The Tethered Aminohydroxylation (TA) of Cyclic Allylic Carbamates

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Supplementary Material

The stereochemistry of **7**, **9**, **17** and **D** was proven by X-ray crystallography on solid derivatives (details of **D** are given below, the others will be reported in a full account of this work); the nature of **11** and **15** was proven by nOe experiments and *J* values, which were all in accordance with the structures shown. The stereochemistry of **13** was assigned by analogy to **15** and that of **20** proven by hydrolysis (Ba(OH)₂) to an amino-diol which was clearly not a symmetrical compound, thus ruling out the all *syn* isomer. Hydrolysis of **17** and **18** gave a 3:1 mixture of amino diols in which the major compound was symmetrical and the minor compound unsymmetrical.

Experimental Procedures

General Carbamate Formation Procedure

Trichloroacetyl isocyanate (1.2 eq.) was added dropwise to a solution of the alcohol (1 eq.) in dry DCM (1.5 cm³/mmol) at 0 °C. After stirring for 2 h, or until TLC showed no starting material present, the mixture was concentrated under reduced pressure and the residue dissolved in MeOH (2 cm³/mmol). This solution was cooled to 0 °C and an aqueous K₂CO₃ solution (3 eq., 0.5 cm³/mmol) was added. The cooling bath was removed and the mixture allowed to stir for 4h, by which time TLC showed complete conversion. The MeOH was evaporated under reduced pressure and the aqueous residue was extracted with DCM. The combined organics were dried (MgSO₄), filtered and concentrated under reduced pressure to yield the crude carbamate, which was purified by column chromatography or recrystallisation if necessary.

General Aminohydroxylation Procedure

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A fresh, aqueous solution of NaOH (0.08 mol dm^{-3} , 0.9 eq.) was prepared. All but a few drops of this was added in one portion to a magnetically stirred solution of the allylic carbamate (1 eq.) in $^n\text{PrOH}$ ($12 \text{ cm}^3/\text{mmol}$). The solution was allowed to stir for 5 minutes, then *tert*-butyl hypochlorite (1 eq.) was added. The mixture was again allowed to stir for 5 minutes. To this was then added the ligand (either EtN^iPr_2 or $(\text{DHQ})_2\text{PHAL}$) (5 mol %) in one portion. The mixture was allowed to stir for a further 5 minutes before the final addition of a solution of potassium osmate (4 mol%) in the remainder of the NaOH solution made previously. The reaction was followed by TLC until the solution turned black, which denoted the end of turnover. The reaction was quenched by the addition of Na_2SO_3 (500 mg), and allowed to stir for 30 minutes. The mixture was extracted with EtOAc, and the organic layer washed with brine. The organic layer was then collected and concentrated under reduced pressure. The crude product was purified by column chromatography.

General Aza-glycolate Osmate Ester Preparation Procedure

A fresh, aqueous solution of NaOH (0.9 eq.) was prepared using minimal water to dissolve the solid. This was added in one portion to a magnetically stirred solution of the allylic carbamate (1 eq.) in $^n\text{PrOH}$ ($12 \text{ cm}^3/\text{mmol}$). The solution was allowed to stir for 5 minutes, then *tert*-butyl hypochlorite (1 eq.) was added. The mixture was again allowed to stir for 5 minutes. A solution of potassium osmate (4 mol%) in a small amount of the NaOH solution was added and the mixture allowed to stir for a further 5 minutes before the final addition of TMEDA (1 eq.). The reaction mixture was allowed to stir overnight, then the solvents were removed under reduced pressure. The crude product was purified by column chromatography.

Cyclopent-2-enyl carbamate **5**

Cyclopenten-2-ol (643 mg, 7.7 mmol) was subjected to the general carbamate formation procedure, affording the *carbamate 5* as an off-white solid (760 mg, 78%). Recrystallisation from light petrol – CHCl₃ gave the carbamate as white needles (406 mg, 42%).

R_f (EtOAc) 0.56; m.p. 93-95 °C; **IR** $\nu_{\max}$ (film) 3420, 3327 (NH₂), 1683 (C=O) and 1613 (NH₂); **¹H NMR** δ_H (400 MHz; CDCl₃) 6.10 (1 H, m, CH₂CH=CH), 5.84 (1 H, dq, J 6.0 and 2.0, CHORCH), 5.65 (1 H, m, CHOR), 4.74 (2 H, br s, NH₂), 2.53 (1 H), 2.30 (2 H) and 1.84 (1 H) (all m, CH₂CH₂); **¹³C NMR** δ_C (CDCl₃) 157.2 (C=O), 137.5, 129.5 (CH=CH), 81.0 (CHOR), 31.0 (allylic CH₂) and 29.9 (CH₂CHOR); **MS** m/z (CI) 145 (MNH₄⁺) and 84 (100%, MH⁺ – CONH₂); **HRMS (CI)** Found MNH₄⁺, 145.0979. C₆H₁₃N₂O₂⁺ requires M 145.0977.

2-Methylene cyclopentyl carbamate **6**

2-Methylene cyclopentanol (553 mg, 5.6 mmol) was subjected to the general carbamate formation procedure, affording the *carbamate 6* as a white solid (669 mg, 85%). Recrystallisation from light petrol – CHCl₃ gave the carbamate as white flakes (327 mg, 41%).

R_f (EtOAc) 0.63; m.p. 68 °C (dec.); **IR** $\nu_{\max}$ (film) 3410, 3327 (NH₂) and 1682 (C=O); **¹H NMR** δ_H (400 MHz; CDCl₃) 5.34 (1 H, m, CHOR), 5.19 (1 H, t, J 1.0, C=CH_AH_B), 5.09 (1 H, dd, J 1.0 and 0.5, C=CH_AH_B), 4.89 (2 H, br s, NH₂), 2.44 (1 H, m, allylic CH_AH_B), 2.29 (1 H, m, allylic CH_AH_B), 2.02 (1 H, m, CH_AH_BCHOR), 1.85-1.62 (3 H, m, CH₂CH_AH_BCHOR); **¹³C NMR** δ_C (CDCl₃) 157.0 (C=O), 150.3 (R₂C=CH₂), 110.1 (R₂C=CH₂), 77.2 (CHOR), 33.0 (CH₂CHOR), 30.6 and 22.4 (CH₂CH₂); **MS** m/z (CI) 159 (100%, MNH₄⁺), 142 (MH⁺) and 81 (MH⁺ – OCONH₂); **HRMS (CI)** Found MNH₄⁺, 159.1138. C₇H₁₅N₂O₂⁺ requires M 159.1134.

(3aSR, 7aSR)-3a-Hydroxymethyl-hexahydro-cyclopentaoxazol-2-one **7**

2-Methylene cyclopentyl carbamate **6** (185 mg, 1.31 mmol) was subjected to the general cyclising aminohydroxylation procedure, using EtNⁱPr₂ as the ligand. Purification of the crude compound by column chromatography (EtOAc) afforded the *oxazolone 7* as a white crystalline solid (104 mg, 51%).

R_f (EtOAc) 0.10; m.p. 133-135 °C; **IR** $\nu_{\max}$ (film) 3223 (br, OH and NH) and 1716 (C=O); **$^1\text{H NMR}$** δ_{H} (400 MHz; D_2O) 4.75 (1 H, m, CHOR), 3.60 (1 H, d, J 12.0, $\text{CH}_\text{A}\text{H}_\text{B}\text{OH}$), 3.43 (1 H, d, J 12.0, $\text{CH}_\text{A}\text{H}_\text{B}\text{OH}$), 1.87 (1 H), 1.66 (4 H) and 1.40 (1 H) (all m, $\text{CH}_2\text{CH}_2\text{CH}_2$); **$^{13}\text{C NMR}$** δ_{C} (D_2O) 161.9 (C=O), 85.6 (CHOR), 70.7 (CNR), 64.6 (CHOH), 35.2, 33.6 (CH_2CHOR and $\text{CH}_2\text{CRNR}'$) and 22.6 ($\text{CH}_2\text{CH}_2\text{CH}_2$); **MS** m/z (CI) 175 (MNH_4^+) and 158 (100%, MH^+); **HRMS (CI)** Found MH^+ , 158.0821. $\text{C}_7\text{H}_{12}\text{NO}_3$ requires M 158.0817.

Cyclohex-2-enyl carbamate **8**

Crude cyclohexen-2-ol (2.2 g, 22.3 mmol) was subjected to the general carbamate formation procedure, affording the *carbamate 8* as a white solid (2.18 g, 74%).

R_f (EtOAc) 0.70; m.p. 106-108 °C; **IR** $\nu_{\max}$ (film) 3424, 3387 (NH_2) and 1678 (C=O); **$^1\text{H NMR}$** δ_{H} (300 MHz; CDCl_3) 5.98 (1 H, dtd, J 10.0, 3.5 and 1.0, $\text{H}_2\text{CCH}=\text{CH}$), 5.76 (1 H, dtd, J 10.0, 4.0 and 2.0, CHCHOR), 5.19 (1 H, dtd, J 6.0, 3.5 and 1.5, CHOR), 4.78 (2 H, br s, NH_2) and 2.17-1.59 (6 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$); **$^{13}\text{C NMR}$** δ_{C} (CDCl_3) 156.9 (C=O), 132.4 ($\text{C}_\text{A}=\text{C}_\text{B}$), 125.8 ($\text{C}_\text{A}=\text{C}_\text{B}$), 68.6 (CHOR), 28.4 (CH_2CHOR), 24.8 and 18.7 (CH_2CH_2); **MS** m/z (CI) 142 (MH^+) and 98 (100%, $\text{MH}^+ - \text{CONH}_2$); **HRMS (CI)**; **Elemental analysis** Found: C, 59.3; H, 7.78; N, 9.6. $\text{C}_7\text{H}_{11}\text{NO}_2$ requires C, 59.6; H, 7.85; N, 9.9.

(3*SR*, 4*SR*, 8*RS*)-4-Hydroxy-hexahydro-benzooxazol-2-one **9**

Cyclohex-2-enyl carbamate **8** (200 mg, 1.41 mmol) was subjected to the general cyclising aminohydroxylation procedure, using $(\text{DHQ})_2\text{PHAL}$ as the ligand.

Purification of the crude compound by column chromatography (EtOAc) afforded the *oxazolone 9* as a white crystalline solid (136 mg, 61%).

R_f (EtOAc) 0.17; m.p. 81-83 °C; **IR** $\nu_{\max}$ (film) 3399 (br, OH, NH) and 1746 (C=O); **$^1\text{H NMR}$** δ_{H} (400 MHz; CDCl_3) 6.36 (1 H, s, NH), 4.70 (1 H, dt, J 7.0 and 5.0, CHOR), 3.95 (1 H, dd, J 7.0 and 4.5, CHNH), 3.75 (1 H, d, J 4.5, OH), 3.86 (1 H, dq, J 8.5 and 4.5, CHOH), 1.77 (3 H, m), 1.66 (2 H, m), 1.33 (1 H, m) ($\text{CH}_2\text{CH}_2\text{CH}_2$); **$^{13}\text{C NMR}$** δ_{C} (CDCl_3) 161.3 (C=O), 76.3, 66.9 (CHOR and CHNR), 55.8 (CHOH), 26.5, 25.7 (CHCHOR and CHCHNR) and 15.6 ($\text{CH}_2\text{CH}_2\text{CH}_2$); **MS** m/z (CI) 175 (MNH_4^+) and 158 (100%, MH^+); **HRMS (CI)** Found MH^+ , 158.0822. $\text{C}_7\text{H}_{12}\text{NO}_3$ requires M 158.0817.

(1*R*, 5*R*)-5-Isopropyl-2-methyl-cyclohex-2-enyl carbamate 10

Carvotanacetol (500 mg, 3.2 mmol) was subjected to the general carbamate formation procedure, affording the *carbamate* **10** as a white solid (624 mg, 99%).

R_f (EtOAc) 0.66; m.p. 86-88 °C; $[\alpha]_D +31.2$ (c 0.8 in CH₂Cl₂); **IR** $\nu_{\max}$ (film) 3435, 3332 (NH₂), 1687 (C=O) and 1611 (NH₂); **¹H NMR** δ_H (400 MHz; CDCl₃) 5.56 (1 H, m, C=CH), 5.29 (1 H, m, CHOR), 4.79 (2 H, br s, NH₂), 2.15 (1 H, ddt, J 12.0, 6.0 and 2.0, C⁶H_AH_B), 1.98 (1 H, m, C⁴H_AH_B), 1.76 (1 H, m, C⁴H_AH_B), 1.66 (3 H, t, J 1.0, C=CMe), 1.49 (2 H, m, CHMe₂ and CH^{*i*}Pr), 1.26 (1 H, dt, J 12.0 and 10.0, C⁶H_AH_B) and 0.88 (6 H, dd, J 6.5 and 5.0 CHMe₂); **¹³C NMR** δ_C (CDCl₃) 157.2 (C=O), 133.2 (C_A=C_B), 126.0 (C_A=C_B), 74.3 (CHOR), 39.2, 33.0, 32.0, 28.7, 19.6, 19.3 and 18.6; **MS** m/z (EI) 197 (100%, M⁺); **HRMS (EI)** Found M⁺, 197.1417. C₁₁H₁₉NO₂ requires M 197.1416.

(3*aS*, 4*S*, 6*R* 8*aR*)-4-Hydroxy-6-isopropyl-3*a*-methyl-hexahydro-benzooxazol-2-one 11

Carbamate **10** (200 mg, 1.02 mmol) was subjected to the general cyclising aminohydroxylation procedure, using (DHQ)₂PHAL as the ligand. Purification of the crude compound by column chromatography (60:40, EtOAc – light petrol) afforded the *oxazolone* **11** as a yellow oil (119 mg, 55%).

R_f (EtOAc) 0.33; $[\alpha]_D -30.3$ (c 0.8 in CH₂Cl₂); **IR** $\nu_{\max}$ (film) 3324 (br, OH, NH) and 1737 (C=O); **¹H NMR** δ_H (400 MHz; CDCl₃) 5.68 (1 H, br s, NH), 4.28 (1 H, ddd, J 9.0, 6.5 and 1.0, CHOR), 3.58 (1 H, dd, J 12.5 and 5.0, CHOH), 2.74 (1 H, br s, OH), 2.02 (1 H, m, C⁷H_AH_B), 1.81 (1 H, m, C⁵H_AH_B), 1.54 (1 H, heptet, J 7.0, CHMe₂), 1.43 (3 H, s, CNRMe), 1.35 (2 H, m, C⁵H_AH_B and C⁷H_AH_B), 1.18 (1 H, m, CH^{*i*}Pr), 0.89 (6 H, dd, J 7.0 and 3.0, CMe₂); **¹³C NMR** δ_C (CDCl₃) 159.5 (C=O), 82.5, 73.2 (CHOR and CMeNR), 60.8 (CHOH), 36.2, 32.5, 32.1, 31.2, 25.0, 19.5 and 19.4 (CMe₂); **MS** m/z (CI) 214 (100%, MH⁺) and 170 (M⁺ - ^{*i*}Pr); **HRMS (CI)** Found MH⁺, 214.1444. C₁₁H₂₀NO₃ requires M 214.1443.

(2*R*, 3*S*)-6-(*tert*-Butyldimethylsilanyloxy)methyl-3,6-dihydro-2*H*-pyran-3-ol carbamate 12

(2*R*, 3*S*)-6-(*tert*-Butyldimethylsilanyloxy)methyl-3,6-dihydro-2*H*-pyran-3-ol (800 mg, 3.2 mmol) was subjected to the general carbamate formation procedure, affording the *carbamate* **12** as a pale yellow solid (870 mg, 95%).

R_f (EtOAc) 0.68; m.p. 100-102 °C; $[\alpha]_D^{25} +76.0$ (c 0.7 in CH₂Cl₂); **IR** $\nu_{\max}$ (film) 3455, 3353 (NH₂) and 1716 (C=O); **¹H NMR** δ_H (400 MHz; CDCl₃) 5.93 (1 H, ddd, J 10.5, 4.0 and 2.5, C=CHCH₂), 5.82 (1 H, ddd, J 10.5, 4.5 and 2.0, CHOC(=O)NH₂), 5.11 (1 H, m, CHOR), 4.80 (2 H, br s, NH₂), 4.19 (2 H, m, allylic CH₂OR), 3.81 (1 H, dd, J 11.5 and 3.0, CH_AH_BOSi), 3.74 (1 H, dd, J 11.5 and 6.0, CH_AH_BOSi), 3.56 (1 H, ddd, J 7.5, 6.0 and 3.0, CHCH₂OSi), 0.90 (9 H, s, ^{*t*}Bu) and 0.08 (6 H, s, SiMe₂); **¹³C NMR** δ_C (CDCl₃) 156.1 (C=O), 129.6 (C_A=C_B), 124.6 (C_A=C_B), 77.0 (CHOCO), 66.1 (CHOR), 64.8 (CH₂OR), 63.3 (CH₂OSi), 25.9 (CMe₃), 18.4 (CMe₃), -5.3 and -5.4 (SiMe₂); **MS** m/z (electrospray) 310 (100%, MNa⁺) and 288 (MH⁺); **HRMS** (electrospray) Found MH⁺, 288.1640. C₁₃H₂₆NO₄Si requires M 288.1631.

(3*aS*, 4*R*, 7*S*, 8*aS*)-4-(*tert*-Butyl-dimethyl-silanyloxymethyl)-7-hydroxy-hexahydro-pyran-[4,3-*d*]-oxazol-2-one **13**

Carbamate **12** (150 mg, 0.52 mmol) was subjected to the general cyclising aminohydroxylation procedure, using (DHQ)₂PHAL as the ligand. Purification of the crude compound by column chromatography (60:40, EtOAc – light petrol) afforded the *oxazolone* **13** as a white crystalline solid (78 mg, 50%).

R_f (EtOAc) 0.38; m.p. 153 °C; $[\alpha]_D^{25} +35.2$ (c 0.8 in CH₂Cl₂); **IR** $\nu_{\max}$ (film) 3297 (br, OH, NH), 1753 (C=O) and 1723; **¹H NMR** δ_H (400 MHz; CDCl₃) 6.22 (1 H, br s, NH), 4.62 (1 H, dd, J 7.5 and 7.0, CHOCO), 4.29 (1 H, dd, J 7.0 and 4.0, CHNR), 3.97 (1 H, m, CHOH), 3.93 (1 H, dd, J 11.0 and 1.0, CH_AH_BOR), 3.88 (1 H, dd, J 11.5 and 2.5, CH_AH_BOSi), 3.76 (1 H, dd, J 11.5 and 4.0, CH_AH_BOR), 3.57 (1 H, dd, J 11.0 and 9.0, CH_AH_BOR), 3.52 (1 H, ddd, J 8.0, 4.5 and 2.5, CHCH₂OSi), 3.43 (1 H, br s, OH), 0.90 (9 H, s, ^{*t*}Bu) and 0.08 (3 H, s, SiMe₂), 0.08 (3 H, s, SiMe₃); **¹³C NMR** δ_C (CDCl₃) 160.4 (C=O), 76.6, 72.2 (CHOR and CNR), 66.4, 64.6, 63.3 (C³, C⁴ and C⁶), 54.8 (COSi), 26.0 (CMe₃), 18.5 (CMe₃) and -5.3 (2 peaks, SiMe₂); **MS** m/z (electrospray) 326 (100%, MNa⁺), 321 (MNH₄⁺) and 304 (MH⁺); **HRMS** (electrospray) Found MH⁺, 304.1571. C₁₃H₂₆NO₅Si requires M 304.1580.

(2*R*, 3*S*, 6*S*)-6-(*tert*-Butyldimethylsilanyloxy)methyl-6-benzyloxy-3,6-dihydro-2*H*-pyran-3-ol carbamate **14**

(2*R*, 3*S*, 6*S*)-2-(*tert*-Butyldimethylsilanyloxy)methyl-6-benzyloxy-3,6-dihydro-2*H*-pyran-3-ol (1.10 g, 3.14 mmol) was subjected to the general carbamate formation procedure, affording the inseparable mixture of anomeric carbamates (5:1) **14** as an oil (1.25 g, 100%).

R_f (Et₂O) 0.42; $[\alpha]_D^{25} +66.4$ (c 0.8 in CH₂Cl₂); **IR** ν_{max} (film) 3464, 3355 (NH₂), 2929, 2857 (CH) and 1716 (C=O); **¹H NMR** δ_H (400 MHz; CDCl₃) 7.39-7.29 (5 H, m, ArH), 6.07 (0.17 H, ddd, J 10.5, 4.0 and 2.0, *minor* C⁵H), 5.97 (0.83 H, ddd, J 10.0, 2.0 and 1.0, *major* C⁵H), 5.94 (0.17 H, ddd, J 10.0, 2.0 and 1.0, *minor* C⁴H), 5.84 (0.83 H, ddd, J 10.0, 3.0 and 2.0, *major* C⁴H), 5.17 (1 H, m, *major/minor* CHOBn), 5.12 (1 H, m, *major/minor* CHOCO), 4.87 (0.17 H, d, J 11.5, *minor* CH_AH_BPh), 4.85 (0.83 H, d, J 11.5, *major* CH_AH_BPh), 4.71 (2 H, br s, NH₂), 4.62 (0.17 H, d, J 12.0, *minor* CH_AH_BPh), 4.59 (0.83 H, d, J 11.5, *major* CH_AH_BPh), 4.00 (0.83 H, m, *major* CHCH₂OSi), 3.93 (0.17 H, m, *minor* CHCH₂OSi), 3.84-3.72 (2 H, m, CH₂OSi), 0.92 (9 H, s, CMe₃), 0.10 (3 H) and 0.10 (3 H) (SiMe₂); **¹³C NMR** δ_C (CDCl₃) 157.2, 156.4 (2 × C=O), 137.8, 136.3 (2 × 4° aryl), 130.0 (2 peaks), 128.6, 128.4 (2 peaks), 128.2 (2 peaks), 128.1 (2 peaks), 127.9, 127.8 (2 peaks), 127.6, 126.7 (all sp²), 93.8, 93.3 (2 × CHOCO), 76.2, 70.0 (COBn), 69.9, 69.4 (CH₂Ph), 66.2, 64.9 (CHCH₂OSi), 63.1, 62.9 (CH₂OSi), 26.0, 25.9 (CMe₃), 18.5, 18.3 (CMe₃), -5.2, -5.3 (3 peaks) (SiMe₂); **MS** m/z (electrospray) 416 (MNa⁺) and 411 (100%, MNH₄⁺); **HRMS** (electrospray) Found MNa⁺, 416.1870. C₂₀H₃₁NO₅NaSi requires M 416.1869.

(3*aS*, 4*R*, 6*S*, 7*S*, 8*aS*)-4-(*tert*-Butyl-dimethyl-silanyloxymethyl)-6-benzyloxy-7-hydroxy-hexahydro-pyran-[4,3-*d*]-oxazol-2-one **15**

Carbamate **14** (793 mg, 2.02 mmol) was subjected to the general cyclising aminohydroxylation procedure, using (DHQ)₂PHAL as the ligand. Purification of the crude compound by column chromatography (1:1, EtOAc – light petrol) afforded the oxazolone **15** as a white crystalline solid (541 mg, 65%).

R_f (Et₂O) 0.06; m.p. 131-133 °C; $[\alpha]_D^{25} +87.2$ (c 0.8 in CH₂Cl₂); **IR** ν_{max} (film) 3385 (br, OH, NH) and 1717 (br, C=O); **¹H NMR** δ_H (400 MHz; CDCl₃) 7.36-7.28 (5 H, m, ArH), 6.28 (1 H, br s, NH), 4.87 (1 H, d, J 4.0, CHOBn), 4.82 (1 H, d, J 12.0, CH_AH_BPh), 4.63 (1 H, m, CHOCO), 5.58 (1 H, d, J 11.5, CH_AH_BPh), 4.06 (1 H, ddd,

J 8.5, 4.5 and 2.0, *CHCH*₂OSi), 4.00 (1 H, dd, *J* 8.0 and 4.5, *CHNH*), 3.89 (1 H, q, *J* 4.0, *CHOH*), 3.81 (1 H, dd, *J* 12.0 and 2.5, *CH*_A*H*_BOSi), 3.74 (1 H, dd, *J* 11.5 and 5.0, *CH*_A*H*_BOSi), 3.30 (1 H, d, *J* 4.0, OH), 0.91 (9 H, s, *CMe*₃), 0.09 (3 H, s) and 0.08 (3 H, s) (*SiMe*₂); **¹³C NMR** δ_{C} (CDCl₃) 159.8 (C=O), 136.8, 128.5, 128.1, 128.0 (4 $\times$ aryl C), 94.9 (COBn), 71.4, 69.5 (CH₂Ph), 69.2, 65.7, 63.0 (CH₂OSi), 52.8, 25.9 (*CMe*₃), 184 (*CMe*₃) –5.30 and –5.33 (*SiMe*₂); **MS** *m/z* (electrospray) 432 (MNa⁺), 427 (MNH₄⁺) and 410 (100%, MH⁺); **HRMS (electrospray)** Found MH⁺, 410.1996. C₂₀H₃₂NO₆Si requires *M* 410.1999.

Cyclohept-2-enyl carbamate **16**

Crude cyclohepten-2-ol (1.02 g, 9.1 mmol) was subjected to the general carbamate formation procedure, affording the *carbamate* **16** as a white solid (1.15 g, 81%). *R*_f (EtOAc) 0.67; m.p. 84–85 °C; **IR** ν_{max} (film) 3440, 3321 (NH₂), 1684 (C=O) and 1609 (NH₂); **¹H NMR** δ_{H} (400 MHz; CDCl₃) 5.81 (1 H, m, CH₂CH=CH), 5.67 (1 H, dddd, *J* 11.5, 3.0, 2.0 and 1.0, CH=CHOR), 5.29 (1 H, m, CHOR), 4.85 (2 H, br s, NH₂), 2.19 (1 H), 2.08 (1 H), 1.91 (2 H), 1.68 (3 H) and 1.38 (1 H) (all m, CH₂CH₂CH₂CH₂); **¹³C NMR** δ_{C} (CDCl₃) 156.9 (C=O), 134.0 (C_A=C_B), 131.2 (C_A=C_B), 75.1 (CHOR), 33.1 (CH₂CHOR), 28.5, 26.6 and 26.5 (CH₂CH₂CH₂); **MS** *m/z* (CI) 173 (MNH₄⁺) and 112 (100%, MH⁺ – CONH₂); **HRMS (CI)** Found MNH₄⁺, 173.1294. C₈H₁₇N₂O₂ requires *M* 173.1290.

(**3RS**, **4RS**, **9SR**)-4-Hydroxy-octahydro-cycloheptaoxazol-2-one **17**

(**3RS**, **4RS**, **9RS**)-4-Hydroxy-octahydro-cycloheptaoxazol-2-one **18**

Cyclohept-2-enyl carbamate **16** (1.24 g, 8.0 mmol) was subjected to the general cyclising aminohydroxylation procedure, using EtNⁱPr₂ as the ligand. Purification of the crude compound by column chromatography (EtOAc) afforded the inseparable *oxazolidinones* **17** and **18** as a white solid (946 mg, 69%, 3:1).

*R*_f (EtOAc) 0.20; **IR** ν_{max} (film) 3326 (br, OH and NH), 2933, 2863 (CH) and 1738 (C=O); **¹H NMR** δ_{H} (400 MHz; CDCl₃); 6.66 (0.75 H, br s, *syn* NH), 6.54 (0.25 H, br s, *anti* NH), 4.86 (0.75 H, ddd, *J* 10.0, 7.5 and 3.0, *syn* CHOCO), 4.80 (0.25 H, m, *anti* CHOCO), 4.13 (0.25 H, td, *J* 5.5 and 3.0, *anti* CHNH), 4.08 (0.75 H, dd, *J* 6.5 and 3.0, *syn* CHNH), 3.86 (0.75 H, d, *J* 10.0, *anti* CHOH), 3.76 (0.25 H, ddd, *J* 10.5, 3.0 and 1.0, *anti* CHOH), 3.68 (0.75 H, br s, *syn* OH), 3.59 (0.25 H, br s, *anti* OH),

2.22 (1 H, m, CH_AH_BCHOCO), 1.88 (1 H, m, CH_AH_BCHOH), 1.82-1.56 (4 H, m) and 1.43 (2 H, m) (remaining methylene H); **^{13}C NMR** $\delta_C(CDCl_3)$ 160.8, 160.1(C=O), 77.7, 76.3, 71.9, 64.8, 63.0, 60.2 (CHOH, CHNH and CHOCO), 34.8, 32.3, 30.5, 29.9, 25.4, 24.3, 22.2 and 20.3 ($CH_2CH_2CH_2CH_2$); **MS** m/z (CI) 189 (MNH_4^+) and 172 (100%, MH^+); **HRMS (CI)** Found MH^+ , 172.0975. $C_8H_{14}NO_3$ requires M 172.0974.

Cyclooct-2-enyl carbamate **19**

Crude cyclooct-2-enol (250 mg, 1.98 mmol) was subjected to the general carbamate formation procedure, affording the *carbamate* **18** as a white solid (316 mg, 94%). R_f (EtOAc) 0.51; m.p. 49-51 °C; **IR** ν_{max} (film) 3477, 3351 (NH_2), 2928, 2857 (CH), 1709 (C=O) and 1601 (NH_2); **1H NMR** δ_H (400 MHz; $CDCl_3$) 5.64 (1 H, m, $CH_2CH=CH$), 5.51 (2 H, m, $CH=CHCHOR$), 4.85 (2 H, br s, NH_2), 2.26 (1 H, tddd, J 13.0, 9.0, 4.0 and 1.0, $CH_AH_BCH=CH$), 2.10 (1 H, m, $CH_AH_BCH=CH$), 1.94 (1 H, m), 1.67 (1 H, m) and 1.61-1.34 (6 H, m) ($CH_2CH_2CH_2$); **^{13}C NMR** $\delta_C(CDCl_3)$ 156.7 (C=O), 130.9 ($C_A=C_B$), 129.4 ($C_A=C_B$), 73.1 (CHOR), 35.3 (CH_2CHOR), 28.7, 26.3, 25.7 and 23.2 ($CH_2CH_2CH_2CH_2$); **MS** m/z (CI) 187 (MNH_4^+) and 126 (100%, $MH^+ - CONH_2$); **HRMS (CI)** Found MNH_4^+ , 187.1452. $C_9H_{19}N_2O_2$ requires M 187.1447.

(3*RS*, 4*RS*, 9*SR*)-4-Hydroxy-octahydro-cycloheptaoxazol-2-one **20**

Cyclooct-2-enyl carbamate **18** (249 mg, 1.47 mmol) was subjected to the general cyclising aminohydroxylation procedure, using (DHQ)₂PHAL as the ligand. Purification of the crude compound by column chromatography (EtOAc) afforded the *oxazolidinone* **19** as a white crystalline solid (157 mg, 58%). R_f (EtOAc) 0.16; m.p. 136-137 °C; **IR** ν_{max} (film) 3312 (br, OH and NH), 2932, 2864 (CH) and 1745 (C=O); **1H NMR** δ_H (400 MHz; $CDCl_3$) 6.91 (1 H, br s, NH), 4.95 (1 H, ddd, J 11.0, 8.5 and 4.5, $CHOCO$), 4.06 (1 H, d, J 3.0, OH), 3.95 (1 H, dd, J 7.0 and 2.5, $CHOH$), 3.85 (1 H, dd, J 8.5 and 1.0, $CHNH$), 2.17 (1 H, m), 1.88 (1 H, m), 1.72 (3 H, m), 1.59 (4 H, m) and 1.36 (1 H, m) (methylene CH_2); **^{13}C NMR** $\delta_C(CDCl_3)$ 160.3, (C=O), 76.5, 67.3, 61.5, (CHOH, CHNH and CHOCO), 33.8, 29.4, 26.5, 21.5 and 19.4 ($CH_2CH_2CH_2CH_2CH_2$); **MS** m/z (CI) 203 (MNH_4^+) and 186 (100%, MH^+); **HRMS (CI)** Found MH^+ , 186.1130. $C_9H_{16}NO_3$ requires M 186.1130.

Osmate Ester D

Cyclohex-2-enyl carbamate **8** (114 mg, 0.81 mmol) was subjected to the general azaglycolate osmate ester formation procedure. Purification of the crude compound by column chromatography (9:1, CH₂Cl₂:MeOH) afforded the *osmate ester* **20** as an orange crystalline solid (186 mg, 47%).

R_f (9:1, CH₂Cl₂:MeOH) 0.33; m.p. 176 °C (dec.); **IR** $\nu_{\max}$ (film) 2935, 2864 (CH) and 1711 (C=O); **¹H NMR** δ_H (400 MHz; CDCl₃) 4.92 (1 H, dt, J 9.0 and 7.5, CHOOs), 4.28 (1 H, dd, J 7.0 and 7.0, CHNR), 4.04 (1 H, dt, J 11.0 and 6.0, CHOCO), 3.27 (2 H, m, TMEDA $CH_AH_BCH_A\cdot H_B\cdot$), 3.22 (3 H, s, Me), 3.02 (3 H, s, Me), 2.94 (3 H, s, Me), 2.89 (2 H, m, TMEDA $CH_AH_BCH_A\cdot H_B\cdot$), 2.79 (3 H, s, Me), 2.08 (1 H, m), 1.72 (2 H, m), 1.42 (2 H, m), 1.20 (1 H, m) (ring CH₂); **¹³C NMR** δ_C (CDCl₃) 164.3 (C=O), 83.0 (CHOCO), 75.4 (CHNR), 70.3 (CHOOs), 64.7, 63.3 (TMEDA CH₂CH₂), 53.2, 52.2, 49.6, 49.5 (2 $\times$ NMe₂), 29.4, 27.1 and 18.6 (CH₂CH₂CH₂); **MS** m/z (electrospray) 1009 (M₂NH₄⁺), 987, 863, 518 (MNa⁺), 496 (100%, MH⁺) and 340; **HRMS (electrospray)** Found MH⁺, 496.1484. C₁₃H₂₆N₃O₅¹⁹²Os requires M 496.1487.

NMR Spectra for Cyclised Compounds

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Single-crystal X-ray diffraction report for $C_{13}H_{25}N_3O_5Os \cdot 0.5H_2O$
(ARC339) Intermediate D

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Views of the two molecules of Os complex, each viewed along a similar axis with respect to the OsN_3O_3 unit. H atoms and solvent have been omitted.

Crystals of **ARC339** were grown by *. A single crystal having dimensions approximately 0.06 x 0.06 x 0.10 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150K in a stream of

cold N₂ using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package¹.

Examination of the systematic absences of the intensity data showed the space group to be $P 2_1/c$. The structure was solved using the direct-methods program SIR92², which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite³. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. The hydrogen atoms of the solvent were located in a difference Fourier map and their coordinates subsequently refined. Other hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give $R = 0.0318$, $wR = 0.0360$.

Attached is a thermal ellipsoid plot (ORTEP-3⁴) at 40% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

Comments:

The asymmetric unit contains two crystallographically-distinct Os complexes and a single molecule of water. The two complexes are structurally similar, but differ in the conformation of the TMEDA ligand. This difference is essentially the result of a reflection of the entire ligand in the NOsN plane.

The water molecule forms hydrogen bonds to O atoms of two neighbouring complexes (O(11)···O(7)' 2.906(10), O(11)···O(9) 2.889(12) Å). These link molecules of one type of complex (Os(2) *etc.*) to form infinite helical chains running parallel to the *b* axis, adjacent members of which are related by a crystallographic screw axis. The molecules of the second type of complex are stacked in a similar way but do not participate in hydrogen bonding.

References:

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- 2 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.* 1994, **27**, 435.
- 3 D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, CRYSTALS issue 11, Chemical Crystallography Laboratory, Oxford, UK, 2001.
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Table 1: Crystal data and refinement details

Crystal identification	ARC339
Chemical formula	$\text{C}_{26}\text{H}_{52}\text{N}_6\text{O}_{11}\text{Os}_2$
Formula weight	1005.13
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P 2_1/c$
a (Å)	14.3533(3)
b (Å)	10.2682(2)
c (Å)	22.1176(5)
α (°)	90
β (°)	97.8921(9)
γ (°)	90
Cell volume (Å ³)	3228.9
Z	4
Calculated density (Mg/m ³)	2.068
Absorption coefficient (mm ⁻¹)	7.929
F_{000}	1946.457
Crystal size (mm)	0.06 x 0.06 x 0.10
Description of crystal	Red-brown block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.45, 0.62
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-18 \leq h \leq 18, 0 \leq k \leq 13, 0 \leq l \leq 28$
Reflections measured	24579
Unique reflections	7724
R_{int}	0.067
Observed reflections ($I > 3\sigma(I)$)	4109
Refinement method	Full-matrix least-squares on F
Parameters refined	412
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.0521
R	0.0318
wR	0.0360
Residual electron density (min,max) (eÅ ⁻³)	-1.73, 2.46

Table 2: Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$) of non-hydrogen atoms

Atom	x	y	z	U_{equiv}
Os(1)	0.45274(2)	0.31164(4)	0.369564(13)	0.0158
O(1)	0.5150(4)	0.3267(6)	0.4421(3)	0.0244
O(2)	0.4137(4)	0.3256(7)	0.2917(3)	0.0246
O(3)	0.3272(4)	0.3068(6)	0.3956(3)	0.0262
C(1)	0.2962(5)	0.1827(9)	0.4134(4)	0.0239
C(2)	0.3263(7)	0.1583(8)	0.4814(4)	0.0286
C(3)	0.3043(7)	0.0157(9)	0.4968(4)	0.0293
C(4)	0.3656(6)	-0.0753(9)	0.4643(4)	0.0274
C(5)	0.3482(6)	-0.0600(9)	0.3954(4)	0.0234
C(6)	0.3373(6)	0.0811(9)	0.3741(4)	0.0229
N(1)	0.4361(6)	0.1195(8)	0.3714(4)	0.0252
C(7)	0.4852(7)	0.0103(11)	0.3617(5)	0.0308
O(4)	0.5637(5)	-0.0004(6)	0.3479(3)	0.0303
O(5)	0.4333(5)	-0.0989(6)	0.3700(3)	0.0279
N(2)	0.4531(5)	0.5266(8)	0.3652(3)	0.0172
C(8)	0.5276(6)	0.5619(9)	0.3264(4)	0.0232
C(9)	0.6154(6)	0.4838(9)	0.3458(5)	0.0269
N(3)	0.5954(5)	0.3401(7)	0.3415(3)	0.0214
C(10)	0.3607(6)	0.5747(8)	0.3357(5)	0.0261
C(11)	0.4715(7)	0.5894(9)	0.4263(4)	0.0301
C(12)	0.6719(6)	0.2719(9)	0.3810(5)	0.0284
C(13)	0.5995(6)	0.2963(11)	0.2775(4)	0.0302
Os(2)	0.024082(19)	0.18790(4)	0.636290(13)	0.0156
O(6)	0.0694(4)	0.1766(6)	0.5679(3)	0.0219
O(7)	0.0055(4)	0.1718(6)	0.7118(3)	0.0238
O(8)	-0.1104(4)	0.1788(6)	0.6027(3)	0.0258
C(14)	-0.1519(6)	0.3033(9)	0.5839(4)	0.0246
C(15)	-0.1485(6)	0.3293(9)	0.5172(4)	0.0249
C(16)	-0.1834(7)	0.4680(9)	0.5004(4)	0.0288
C(17)	-0.1174(6)	0.5661(9)	0.5362(4)	0.0285
C(18)	-0.1075(6)	0.5477(9)	0.6046(5)	0.0265
C(19)	-0.1054(6)	0.4064(8)	0.6250(4)	0.0216
N(4)	-0.0028(5)	0.3799(7)	0.6331(3)	0.0176
C(20)	0.0445(6)	0.4931(9)	0.6410(4)	0.0192
O(9)	0.1278(4)	0.5127(6)	0.6540(3)	0.0318
O(10)	-0.0175(5)	0.5973(6)	0.6321(3)	0.0290
N(5)	0.0380(5)	-0.0266(8)	0.6368(3)	0.0208
C(21)	0.1404(6)	-0.054(1)	0.6478(5)	0.0308
C(22)	0.1917(6)	0.0358(9)	0.6959(5)	0.0303
N(6)	0.1742(4)	0.1748(7)	0.6788(3)	0.0195
C(23)	-0.0130(7)	-0.089(1)	0.6843(5)	0.0351
C(24)	-0.0019(7)	-0.0814(9)	0.5781(4)	0.0291
C(25)	0.2415(6)	0.2147(9)	0.6372(5)	0.0299
C(26)	0.1949(7)	0.2529(11)	0.7357(5)	0.0340
O(11)	0.1873(6)	0.6659(12)	0.7619(5)	0.0685

Table 3: Atomic coordinates and isotropic thermal parameters ($\text{\AA}^2$) of hydrogen atoms

Atom	x	y	z	U_{iso}
H(11)	0.2260	0.1779	0.4070	0.0293
H(21)	0.3954	0.1744	0.4917	0.0360
H(22)	0.2912	0.2185	0.5058	0.0360
H(31)	0.3181	0.0020	0.5419	0.0361
H(32)	0.2364	-0.0031	0.4828	0.0361
H(41)	0.4332	-0.0557	0.4788	0.0322
H(42)	0.3516	-0.1673	0.4748	0.0322
H(51)	0.2900	-0.1121	0.3824	0.0277
H(61)	0.2904	0.0812	0.3362	0.0272
H(81)	0.5424	0.6568	0.3313	0.0277
H(82)	0.5040	0.5428	0.2827	0.0277
H(91)	0.6404	0.5062	0.3890	0.0322
H(92)	0.6635	0.5061	0.3188	0.0322
H(101)	0.3112	0.5513	0.3614	0.0323
H(102)	0.3632	0.6715	0.3312	0.0323
H(103)	0.3454	0.5339	0.2945	0.0323
H(111)	0.4209	0.5643	0.4510	0.0354
H(112)	0.5338	0.5600	0.4477	0.0354
H(113)	0.4720	0.6862	0.4214	0.0354
H(121)	0.6603	0.1758	0.3789	0.0330
H(122)	0.6735	0.3022	0.4241	0.0330
H(123)	0.7335	0.2915	0.3667	0.0330
H(131)	0.5863	0.2008	0.2741	0.0362
H(132)	0.6635	0.3142	0.2664	0.0362
H(133)	0.5514	0.3447	0.2490	0.0362
H(141)	-0.2204	0.3029	0.5879	0.0300
H(151)	-0.0822	0.3199	0.5085	0.0290
H(152)	-0.1895	0.2650	0.4921	0.0290
H(161)	-0.2484	0.4793	0.5109	0.0335
H(162)	-0.1839	0.4825	0.4556	0.0335
H(171)	-0.1422	0.6557	0.5263	0.0341
H(172)	-0.0537	0.5572	0.5231	0.0341
H(181)	-0.1635	0.5931	0.6170	0.0316
H(191)	-0.1417	0.4002	0.6604	0.0257
H(211)	0.1500	-0.1463	0.6620	0.0372
H(212)	0.1671	-0.0422	0.6088	0.0372
H(221)	0.1688	0.0189	0.7359	0.0353
H(222)	0.2607	0.0179	0.6998	0.0353
H(231)	-0.0816	-0.0681	0.6754	0.0429
H(232)	0.0127	-0.0543	0.7255	0.0429
H(233)	-0.0039	-0.1853	0.6836	0.0429
H(241)	-0.0710	-0.0628	0.5706	0.0345
H(242)	0.0085	-0.1777	0.5785	0.0345
H(243)	0.0293	-0.0411	0.5449	0.0345
H(251)	0.2304	0.3080	0.6254	0.0358
H(252)	0.3072	0.2040	0.6583	0.0358
H(253)	0.2322	0.1590	0.5998	0.0358
H(261)	0.1839	0.3472	0.7260	0.0391
H(262)	0.1527	0.2244	0.7656	0.0391
H(263)	0.2620	0.2395	0.7537	0.0391

H(1)	0.161(9)	0.628(13)	0.727(6)	0.05
H(2)	0.148(9)	0.671(13)	0.781(6)	0.05

Table 4: Anisotropic thermal parameters ($\text{\AA}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	0.01831(16)	0.01321(17)	0.01640(17)	0.00115(16)	0.00381(12)	0.00195(15)
O(1)	0.034(3)	0.023(3)	0.016(3)	-0.001(3)	0.001(2)	0.001(3)
O(2)	0.023(3)	0.024(3)	0.026(3)	-0.002(3)	0.001(2)	0.001(3)
O(3)	0.030(3)	0.014(3)	0.037(3)	0.002(3)	0.013(3)	-0.002(3)
C(1)	0.017(4)	0.018(4)	0.038(5)	0.003(4)	0.009(3)	0.010(3)
C(2)	0.041(5)	0.019(5)	0.030(5)	0.001(4)	0.020(4)	0.006(4)
C(3)	0.032(5)	0.029(5)	0.030(5)	0.012(4)	0.013(4)	0.007(4)
C(4)	0.036(5)	0.018(4)	0.026(5)	0.002(4)	-0.001(4)	0.005(4)
C(5)	0.030(4)	0.018(4)	0.022(4)	-0.000(4)	-0.001(3)	-0.003(4)
C(6)	0.029(4)	0.017(4)	0.022(4)	0.002(4)	0.001(4)	-0.003(3)
N(1)	0.032(4)	0.022(4)	0.022(4)	0.002(3)	0.005(3)	-0.002(3)
C(7)	0.035(6)	0.028(6)	0.030(5)	-0.002(4)	0.005(4)	0.002(4)
O(4)	0.033(4)	0.025(3)	0.035(4)	0.001(3)	0.010(3)	0.003(3)
O(5)	0.041(4)	0.015(3)	0.029(3)	-0.003(3)	0.010(3)	-0.003(3)
N(2)	0.023(4)	0.014(4)	0.015(4)	-0.000(3)	0.006(3)	0.002(3)
C(8)	0.024(4)	0.016(4)	0.029(5)	0.008(4)	0.002(4)	-0.001(3)
C(9)	0.015(4)	0.023(5)	0.043(6)	0.000(4)	0.003(4)	-0.004(3)
N(3)	0.017(3)	0.019(4)	0.028(4)	0.001(3)	0.001(3)	-0.001(3)
C(10)	0.026(4)	0.008(4)	0.047(6)	0.008(4)	0.014(4)	0.007(3)
C(11)	0.053(6)	0.013(4)	0.022(5)	-0.004(4)	-0.001(4)	0.006(4)
C(12)	0.022(4)	0.021(5)	0.039(5)	0.001(4)	-0.005(4)	0.003(3)
C(13)	0.023(4)	0.050(6)	0.018(4)	-0.013(4)	0.002(3)	-0.003(4)
Os(2)	0.01499(15)	0.01235(17)	0.01899(17)	0.00092(15)	0.00083(12)	0.00194(14)
O(6)	0.027(3)	0.018(3)	0.021(3)	-0.002(3)	0.006(2)	-0.002(2)
O(7)	0.022(3)	0.021(3)	0.029(3)	-0.004(3)	0.004(2)	0.006(2)
O(8)	0.023(3)	0.018(3)	0.035(3)	-0.000(3)	-0.002(2)	0.001(3)
C(14)	0.025(4)	0.019(4)	0.031(4)	0.010(4)	0.008(3)	0.009(4)
C(15)	0.024(4)	0.026(5)	0.022(4)	-0.002(4)	-0.005(3)	-0.001(4)
C(16)	0.036(5)	0.019(5)	0.029(5)	-0.003(4)	-0.005(4)	-0.001(4)
C(17)	0.032(5)	0.020(4)	0.034(5)	0.008(4)	0.004(4)	-0.003(4)
C(18)	0.021(4)	0.020(4)	0.038(5)	-0.001(4)	0.002(4)	0.007(3)
C(19)	0.026(4)	0.015(4)	0.023(4)	-0.006(3)	0.002(3)	0.002(3)
N(4)	0.020(3)	0.007(3)	0.025(4)	-0.001(3)	-0.000(3)	0.003(3)
C(20)	0.024(4)	0.012(4)	0.020(4)	-0.002(3)	-0.004(3)	-0.005(3)
O(9)	0.026(3)	0.023(3)	0.044(4)	-0.002(3)	-0.001(3)	-0.006(3)
O(10)	0.036(4)	0.017(3)	0.031(4)	0.001(3)	-0.004(3)	-0.001(3)
N(5)	0.023(4)	0.013(4)	0.026(4)	0.004(3)	0.000(3)	0.008(3)
C(21)	0.027(5)	0.024(5)	0.042(6)	0.003(4)	0.007(4)	0.012(4)
C(22)	0.029(5)	0.017(5)	0.042(6)	0.008(4)	-0.004(4)	0.006(3)
N(6)	0.018(3)	0.020(4)	0.019(3)	-0.000(3)	-0.002(3)	0.007(3)
C(23)	0.045(6)	0.024(5)	0.038(6)	0.008(4)	0.012(5)	0.005(4)
C(24)	0.041(5)	0.016(5)	0.029(5)	0.000(4)	0.001(4)	-0.004(4)
C(25)	0.020(4)	0.033(6)	0.037(5)	-0.007(4)	0.004(4)	0.002(4)
C(26)	0.030(5)	0.041(6)	0.027(5)	-0.012(5)	-0.011(4)	0.008(4)
O(11)	0.031(4)	0.106(9)	0.073(6)	-0.040(6)	0.025(4)	-0.022(5)

Table 5: Bond lengths (Å)

Os(1) - O(1)	1.732(6)	Os(2) - O(6)	1.730(5)
Os(1) - O(2)	1.742(6)	Os(2) - O(7)	1.735(6)
Os(1) - O(3)	1.966(5)	Os(2) - O(8)	1.973(6)
Os(1) - N(1)	1.988(9)	Os(2) - N(4)	2.009(7)
Os(1) - N(2)	2.210(8)	Os(2) - N(5)	2.211(8)
Os(1) - N(3)	2.240(7)	Os(2) - N(6)	2.234(6)
O(3) - C(1)	1.423(11)	O(8) - C(14)	1.45(1)
C(1) - C(2)	1.528(13)	C(14) - C(15)	1.506(12)
C(1) - C(6)	1.528(12)	C(14) - C(19)	1.493(13)
C(2) - C(3)	1.545(13)	C(15) - C(16)	1.538(13)
C(3) - C(4)	1.530(12)	C(16) - C(17)	1.528(13)
C(4) - C(5)	1.516(12)	C(17) - C(18)	1.511(13)
C(5) - C(6)	1.525(12)	C(18) - C(19)	1.519(12)
C(5) - O(5)	1.470(11)	C(18) - O(10)	1.443(11)
C(6) - N(1)	1.481(11)	C(19) - N(4)	1.484(11)
N(1) - C(7)	1.357(13)	N(4) - C(20)	1.345(11)
C(7) - O(4)	1.212(11)	C(20) - O(9)	1.21(1)
C(7) - O(5)	1.372(12)	C(20) - O(10)	1.389(11)
N(2) - C(8)	1.50(1)	N(5) - C(21)	1.484(11)
N(2) - C(10)	1.480(11)	N(5) - C(23)	1.502(12)
N(2) - C(11)	1.490(11)	N(5) - C(24)	1.458(12)
C(8) - C(9)	1.505(12)	C(21) - C(22)	1.520(14)
C(9) - N(3)	1.504(11)	C(22) - N(6)	1.490(11)
N(3) - C(12)	1.483(11)	N(6) - C(25)	1.479(11)
N(3) - C(13)	1.494(11)	N(6) - C(26)	1.487(11)
O(11) - H(1)	0.90(13)	O(11) - H(2)	0.75(13)

Note – Geometrically-positioned H atoms have been excluded

Table 6: Bond angles (°)

O(1) - Os(1) - O(2)	164.3(3)	O(6) - Os(2) - O(7)	163.9(3)
O(1) - Os(1) - O(3)	96.2(3)	O(6) - Os(2) - O(8)	97.7(3)
O(2) - Os(1) - O(3)	96.2(3)	O(7) - Os(2) - O(8)	94.9(3)
O(1) - Os(1) - N(1)	96.7(3)	O(6) - Os(2) - N(4)	97.4(3)
O(2) - Os(1) - N(1)	94.5(3)	O(7) - Os(2) - N(4)	94.2(3)
O(3) - Os(1) - N(1)	81.5(3)	O(8) - Os(2) - N(4)	82.0(3)
O(1) - Os(1) - N(2)	87.0(3)	O(6) - Os(2) - N(5)	83.9(3)
O(2) - Os(1) - N(2)	82.9(3)	O(7) - Os(2) - N(5)	85.7(3)
O(3) - Os(1) - N(2)	92.6(3)	O(8) - Os(2) - N(5)	92.2(3)
N(1) - Os(1) - N(2)	173.3(3)	N(4) - Os(2) - N(5)	174.1(3)
O(1) - Os(1) - N(3)	82.5(3)	O(6) - Os(2) - N(6)	84.7(3)
O(2) - Os(1) - N(3)	84.1(3)	O(7) - Os(2) - N(6)	81.7(2)
O(3) - Os(1) - N(3)	173.9(3)	O(8) - Os(2) - N(6)	173.2(3)
N(1) - Os(1) - N(3)	104.6(3)	N(4) - Os(2) - N(6)	104.1(3)
N(2) - Os(1) - N(3)	81.3(3)	N(5) - Os(2) - N(6)	81.8(3)
Os(1) - O(3) - C(1)	115.9(5)	Os(2) - O(8) - C(14)	114.2(5)
O(3) - C(1) - C(2)	111.3(7)	O(8) - C(14) - C(15)	111.8(7)
O(3) - C(1) - C(6)	107.1(6)	O(8) - C(14) - C(19)	108.6(7)
C(2) - C(1) - C(6)	111.7(7)	C(15) - C(14) - C(19)	113.5(8)
C(1) - C(2) - C(3)	109.5(8)	C(14) - C(15) - C(16)	110.4(8)
C(2) - C(3) - C(4)	109.1(7)	C(15) - C(16) - C(17)	109.1(7)
C(3) - C(4) - C(5)	112.5(7)	C(16) - C(17) - C(18)	113.8(8)
C(4) - C(5) - C(6)	113.9(7)	C(17) - C(18) - C(19)	114.4(8)
C(4) - C(5) - O(5)	109.0(7)	C(17) - C(18) - O(10)	109.5(7)
C(6) - C(5) - O(5)	101.2(7)	C(19) - C(18) - O(10)	103.4(7)
C(1) - C(6) - C(5)	120.2(7)	C(14) - C(19) - C(18)	120.4(8)
C(1) - C(6) - N(1)	106.7(7)	C(14) - C(19) - N(4)	107.3(7)
C(5) - C(6) - N(1)	102.0(7)	C(18) - C(19) - N(4)	100.9(7)
Os(1) - N(1) - C(6)	112.5(6)	Os(2) - N(4) - C(19)	111.5(5)
Os(1) - N(1) - C(7)	138.6(7)	Os(2) - N(4) - C(20)	138.8(6)
C(6) - N(1) - C(7)	107.9(8)	C(19) - N(4) - C(20)	109.4(7)
N(1) - C(7) - O(4)	129.4(10)	N(4) - C(20) - O(9)	129.8(9)
N(1) - C(7) - O(5)	110.6(8)	N(4) - C(20) - O(10)	110.2(7)
O(4) - C(7) - O(5)	120.0(9)	O(9) - C(20) - O(10)	120.0(8)
C(5) - O(5) - C(7)	108.9(7)	C(18) - O(10) - C(20)	107.9(7)
Os(1) - N(2) - C(8)	105.8(5)	Os(2) - N(5) - C(21)	106.1(6)
Os(1) - N(2) - C(10)	110.2(5)	Os(2) - N(5) - C(23)	112.0(6)
C(8) - N(2) - C(10)	109.4(7)	C(21) - N(5) - C(23)	111.7(7)
Os(1) - N(2) - C(11)	113.2(5)	Os(2) - N(5) - C(24)	110.8(5)
C(8) - N(2) - C(11)	111.2(7)	C(21) - N(5) - C(24)	109.4(7)
C(10) - N(2) - C(11)	107.0(7)	C(23) - N(5) - C(24)	106.8(8)
N(2) - C(8) - C(9)	110.0(7)	N(5) - C(21) - C(22)	111.9(7)
C(8) - C(9) - N(3)	111.1(7)	C(21) - C(22) - N(6)	110.9(7)
Os(1) - N(3) - C(9)	106.5(5)	Os(2) - N(6) - C(22)	106.5(5)
Os(1) - N(3) - C(12)	113.9(5)	Os(2) - N(6) - C(25)	113.3(5)
C(9) - N(3) - C(12)	107.9(7)	C(22) - N(6) - C(25)	108.8(7)
Os(1) - N(3) - C(13)	112.3(5)	Os(2) - N(6) - C(26)	113.1(5)
C(9) - N(3) - C(13)	108.9(7)	C(22) - N(6) - C(26)	107.1(7)
C(12) - N(3) - C(13)	107.2(7)	C(25) - N(6) - C(26)	107.8(7)
H(1) - O(11) - H(2)	105.(12)		

Note – Geometrically-positioned H atoms have been excluded