)   | 117.7(4)     |
| C(34)-C(33)-C(38)   | 121.3(3)     |
| C(33)-C(34)-C(35)   | 119.5(3)     |
| C(37)-C(36)-C(35)   | 120.4(3)     |
| C(33)-C(38)-C(37)   | 118.9(3)     |

| Bond          | Distance (Å) |
|---------------|--------------|
| C(21)-Bi(1)-Cl(2) | 93.19(7)     |
| C(13)-Bi(2)-Cl(3) | 91.39(7)     |
| C(27)-Bi(2)-Cl(3) | 90.69(9)     |
| C(27)-Bi(2)-C(13) | 138.46(10)   |
| C(33)-Bi(2)-Cl(4) | 88.07(7)     |
| C(33)-Bi(2)-C(27) | 110.60(11)   |
| O(1)-C(1)-C(2)   | 113.8(2)     |
| C(2)-C(1)-C(6)   | 119.4(2)     |
| C(3)-C(2)-Bi(1)  | 119.50(19)   |
| C(2)-C(3)-C(4)   | 117.8(2)     |
| C(4)-C(5)-C(6)   | 123.1(3)     |
| C(5)-C(6)-C(1)   | 117.1(3)     |
| C(6)-C(7)-C(8)   | 110.1(2)     |
| C(10)-C(9)-C(8)  | 120.7(2)     |
| C(14)-C(9)-C(8)  | 121.4(2)     |
| C(10)-C(11)-C(12)| 119.3(3)     |
| C(12)-C(13)-Bi(2)| 114.97(19)   |
| C(14)-C(13)-Bi(2)| 121.05(19)   |
| O(1)-C(14)-C(13)| 115.2(2)     |
| C(16)-C(15)-Bi(1)| 121.55(19)   |
| C(20)-C(15)-C(16)| 122.4(2)     |
| C(18)-C(17)-C(16)| 120.5(3)     |
| C(18)-C(19)-C(20)| 120.2(3)     |
| C(22)-C(21)-Bi(1)| 118.0(2)     |
| C(26)-C(21)-C(22)| 122.1(3)     |
| C(24)-C(23)-C(22)| 120.3(3)     |
| C(24)-C(25)-C(26)| 120.9(3)     |
| C(28)-C(27)-Bi(2)| 120.7(2)     |
| C(32)-C(27)-Bi(2)| 116.1(3)     |
| C(30)-C(29)-C(28)| 120.3(4)     |
| C(30)-C(31)-C(32)| 120.8(4)     |
| C(34)-C(33)-Bi(2)| 117.5(2)     |
| C(38)-C(33)-Bi(2)| 121.1(2)     |
| C(36)-C(35)-C(34)| 120.0(3)     |
| C(36)-C(37)-C(38)| 119.9(3)     |
| C(53)-C(51)-C(52)| 120.1(3)     |
| Bond                  | Angle (°)  | Bond                  | Angle (°)  |
|-----------------------|------------|-----------------------|------------|
| C(53)-C(52)-C(51)     | 119.7(3)   | C(51)^*-C(53)-C(52)   | 120.2(3)   |
| C(62)-C(61)-C(63)**   | 120.0(4)   | C(61)-C(62)-C(63)     | 120.4(3)   |
| C(62)-C(63)-C(61)**   | 119.6(4)   |                       |            |

Symmetry transformations used to generate equivalent atoms:
* -x,-y+1,-z+1  ** -x,-y+2,-z
Single crystal structure analysis of 12 (13386)

**Figure 15.** The molecular structure of complex 12. H atoms have been removed for clarity.

**X-ray Crystal Structure Analysis of complex 12:** C$_{36}$H$_{28}$Bi$_2$Cl$_4$O, $M_r = 1036.34$ g mol$^{-1}$, colourless prism, crystal size $0.046 \times 0.024 \times 0.022$ mm$^3$, monoclinic, $P2_1/n$ [14], $a = 8.4334(5)$ Å, $b = 25.9105(15)$ Å, $c = 15.5944(9)$ Å, $\beta = 91.060(2)$°, $V = 3407.0(3)$ Å$^3$, $T = 100(2)$ K, $Z = 4$, $D_{calc} = 2.020$ g·cm$^{-3}$, $\lambda = 0.71073$ Å, $\mu$($Mo-K\alpha$)= 10.658 mm$^{-1}$, Gaussian absorption correction ($T_{min} = 0.67881$, $T_{max} = 0.85075$), Bruker-AXS Mach3 diffractometer with APEX-II detector and \(\mu\)S microfocus Mo-anode X-ray source, $1.524 < \theta < 30.508$°, 151031 measured reflections, 10382 independent reflections, 9085 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0595$. The structure was solved by SHELXT and refined by full-matrix least-squares (SHELXL) against $F^2$ to $R_I = 0.0253$ [$I > 2\sigma(I)$], $wR_2 = 0.0521$, 388 parameters.
Figure 16. Crystal faces and unit cell determination of complex 12.

### INTENSITY STATISTICS FOR DATASET

| Resolution | #Data | #Theory | %Complete | Redundancy | Mean I | Mean I/s | Rmerge | Rsigma |
|------------|-------|---------|-----------|------------|--------|----------|--------|--------|
| Inf - 2.45 | 267   | 267     | 100.0     | 20.20      | 103.09 | 56.90    | 0.0462 | 0.0144 |
| 2.45 - 1.62| 616   | 616     | 100.0     | 23.06      | 72.24  | 58.09    | 0.0399 | 0.0137 |
| 1.62 - 1.11| 895   | 895     | 100.0     | 23.17      | 46.06  | 51.39    | 0.0389 | 0.0146 |
| 1.11 - 1.01| 877   | 877     | 100.0     | 17.24      | 26.65  | 32.97    | 0.0588 | 0.0210 |
| 1.01 - 0.93| 981   | 981     | 100.0     | 14.04      | 22.64  | 27.09    | 0.0690 | 0.0262 |
| 0.93 - 0.88| 830   | 830     | 100.0     | 12.06      | 17.49  | 21.36    | 0.0862 | 0.0333 |
| 0.88 - 0.83| 1012  | 1012    | 100.0     | 11.32      | 16.19  | 18.62    | 0.0963 | 0.0377 |
| 0.83 - 0.80| 755   | 755     | 100.0     | 10.72      | 13.84  | 16.33    | 0.1110 | 0.0444 |
| 0.80 - 0.77| 834   | 834     | 100.0     | 10.42      | 13.17  | 15.62    | 0.1263 | 0.0490 |
| 0.77 - 0.74| 1021  | 1021    | 100.0     | 9.80       | 10.77  | 12.97    | 0.1454 | 0.0598 |
| 0.74 - 0.72| 768   | 768     | 100.0     | 9.54       | 10.42  | 12.18    | 0.1553 | 0.0646 |
| 0.72 - 0.70| 832   | 832     | 100.0     | 9.15       | 8.45   | 8.98     | 0.1810 | 0.0805 |
| 0.70 - 0.68| 985   | 985     | 100.0     | 8.90       | 7.63   | 8.96     | 0.2039 | 0.0909 |
| 0.68 - 0.66| 1071  | 1071    | 100.0     | 8.51       | 7.31   | 8.15     | 0.2203 | 0.1012 |
| 0.66 - 0.65| 563   | 563     | 100.0     | 8.32       | 5.96   | 6.93     | 0.2573 | 0.1267 |
| 0.65 - 0.63| 1322  | 1322    | 100.0     | 7.90       | 5.42   | 6.03     | 0.2729 | 0.1441 |
| 0.63 - 0.62| 725   | 725     | 100.0     | 7.75       | 5.22   | 5.68     | 0.2990 | 0.1563 |
| 0.62 - 0.61| 750   | 750     | 100.0     | 7.42       | 4.74   | 5.04     | 0.3239 | 0.1810 |
| 0.61 - 0.60| 781   | 781     | 100.0     | 7.17       | 4.39   | 4.47     | 0.3471 | 0.2085 |
| 0.60 - 0.59| 834   | 1025    | 81.4      | 3.23       | 3.14   | 2.26     | 0.4051 | 0.4727 |
| 0.59 - 0.59| 6537  | 6728    | 97.2      | 7.23       | 5.43   | 5.83     | 0.2715 | 0.1631 |
| Inf         | 17643 | 17834   | 98.9      | 11.55      | 17.54  | 18.61    | 0.0711 | 0.0426 |

A resolution cut off (SHEL 99 0.7) was applied to suppress poorly measured intensities at higher diffraction angles. The high residual electron density (highest peak: 3.13 at 0.78 Å from Bi1 and deepest hole: -1.09 at 1.28 Å from Bi1) could possibly be caused by anharmonic displacement of the Bi atom.

Complete .cif-data of the compound are available under the CCDC number CCDC-2063979.
| Identification code | 13386 |
|---------------------|-------|
| Empirical formula   | C_{36}H_{28}Bi_{2}Cl_{4}O |
| Color               | colourless |
| Formula weight      | 1036.34 g·mol^{-1} |
| Temperature         | 100(2) K |
| Wavelength          | 0.71073 Å |
| Crystal system      | Monoclinic |
| Space group         | P 2_1/n, (No. 14) |
| Unit cell dimensions| a = 8.4334(5) Å, α= 90°. |
|                     | b = 25.9105(15) Å, β= 91.060(2)°. |
|                     | c = 15.5944(9) Å, γ = 90°. |
| Volume              | 3407.0(3) Å^3 |
| Z                   | 4 |
| Density (calculated)| 2.020 Mg·m^3 |
| Absorption coefficient | 10.658 mm^{-1} |
| F(000)              | 1944 e |
| Crystal size        | 0.046 x 0.024 x 0.022 mm^3 |
| θ range for data collection | 1.524 to 30.508°. |
| Index ranges        | -12 ≤ h ≤ 12, -37 ≤ k ≤ 37, -22 ≤ l ≤ 22 |
| Reflections collected | 151031 |
| Independent reflections | 10382 [R_{int} = 0.0595] |
| Reflections with I>2σ(I) | 9085 |
| Completeness to θ = 25.242° | 100.0 % |
| Absorption correction | Gaussian |
| Max. and min. transmission | 0.85075 and 0.67881 |
| Refinement method   | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 10382 / 0 / 388 |
| Goodness-of-fit on F^2 | 1.089 |
| Final R indices [I>2σ(I)] | R_1 = 0.0253, wR^2 = 0.0521 |
| R indices (all data) | R_1 = 0.0327, wR^2 = 0.0542 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 3.134 and -1.090 e·Å^{-3} |
Table 16. Bond lengths [Å] and angles [°].

| Bond | Length [Å] | Bond | Length [Å] |
|------|------------|------|------------|
| Bi(1)-Cl(2) | 2.5892(8) | Bi(1)-Cl(1) | 2.5862(8) |
| Bi(1)-C(13) | 2.199(3) | Bi(1)-C(1) | 2.184(3) |
| Bi(1)-C(19) | 2.204(3) | Bi(2)-Cl(4) | 2.6191(8) |
| Bi(2)-Cl(3) | 2.5677(8) | Bi(2)-C(7) | 2.189(3) |
| Bi(2)-C(31) | 2.214(3) | Bi(2)-C(25) | 2.205(3) |
| O(1)-C(2) | 1.399(4) | O(1)-C(8) | 1.396(4) |
| C(33)-H(33) | 0.9500 | C(33)-C(32) | 1.391(5) |
| C(33)-C(34) | 1.380(5) | C(7)-C(8) | 1.385(4) |
| C(7)-C(12) | 1.388(5) | C(4)-H(4) | 0.9500 |
| C(4)-C(3) | 1.386(5) | C(4)-C(5) | 1.383(5) |
| C(13)-C(18) | 1.385(4) | C(13)-C(14) | 1.380(4) |
| C(2)-C(1) | 1.377(4) | C(2)-C(3) | 1.392(4) |
| C(1)-C(6) | 1.389(4) | C(3)-H(3) | 0.9500 |
| C(19)-C(24) | 1.392(4) | C(19)-C(20) | 1.382(5) |
| C(5)-H(5) | 0.9500 | C(5)-C(6) | 1.382(5) |
| C(17)-H(17) | 0.9500 | C(17)-C(18) | 1.390(5) |
| C(17)-C(16) | 1.377(5) | C(8)-C(9) | 1.384(5) |
| C(24)-H(24) | 0.9500 | C(24)-C(23) | 1.393(5) |
| C(15)-H(15) | 0.9500 | C(15)-C(16) | 1.386(5) |
| C(15)-C(14) | 1.394(5) | C(32)-H(32) | 0.9500 |
| C(32)-C(31) | 1.380(5) | C(34)-H(34) | 0.9500 |
| C(34)-C(35) | 1.379(5) | C(31)-C(36) | 1.387(4) |
| C(18)-H(18) | 0.9500 | C(36)-H(36) | 0.9500 |
| C(36)-C(35) | 1.396(5) | C(16)-H(16) | 0.9500 |
| C(25)-C(30) | 1.375(5) | C(25)-C(26) | 1.385(5) |
| C(9)-H(9) | 0.9500 | C(9)-C(10) | 1.383(5) |
| C(14)-H(14) | 0.9500 | C(35)-H(35) | 0.9500 |
| C(23)-H(23) | 0.9500 | C(23)-C(22) | 1.384(6) |
| C(6)-H(6) | 0.9500 | C(30)-H(30) | 0.9500 |
| C(30)-C(29) | 1.404(5) | C(11)-H(11) | 0.9500 |
| C(11)-C(12) | 1.382(6) | C(11)-C(10) | 1.381(6) |
| C(12)-H(12) | 0.9500 | C(10)-H(10) | 0.9500 |
| C(28)-H(28) | 0.9500 | C(28)-C(29) | 1.366(6) |
| C(28)-C(27) | 1.375(6) | C(20)-H(20) | 0.9500 |
| Bond                  | Distance | Bond                  | Distance |
|-----------------------|----------|-----------------------|----------|
| C(20)-C(21)           | 1.392(5) | C(29)-H(29)           | 0.9500   |
| C(22)-H(22)           | 0.9500   | C(22)-C(21)           | 1.384(6) |
| C(26)-H(26)           | 0.9500   | C(26)-C(27)           | 1.390(6) |
| C(21)-H(21)           | 0.9500   | C(27)-H(27)           | 0.9500   |
| Cl(1)-Bi(1)-Cl(2)     | 175.42(3)| C(13)-Bi(1)-Cl(2)    | 88.59(8) |
| C(13)-Bi(1)-Cl(1)     | 92.04(8) | C(13)-Bi(1)-C(19)    | 120.09(12)|
| C(1)-Bi(1)-Cl(2)      | 90.01(8) | C(1)-Bi(1)-C(19)     | 86.12(8) |
| C(1)-Bi(1)-C(13)      | 130.36(11)| C(1)-Bi(1)-C(19)    | 109.56(12)|
| C(19)-Bi(1)-Cl(2)     | 91.13(9) | C(19)-Bi(1)-Cl(1)    | 92.47(9) |
| Cl(3)-Bi(2)-Cl(4)     | 176.06(3)| C(7)-Bi(2)-Cl(4)     | 83.75(9) |
| Cl(7)-Bi(2)-Cl(3)     | 93.06(9) | C(7)-Bi(2)-C(31)     | 114.23(12)|
| Cl(7)-Bi(2)-C(25)     | 128.79(12)| C(7)-Bi(2)-C(31)    | 91.96(9) |
| C(31)-Bi(2)-Cl(3)     | 91.45(8) | C(25)-Bi(2)-Cl(4)    | 90.22(9) |
| C(25)-Bi(2)-Cl(3)     | 89.99(9) | C(25)-Bi(2)-C(31)    | 116.77(12)|
| C(8)-O(1)-C(2)        | 115.0(2) | C(32)-C(33)-H(33)    | 119.9    |
| C(34)-C(33)-H(33)     | 119.9    | C(34)-C(33)-C(32)    | 120.3(3) |
| C(8)-C(7)-Bi(2)       | 120.0(2) | C(8)-C(7)-C(12)      | 120.5(3) |
| C(12)-C(7)-Bi(2)      | 119.2(2) | C(3)-C(4)-H(4)       | 119.4    |
| C(5)-C(4)-H(4)        | 119.4    | C(5)-C(4)-C(3)       | 121.1(3) |
| C(18)-C(13)-Bi(1)     | 117.5(2) | C(14)-C(13)-Bi(1)    | 119.6(2) |
| C(14)-C(13)-C(18)     | 122.9(3) | C(1)-C(2)-O(1)       | 118.7(3) |
| C(1)-C(2)-C(3)        | 120.1(3) | C(3)-C(2)-O(1)       | 121.1(3) |
| C(2)-C(1)-Bi(1)       | 121.2(2) | C(2)-C(1)-C(6)       | 121.2(3) |
| C(6)-C(1)-Bi(1)       | 117.6(2) | C(4)-C(3)-C(2)       | 118.6(3) |
| C(4)-C(3)-H(3)        | 120.7    | C(2)-C(3)-H(3)       | 120.7    |
| C(24)-C(19)-Bi(1)     | 119.3(2) | C(20)-C(19)-Bi(1)    | 118.5(2) |
| C(20)-C(19)-C(24)     | 122.2(3) | C(4)-C(5)-H(5)       | 119.9    |
| C(6)-C(5)-C(4)        | 120.2(3) | C(6)-C(5)-H(5)       | 119.9    |
| C(18)-C(17)-H(17)     | 119.8    | C(16)-C(17)-H(17)    | 119.8    |
| C(16)-C(17)-C(18)     | 120.4(3) | C(7)-C(8)-O(1)       | 118.7(3) |
| C(9)-C(8)-O(1)        | 121.2(3) | C(9)-C(8)-C(7)       | 120.1(3) |
| C(19)-C(24)-H(24)     | 121.0    | C(19)-C(24)-C(23)    | 118.0(3) |
| C(23)-C(24)-H(24)     | 121.0    | C(16)-C(15)-H(15)    | 119.7    |
| C(16)-C(15)-C(14)     | 120.6(3) | C(14)-C(15)-H(15)    | 119.7    |
| C(33)-C(32)-H(32)     | 120.4    | C(31)-C(32)-C(33)    | 119.1(3) |
