Electronic Supplementary Information

A Ternary Supramolecular System Containing a Boronated DNA-Metallointercalator, *β*-Cyclodextrin and the Hexanucleotide d(GTCGAC)$_2$

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Contents

Synthesis and characterisation

High resolution ESI-MS were recorded on a Bruker 7T FTICR mass spectrometer in the ESI mode. Elemental analysis was performed by Campbell Microanalytical Laboratory, Chemistry Department, The University of Otago, Dunedin, New Zealand. Normal phase HPLC was performed on a Waters 2525 Binary Gradient Module equipped with a Waters 2996 Photodiode Array Detector and an automated Waters 2767 Sample Manager. A ZORBAX® RX-SIL column (5 μm, 21.2 mm × 250 mm) was used. The results were analysed by means of Waters MassLynx 4.1 software. Chiral HPLC was performed by using a Waters 510 HPLC Pump equipped with a Waters 2487 Dual λ Absorbance Detector. A DAICEL® CHIRALCEL OD-H column (5 μm, 4.6 mm × 250 mm) was used. The results were analysed by means of Waters Empower® software.

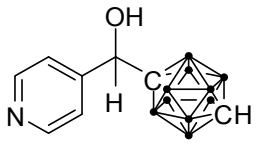
Commercially available deuterated solvents of 99.5% isotopic purity or higher were used for all NMR spectra. All NMR spectra were recorded at 300 K on a Bruker AVANCE 400 MHz DRX spectrometer (^{1}H at 400 MHz, ^{13}C at 101 MHz, ^{11}B at 128 MHz and ^{195}Pt at 85 MHz). All NMR signals are reported in ppm. ^{1}H, ^{1}H{^{11}B} and ^{13}C{^{1}H} NMR spectra were referenced to TMS (0 ppm), except for spectra in D_2O which were referenced to TSP (0 ppm). ^{11}B{^{1}H} NMR spectra were referenced to an external standard BF_3•OEt_2 (0 ppm). ^{195}Pt{^{1}H} NMR spectra were referenced to external standard of $K_2[PtCl_4]$ with KCl in D_2O (-1628 ppm). ^{1}H{^{11}B} NOESY spectra were recorded with 4096 points in t_2 for 256 t_1 values with a pulse repetition delay of 1.5 s and a mixing time of 300 ms. ^{1}H{^{11}B} ROESY spectra were recorded with 4096 points in t_2 for 512 t_1 values with a pulse repetition delay of 2 s. Coupling constants ($^{n}\boldsymbol{J}$ [ij]) are reported in Hz. Peak multiplicities have been abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet - unassignable multiplicity or overlapping signals), and b (broad).

Materials

MilliQ™ water was used for all experiments requiring water. THF was dried over sodium wire and distilled from benzophenone ketyl in accordance with Perrin *et. al.*[1] All other solvents were used without further purification. 1,12-dicarba-*closo*-dodecaborane(12) was obtained from Katchem Pty Ltd (Czech Republic). Potassium tetrachloridoplatinate(II) was kindly loaned from Johnson Matthey. Acetonitrile(2,2':6',2"-terpyridine)platinum(II) nitrate

was synthesised by following the method of Lowe *et al.*[2] All other reagents were purchased from Sigma Aldrich and were used without further purification.

rac-(1,12-Dicarba-_closo_-dodecaboran-1-yl)(pyrid-4-yl) methanol



n-BuLi (1.60 M in hexane, 3.10 mL, 4.96 mmol) was added dropwise to a stirred solution of the 1,12-dicarba-*closo*-dodecaborane (720 mg, 5.00 mmol) in THF (50 mL) at -78 °C. After 30 min, 4-pyridinecarboxaldehyde (590 mg, 0.661 mL, 5.50 mmol) was added and the mixture was stirred for 1 h. The mixture was warmed to room temperature and quenched with water (10 mL). The solution was extracted with diethyl ether (4×150 mL) and dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* followed by recrystallisation from acetone yielded the desired product as colourless crystals which were dried *in vacuo* (850 mg, 66 %). ^{1}H NMR (acetone-d_6) δ: 8.51 (m, 2H, H2$_{py}$), 7.19 (m, 2H, H3$_{py}$), 5.48 (d, $^{3}\boldsymbol{J}$ [H$_{OH}$, H$_{methine}$] = 5.1 Hz, 1H, OH), 4.67 (d, $^{3}\boldsymbol{J}$ [H$_{OH}$, H$_{methine}$] = 5.1 Hz, 1H, methine), 3.37 (bs, 1H, H12$_{CB}$), 3.0-1.3 (m, 10H, BH$_{CB}$). ^{13}C{^{1}H} NMR (acetone-d_6) δ: 150.4 (1C, C4$_{py}$), 150.3 (2C, C2$_{py}$), 122.8 (2C, C3$_{py}$), 90.1 (1C, C1$_{CB}$), 74.9 (1C, methine), 62.3 (1C, C12$_{CB}$). ^{11}B{^{1}H} NMR (acetone-d_6) δ: -12.9 (5B), -14.8 (5B). HR-ESI-MS Calcd for [M + H^{+}]$^{+}$, $C_8H_{18}B_{10}NO$: *m/z* 252.23861. Found *m/z* 252.23879. Anal. Calcd for $C_8H_{17}B_{10}NO$: C, 38.23; H, 6.81; N, 5.57. Found: C, 38.58; H, 6.78; N, 5.61.

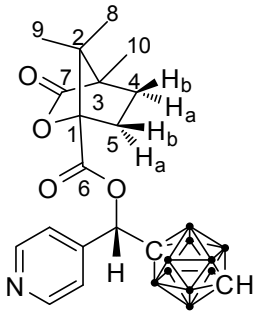
Chiral resolution

(1*S*)-(–)-camphanic acid chloride (1.18 g, 5.40 mmol) was added to a stirred solution of *rac*-(1,12-dicarba-*closo*-dodecaboran-1-yl)pyrid-4-yl methanol ligand (650 mg, 2.58 mmol) in dry pyridine (10 mL). After 2 h, the volatiles were removed *in vacuo*. Water (50 mL) was added to the residue and the mixture was extracted with DCM (3×50 mL) and dried over anhydrous sodium sulfate. Removal of the solvent gave a mixture of two diastereomers which were separated by normal phase preparative-HPLC (isocratic Hex:EtOAc:TEA (77:23:0.1 *v/v*). Concentration of each of the fractions *in vacuo* gave enantiopure camphanic esters as colourless crystals which were dried *in vacuo.*

Potassium carbonate (200 mg, 1.44 mmol) in water (2 mL) was added to a stirred solution of (1*S*)-((*R*)-(1,12-dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl)methyl) camphanoate or (1*S*)-

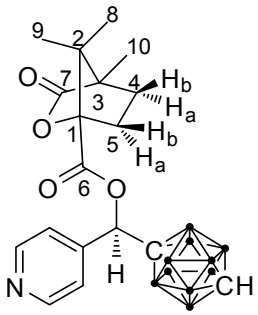
((*S*)-(1,12-dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl)methyl) camphanoate (200 mg, 0.46 mmol) in DCM/MeOH (5 mL/5 mL). After 2 h, the organic solvents were removed *in vacuo* and then water (25 mL) was added to the residue. The mixture was extracted with DCM (3×25 mL) and dried over anhydrous sodium sulphate. Evaporation of the solvent followed by recrystallisation from acetone yielded the desired products as colourless crystals which were dried *in vacuo*.

(1*S*)-((*R*)-(1,12-Dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl)methyl) camphanoate



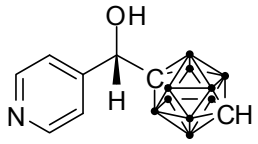
T_R = 38 min, 340 mg, 61 %. Single crystals suitable for X-ray structural analysis were obtained from EtOAc. ^{1}H NMR ($CDCl_3$) δ: 8.58 (m, 2H, $H2_{py}$), 7.08 (m, 2H, $H3_{py}$), 5.72 (s, 1H, methine), 2.79 (bs, 1H, $H12_{CB}$), 3.0-1.3 (m, 10H, BH_{CB}), 2.40 (ddd, $^2\boldsymbol{J}$ [$H5a_{camph}$, $H5b_{camph}$] = 13.5 Hz, $^3\boldsymbol{J}$ [$H4b_{camph}$, $H5b_{camph}$] = 10.8 Hz, $^3\boldsymbol{J}$ [$H4a_{camph}$, $H5b_{camph}$] = 4.2 Hz, 1H, $H5b_{camph}$), 2.09 (ddd, $^2\boldsymbol{J}$ [$H5a_{camph}$, $H5b_{camph}$] = 13.7 Hz, $^3\boldsymbol{J}$ [$H4a_{camph}$, $H5a_{camph}$] = 9.3 Hz, $^3\boldsymbol{J}$ [$H4b_{camph}$, $H5a_{camph}$] = 4.4 Hz, 1H, $H5a_{camph}$), 1.93 (ddd, $^2\boldsymbol{J}$ [$H4a_{camph}$, $H4b_{camph}$] = 13.2 Hz, $^3\boldsymbol{J}$ [$H4b_{camph}$, $H5b_{camph}$] = 10.8 Hz, $^3\boldsymbol{J}$ [$H4b_{camph}$, $H5a_{camph}$] = 4.4 Hz, 1H, $H4b_{camph}$), 1.71 (ddd, $^2\boldsymbol{J}$ [$H4a_{camph}$, $H4b_{camph}$] = 13.2 Hz, $^3\boldsymbol{J}$ [$H4a_{camph}$, $H5a_{camph}$] = 9.3 Hz, $^3\boldsymbol{J}$ [$H4a_{camph}$, $H5b_{camph}$] = 4.2 Hz, 1H, $H4a_{camph}$), 1.10 (s, 3H, $H10_{camph}$), 1.01 (s, 3H, $H8_{camph}$), 0.80 (s, 3H, $H9_{camph}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 177.9 (1C, $C7_{camph}$), 165.6 (1C, $C6_{camph}$), 149.9 (2C, $C2_{py}$), 144.7 (1C, $C4_{py}$), 121.8 (1C, $C3_{py}$), 90.4 (1C, $C1_{camph}$), 83.3 (1C, $C1_{CB}$), 74.8 (1C, methine), 61.7 (C1, $C12_{CB}$), 54.8 (2C, $C2_{camph}$), 54.5 (1C, $C3_{camph}$), 31.0 (1C, $C5_{camph}$), 28.8 (1C, $C4_{camph}$), 16.6 (2C, $C8_{camph}$, $C9_{camph}$), 9.6 (1C, $C10_{camph}$). $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ: -13.4 (5B), -15.0 (5B). HR-ESI-MS Calcd for $[2M + Na]^+$, $C_{36}H_{58}B_{20}N_2O_8Na$: *m/z* 886.60608. Found *m/z* 886.60464. Anal. Calcd for $C_{18}H_{29}B_{10}NO_4$: C, 50.10; H, 6.77; N, 3.25. Found: C, 50.31; H, 6.83; N, 3.30.

(1*S*)-((*S*)-(1,12-Dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl)methyl) camphanoate



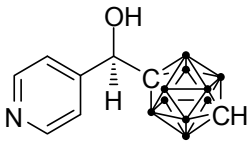
T_R = 49 min, 340 mg, 61 %. ^{1}H NMR ($CDCl_3$) δ: 8.59 (m, 2H, $H2_{py}$), 7.07 (m, 2H, $H3_{py}$), 5.67 (s, 1H, methine), 2.79 (bs, 1H, $H12_{CB}$), 3.0-1.3 (m, 10H, BH_{CB}), 2.37 (ddd, $^2\boldsymbol{J}$ [$H5a_{camph}$, $H5b_{camph}$] = 13.7 Hz, $^3\boldsymbol{J}$ [$H4b_{camph}$, $H5b_{camph}$] = 10.5 Hz, $^3\boldsymbol{J}$ [$H4a_{camph}$, $H5b_{camph}$] = 4.7 Hz, 1H, $H5b_{camph}$), 2.00 (ddd, $^2\boldsymbol{J}$ [$H5a_{camph}$, $H5b_{camph}$] = 13.7 Hz, $^3\boldsymbol{J}$ [$H4a_{camph}$, $H5a_{camph}$] = 9.3 Hz, $^3\boldsymbol{J}$ [$H4b_{camph}$, $H5a_{camph}$] = 4.4 Hz, 1H, $H5a_{camph}$), 1.93 (ddd, $^2\boldsymbol{J}$ [$H4a_{camph}$, $H4b_{camph}$] = 13.2 Hz, $^3\boldsymbol{J}$ [$H4b_{camph}$, $H5b_{camph}$] = 10.8 Hz, $^3\boldsymbol{J}$ [$H4b_{camph}$, $H5a_{camph}$] = 4.4 Hz, 1H, $H4b_{camph}$), 1.70 (ddd, $^2\boldsymbol{J}$ [$H4a_{camph}$, $H4b_{camph}$] = 13.2 Hz, $^3\boldsymbol{J}$ [$H4a_{camph}$, $H5a_{camph}$] = 9.3 Hz, $^3\boldsymbol{J}$ [$H4a_{camph}$, $H5b_{camph}$] = 4.7 Hz, 1H, $H4a_{camph}$), 1.11 (s, 3H, $H10_{camph}$), 1.04 (s, 3H, $H8_{camph}$), 0.92 (s, 3H, $H9_{camph}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 177.6 (1C, $C7_{camph}$), 165.5 (1C, $C6_{camph}$), 150.0 (2C, $C2_{py}$), 144.7 (1C, $C4_{py}$), 121.9 (2C, $C3_{py}$), 90.5 (1C, $C1_{camph}$), 83.0 (1C, $C1_{CB}$), 75.4 (1C, methine), 61.8 (C1, $C12_{CB}$), 54.9 (1C, $C2_{camph}$), 54.5 (1C, $C3_{camph}$), 30.9 (1C, $C5_{camph}$), 28.8 (1C, $C4_{camph}$), 16.9 (2C, $C8_{camph}$, $C9_{camph}$), 9.6 (1C, $C10_{camph}$). $^{11}B\{^1H\}$ NMR ($CDCl_3$) δ: -13.4 (5B), -14.9 (5B). HR-ESI-MS Calcd for $[M + H]^+$, $C_{18}H_{30}B_{10}NO_4$: *m/z* 432.31816. Found *m/z* 432.31729. Anal. Calcd for $C_{18}H_{29}B_{10}NO_4$: C, 50.10; H, 6.77; N, 3.25. Found: C, 50.27; H, 6.81; N, 3.16.

(*R*)-(1,12-Dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl) methanol



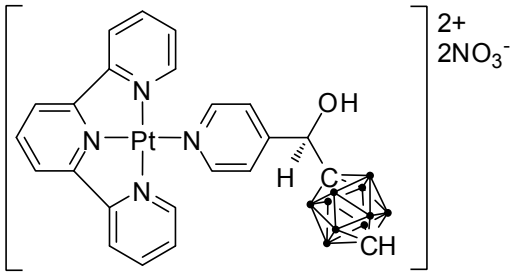
The title compound was prepared from (1*S*)-((*R*)-(1,12-dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl)methyl) camphanoate (80 mg, 69%, >99% ee). HR-ESI-MS Calcd for $[M + H]^+$, $C_8H_{18}B_{10}NO$: *m/z* 252.23861. Found *m/z* 252.23866. Anal. Calcd for $C_8H_{17}B_{10}NO$: C, 38.23; H, 6.81; N, 5.57. Found: C, 38.64; H, 7.14; N, 5.61.

(*S*)-(1,12-Dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl) methanol



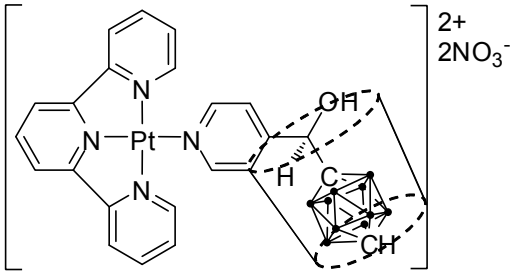
The title compound was prepared from (1*S*)-((*S*)-(1,12-dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl)methyl) camphanoate (90 mg, 78%, >99% ee). HR-ESI-MS Calcd for $[M + H]^+$, $C_8H_{18}B_{10}NO$: *m/z* 252.23861. Found *m/z* 252.23874. Anal. Calcd for $C_8H_{17}B_{10}NO$: C, 38.23; H, 6.81; N, 5.57. Found: C, 38.52; H, 6.78; N, 5.54.

((*S*)-(1,12-Dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl) methanol)(2,2':6',2''-terpyridine)platinum(II) nitrate (*S*-1·2NO$_3$)



A solution of (*S*)-(1,12-dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl) methanol (45 mg, 0.18 mmol) in acetone (10 mL) was added dropwise to a stirred solution of freshly prepared acetonitrile(2,2':6',2''-terpyridine)platinum(II) nitrate (100 mg, 0.17 mmol) in acidified water (2 mL). After 16 h, the volatiles were removed *in vacuo*. Water (20 mL) was added to the residue and the mixture was filtered off. The filtrate was then concentrated with heating (< 90 °C). Upon cooling, the desired product precipitated from the solution and the solid was collected by filtration, washed with water (3 × 0.5 mL), and dried *in vacuo* (beige powder, 64 mg, 47%). ^{1}H NMR (D_2O) δ: 9.12 (m, 2H, $H2_{py}$), 8.52 (t, ^3J [$H3'_{terpy}$, $H4'_{terpy}$] = 8.8 Hz, 1H, $H4'_{terpy}$), 8.42 (m, 6H, $H3_{terpy}$, $H3'_{terpy}$, $H3''_{terpy}$, $H4_{terpy}$, $H4''_{terpy}$, $H5'_{terpy}$), 7.74 (m, 6H, $H3_{py}$, $H5_{terpy}$, $H5''_{terpy}$, $H6_{terpy}$, $H6''_{terpy}$) 4.99 (s, 1H, methine), 3.26 (bs, 1H, $H12_{CB}$), 3.0-1.3 (m, 10H, BH_{CB}). ^{13}C{^{1}H} NMR (D_2O) δ: 158.2 (2C, $C2_{terpy}$, $C2''_{terpy}$), 155.4 (2C, $C2'_{terpy}$, $C6'_{terpy}$), 154.6 (1C, $C4_{py}$), 152.3 (2C, $C2_{py}$), 150.9 (2C, $C6''_{terpy}$, $C6_{terpy}$), 143.6 (1C, $C4'_{terpy}$), 143.1 (2C, $C4_{terpy}$, $C4''_{terpy}$), 129.0 (2C, $C5_{terpy}$, $C5''_{terpy}$), 126.1 (2C, $C3_{py}$), 125.7 (2C, $C3_{terpy}$, $C3''_{terpy}$), 123.9 (2H, $C3'_{terpy}$, $C5'_{terpy}$), 86.5 (1C, $C1_{CB}$), 72.9 (1C, methine), 61.6 (1C, $C12_{CB}$). ^{11}B{^{1}H} NMR (D_2O) δ: -13.6 (5B), -14.8 (5B). ^{195}Pt NMR (D_2O) δ: -2778. HR-ESI-MS Calcd for $[M - 2NO_3]^{2+}$, $C_{23}H_{28}B_{10}N_4OPt$: *m/z* 340.14345. Found *m/z* 340.14416. Anal. Calcd for $C_{23}H_{28}B_{10}N_6O_7Pt$: C, 34.37; H, 3.51; N, 10.46. Found: C, 34.48; H, 3.58; N, 10.47.

((*S*)-(1,12-Dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl)methanol)(2,2':6',2''-terpyridine)platinum(II)·*β*-cyclodextrin nitrate (*S*-1·*β*-CD·2NO$_3$)



S-**1**·2NO$_3$ (4.8 mg, 6.0 μmol) was suspended in a 2.0 mM aqueous solution of *β*-CD (3.0 mL, 6.0 μmol) and placed in an ultrasonic bath for 30 min. Filtration through cellulose followed by lyophilisation gave the desired product as a bisque powder (12 mg, quantitative). ^{1}H NMR (D$_2$O) δ: 9.17 (m, 2H, H2$_{py}$), 8.55 (t, ^{3}***J*** [H3'$_{terpy}$, H4'$_{terpy}$] = 8.1 Hz, 1H, H4'$_{terpy}$), 8.43 (m, 6H, H3$_{terpy}$, H3'$_{terpy}$, H3''$_{terpy}$, H4$_{terpy}$, H4''$_{terpy}$, H5$_{terpy}$), 7.80 (m, 6H, H3$_{py}$, H5$_{terpy}$, H5''$_{terpy}$, H6$_{terpy}$, H6''$_{terpy}$), 5.10 (d, ^{3}***J*** [H1$_{\beta\text{-CD}}$, H2$_{\beta\text{-CD}}$] = 3.4 Hz, 7H, H1$_{\beta\text{-CD}}$), 5.05 (s, 1H, methine), 4.16 (dd, ^{3}***J*** [H2$_{\beta\text{-CD}}$, H3$_{\beta\text{-CD}}$] = 9.5 Hz, ^{3}***J*** [H3$_{\beta\text{-CD}}$, H4$_{\beta\text{-CD}}$] = 9.5 Hz, 7H, H3$_{\beta\text{-CD}}$), 3.91, (m, 14H, H6$_{\beta\text{-CD}}$), 3.85 (m, H5$_{\beta\text{-CD}}$), 3.73 (dd, ^{3}***J*** [H1$_{\beta\text{-CD}}$, H2$_{\beta\text{-CD}}$] = 3.4 Hz, ^{3}***J*** [H2$_{\beta\text{-CD}}$, H3$_{\beta\text{-CD}}$] = 9.5 Hz, 7H, H2$_{\beta\text{-CD}}$), 3.62 (dd, ^{3}***J*** [H3$_{\beta\text{-CD}}$, H4$_{\beta\text{-CD}}$] = 9.5 Hz, ^{3}***J*** [H4$_{\beta\text{-CD}}$, H5$_{\beta\text{-CD}}$] = 9.5 Hz, 7H, H4$_{\beta\text{-CD}}$), 3.27 (bs, 1H, H12$_{CB}$), 3.0-1.3 (m, 10H, BH$_{CB}$). ^{13}C{^{1}H} NMR (D$_2$O) δ: 158.1 (2C, C2$_{terpy}$, C2''$_{terpy}$), 155.4 (2C, C2'$_{terpy}$, C6'$_{terpy}$), 154.6 (1C, C4$_{py}$), 152.4 (2C, C2$_{py}$), 150.9 (2C, C6$_{terpy}$, C6''$_{terpy}$), 143.5 (1C, C4'$_{terpy}$), 143.0 (2C, C4$_{terpy}$, C4''$_{terpy}$), 129.2 (2C, C5$_{terpy}$, C5''$_{terpy}$), 126.3 (2C, C3$_{py}$), 125.6 (2C, C3$_{terpy}$, C3''$_{terpy}$), 123.8 (2C, C3'$_{terpy}$, C5'$_{terpy}$), 102.3 (7C, C1$_{\beta\text{-CD}}$), 87.1 (1C, C1$_{CB}$), 81.9 (7C, C4$_{\beta\text{-CD}}$), 73.3 (7C, C3$_{\beta\text{-CD}}$), 72.9 (1C, methine), 72.1 (7C, C2$_{\beta\text{-CD}}$), 72.0 (7C, C5$_{\beta\text{-CD}}$), 61.8 (1C, C12$_{CB}$), 60.3 (7C, C6$_{\beta\text{-CD}}$). ^{11}B{^{1}H} NMR (D$_2$O) δ: -16.3 (5B), -17.7 (5B). ^{195}Pt NMR (D$_2$O) δ: -2783. HR-ESI-MS Calcd for [M – 2NO$_3^-$]$^{2+}$, C$_{65}$H$_{98}$B$_{10}$N$_4$O$_{36}$Pt: *m/z* 907.33048. Found *m/z* 907.33028. Anal. Calcd C$_{65}$H$_{98}$B$_{10}$N$_6$O$_{42}$Pt·8H$_2$O: C, 37.48; H, 5.52; N, 4.03. Found: C, 37.35; H, 5.14; N, 4.51.

X-ray crystallography

A suitable single crystal of (1*S*)-((*R*)-(1,12-dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl)methyl) camphanoate, selected under the polarizing microscope (Leica M165Z) was picked up on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker kappa-II CCD diffractometer at 150 K by using graphite-monochromated Mo-*K*α radiation (λ = 0.710723 Å). The single crystal, mounted on the goniometer using cryo loops for intensity measurements, was coated with paraffin oil and then quickly transferred to the cold stream using an Oxford Cryo stream attachment. Symmetry related absorption corrections using the program SADABS[3] were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX2 software.[4] All structures were solved by direct methods and the full-matrix least-square refinements were carried out using SHELXL.[5] The non-hydrogen atoms were refined anisotropically. The molecular graphic was generated using OLEX2.[6] Key crystallographic data and refinement details are presented in the Tables S1 - S3. Crystallographic data (without structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 843257. Copies of the data can be obtained free of charge from the CCDC (12 Union Road, Cambridge CB21EZ, UK; Tel: +44-1223-336408; Fax: +44-1223-336003;e-mail: deposit@ccdc.cam.ac.uk).

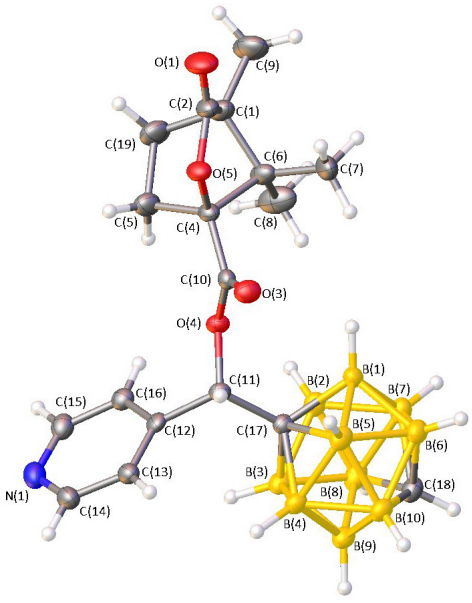


Figure S1. ORTEP representation of (1*S*)-((*R*)-(1,12-dicarba-*closo*-dodecaboran-1-yl)(pyrid-4-yl)methyl) camphanoate with thermal ellipsoids shown at 50% probability.

Table S1. X-ray crystallography data

Crystal data	
Chemical formula	$C_{18}H_{29}B_{10}NO_4$
M_r	431.52
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	150(2)
a, b, c (Å)	6.5549 (11), 11.7027 (19), 31.294 (5)
V (Å^3)	2400.6 (7)
Z	4
Radiation type	Mo K_α
μ (mm^{-1})	0.07
Crystal size (mm)	0.28 × 0.13 × 0.12
Data collection	
Diffractometer	Bruker kappa APEXII CCD Area Detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2003)
T_{min}, T_{max}	0.980, 0.991
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12750, 4195, 3740
Rint	0.070
Refinement	
R[$F^2 > 2\sigma(F^2)$], wR(F^2), *S*	0.040, 0.109, 0.72
No. of reflections	4195
No. of parameters	414
No. of restraints	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.15
Absolute structure	Flack H D (1983), *Acta Cryst.* A39, 876-881

Table S2. Bond distances (Å)

Atom-Atom	Distance	Atom-Atom	Distance
B1—B2	1.815 (3)	B9—B10	1.806 (3)
B1—B5	1.810 (3)	B9—C18	1.739 (3)
B1—B6	1.793 (3)	B10—C18	1.719 (3)
B1—B7	1.790 (3)	C1—C2	1.525 (3)
B1—C17	1.750 (3)	C1—C6	1.582 (3)
B2—B3	1.819 (3)	C1—C9	1.543 (3)
B2—B7	1.804 (3)	C1—C19	1.586 (4)
B2—B8	1.798 (3)	C2—O1	1.218 (3)
B2—C17	1.745 (3)	C2—O5	1.395 (3)
B3—B4	1.811 (3)	C4—C5	1.559 (3)
B3—B8	1.793 (3)	C4—C6	1.586 (3)
B3—B9	1.789 (3)	C4—C10	1.530 (3)
B3—C17	1.750 (3)	C4—O5	1.485 (2)
B4—B5	1.812 (3)	C5—C19	1.578 (3)
B4—B9	1.787 (3)	C6—C7	1.548 (4)
B4—B10	1.796 (3)	C6—C8	1.540 (4)
B4—C17	1.741 (3)	C10—O3	1.216 (3)
B5—B6	1.800 (3)	C10—O4	1.378 (2)
B5—B10	1.792 (3)	C11—C12	1.543 (3)
B5—C17	1.750 (3)	C11—C17	1.569 (3)
B6—B7	1.811 (3)	C11—O4	1.468 (2)
B6—B10	1.817 (3)	C12—C13	1.410 (3)
B6—C18	1.723 (3)	C12—C16	1.406 (3)
B7—B8	1.816 (4)	C13—C14	1.409 (3)
B7—C18	1.739 (3)	C14—N1	1.357 (3)
B8—B9	1.814 (4)	C15—C16	1.409 (3)
B8—C18	1.734 (3)	C15—N1	1.361 (3)

Table S3. Torsion angles (°)

Atom-Atom-Atom	Angle	Atom-Atom-Atom	Angle
B1—B2—B3	107.93 (16)	C2—C1—C9	113.9 (2)
B1—B5—B4	107.89 (16)	C2—C1—C19	103.18 (19)
B1—B6—B5	60.49 (13)	C2—O5—C4	105.85 (15)
B1—B6—B7	59.55 (13)	C4—C5—C19	100.88 (18)
B1—B6—B10	107.69 (16)	C5—C4—C6	105.10 (17)
B1—B7—B2	60.69 (13)	C5—C19—C1	104.23 (18)
B1—B7—B6	59.72 (13)	C6—C1—C19	102.76 (18)
B1—B7—B8	107.85 (16)	C7—C6—C1	112.47 (19)
B1—C17—B3	114.20 (15)	C7—C6—C4	113.43 (19)
B1—C17—B5	62.28 (13)	C8—C6—C1	114.5 (2)
B2—B7—B6	108.32 (16)	C8—C6—C4	114.5 (2)
B2—B7—B8	59.56 (13)	C8—C6—C7	109.8 (2)
B2—B8—B7	59.87 (13)	C9—C1—C6	118.9 (2)
B2—B8—B9	108.19 (16)	C9—C1—C19	116.6 (2)
B2—C17—B1	62.60 (13)	C10—C4—C5	119.15 (16)
B2—C17—B3	62.72 (13)	C10—C4—C6	116.67 (15)
B2—C17—B5	114.26 (15)	C10—O4—C11	116.67 (14)
B3—B4—B5	108.36 (16)	C11—C17—B1	117.66 (15)
B3—B8—B2	60.85 (12)	C11—C17—B2	121.49 (15)
B3—B8—B7	108.67 (16)	C11—C17—B3	120.66 (15)
B3—B8—B9	59.45 (13)	C11—C17—B4	115.89 (15)
B3—B9—B8	59.70 (13)	C11—C17—B5	114.10 (15)
B3—B9—B10	108.62 (16)	C12—C11—C17	115.91 (15)
B4—B3—B2	107.70 (16)	C12—C16—C15	118.68 (19)
B4—B9—B3	60.86 (12)	C13—C12—C11	120.30 (18)
B4—B9—B8	108.12 (16)	C14—C13—C12	119.1 (2)
B4—B9—B10	59.96 (13)	C14—N1—C15	116.43 (18)
B4—B10—B6	108.40 (16)	C16—C12—C11	121.63 (17)
B4—B10—B9	59.52 (13)	C16—C12—C13	118.00 (19)
B4—C17—B1	114.02 (15)	C17—B1—B2	58.55 (12)
B4—C17—B2	114.46 (15)	C17—B1—B5	58.86 (12)

B4—C17—B3	62.50 (13)	C17—B1—B6	105.07 (15)
B4—C17—B5	62.54 (13)	C17—B1—B7	104.92 (15)
B5—B1—B2	108.11 (16)	C17—B2—B1	58.84 (12)
B5—B6—B7	108.02 (16)	C17—B2—B3	58.79 (12)
B5—B6—B10	59.41 (13)	C17—B2—B7	104.55 (15)
B5—B10—B4	60.67 (13)	C17—B2—B8	104.30 (16)
B5—B10—B6	59.85 (13)	C17—B3—B2	58.49 (12)
B5—B10—B9	108.25 (16)	C17—B3—B4	58.51 (12)
B5—C17—B3	114.17 (14)	C17—B3—B8	104.27 (16)
B6—B1—B2	108.60 (16)	C17—B3—B9	104.40 (15)
B6—B1—B5	59.97 (13)	C17—B4—B3	58.99 (12)
B6—B5—B1	59.55 (13)	C17—B4—B5	58.97 (12)
B6—B5—B4	108.38 (16)	C17—B4—B9	104.82 (16)
B6—B7—B8	107.69 (17)	C17—B4—B10	104.71 (16)
B6—C18—B7	63.08 (14)	C17—B5—B1	58.86 (12)
B6—C18—B8	115.78 (16)	C17—B5—B4	58.49 (12)
B6—C18—B9	116.12 (16)	C17—B5—B6	104.74 (16)
B7—B1—B2	60.03 (13)	C17—B5—B10	104.48 (15)
B7—B1—B5	108.55 (16)	C18—B6—B1	103.82 (16)
B7—B1—B6	60.73 (13)	C18—B6—B5	103.45 (16)
B7—B2—B1	59.27 (13)	C18—B6—B7	58.88 (13)
B7—B2—B3	108.10 (16)	C18—B6—B10	58.04 (13)
B7—B6—B10	107.91 (17)	C18—B7—B1	103.31 (16)
B8—B2—B1	107.52 (16)	C18—B7—B2	103.65 (16)
B8—B2—B3	59.45 (13)	C18—B7—B6	58.04 (13)
B8—B2—B7	60.56 (13)	C18—B7—B8	58.36 (13)
B8—B3—B2	59.70 (14)	C18—B8—B2	104.07 (16)
B8—B3—B4	107.98 (16)	C18—B8—B3	104.03 (16)
B8—C18—B7	63.05 (14)	C18—B8—B7	58.59 (13)
B8—C18—B9	62.97 (14)	C18—B8—B9	58.63 (13)
B9—B3—B2	108.39 (16)	C18—B9—B3	104.04 (16)
B9—B3—B4	59.54 (13)	C18—B9—B4	103.73 (16)
B9—B3—B8	60.85 (13)	C18—B9—B8	58.40 (13)

B9—B4—B3	59.60 (13)	C18—B9—B10	57.99 (13)
B9—B4—B5	108.18 (17)	C18—B10—B4	104.19 (16)
B9—B4—B10	60.52 (13)	C18—B10—B5	103.95 (16)
B9—B8—B7	108.35 (16)	C18—B10—B6	58.26 (13)
B9—B10—B6	108.39 (17)	C18—B10—B9	59.05 (13)
B9—C18—B7	115.64 (16)	N1—C14—C13	123.7 (2)
B10—B4—B3	108.07 (16)	N1—C15—C16	124.1 (2)
B10—B4—B5	59.58 (13)	O1—C2—C1	131.7 (2)
B10—B5—B1	108.00 (17)	O1—C2—O5	120.6 (2)
B10—B5—B4	59.75 (13)	O3—C10—C4	125.88 (18)
B10—B5—B6	60.74 (13)	O3—C10—O4	124.76 (17)
B10—B9—B8	107.65 (17)	O4—C10—C4	109.33 (16)
B10—C18—B6	63.71 (14)	O4—C11—C12	106.94 (14)
B10—C18—B7	116.05 (17)	O4—C11—C17	110.11 (15)
B10—C18—B8	115.56 (17)	O5—C2—C1	107.61 (17)
B10—C18—B9	62.95 (14)	O5—C4—C5	105.69 (15)
C1—C6—C4	91.14 (15)	O5—C4—C6	101.71 (14)
C2—C1—C6	98.91 (17)	O5—C4—C10	106.65 (15)

Table S4. Selected ^{1}H NMR chemical shifts (in ppm) of free *S*-**1**·*β*-CD·2NO_3 and the chemical shift differences induced when bound to d(GTCGAC)$_2$ at a metal complex-to-duplex ratio of 1:1 (numbers in parentheses), in 10 mM phosphate buffer (pH 7) containing 20 mM $NaNO_3$ and 0.1 mM EDTA in D_2O at 300 K.

Proton	Chemical shift	Proton	Chemical shift
$H3_{terpy}$	8.43 (-0.56)	$H2_{py}$	9.17 (-0.10)
$H4_{terpy}$	8.43 (-0.48)	$H3_{py}$	7.85 (-0.07)
$H5_{terpy}$	7.78 (-0.27)		
$H6_{terpy}$	7.85 (-0.61)		
$H3'_{terpy}$	8.43 (-0.48)		
$H4'_{terpy}$	8.55 (-0.32)		

Table S5. Selected ^{1}H NMR chemical shifts (in ppm) of d(GTCGAC)$_2$ and the chemical shift differences induced by the addition of *S*-**1**·*β*-CD·2NO_3 at a metal complex-to-duplex ratio of 1:1 (numbers in parentheses), in 10 mM phosphate buffer (pH 7) containing 20 mM $NaNO_3$ and 0.1 mM EDTA in D_2O at 300 K.

	H6/H8	H1'	H2'	H2''	H3'	AH2/CH5/TCH_3
G1	8.01 (-0.11)	6.07 (-0.13)	2.73 (-0.11)	2.81 (-0.07)	4.85 (-0.05)	
T2	7.52 (-0.08)	6.21 (-0.11)	2.25 (-0.11)	2.59 (-0.11)	4.93 (-0.07)	1.40 (-0.11)
C3	7.51 (-0.01)	5.72 (-0.14)*	2.05 (0.09)	2.42 (-0.28)	4.87 (-0.01)	5.72 (-0.14)
G4	7.96 (-0.12)	5.64 (-0.06)*	2.74 (-0.09)	2.79 (-0.14)	5.01 (-0.02)	
A5	8.19 (-0.02)	6.29 (-0.02)	2.65 (0.00)	2.89 (0.00)	5.02 (-0.01)	8.02 (-0.06)
C6	7.35 (-0.03)	6.07 (0.00)	2.09 (0.02)	2.09 (0.02)	4.48 (0.01)	5.39 (-0.13)

* very broad

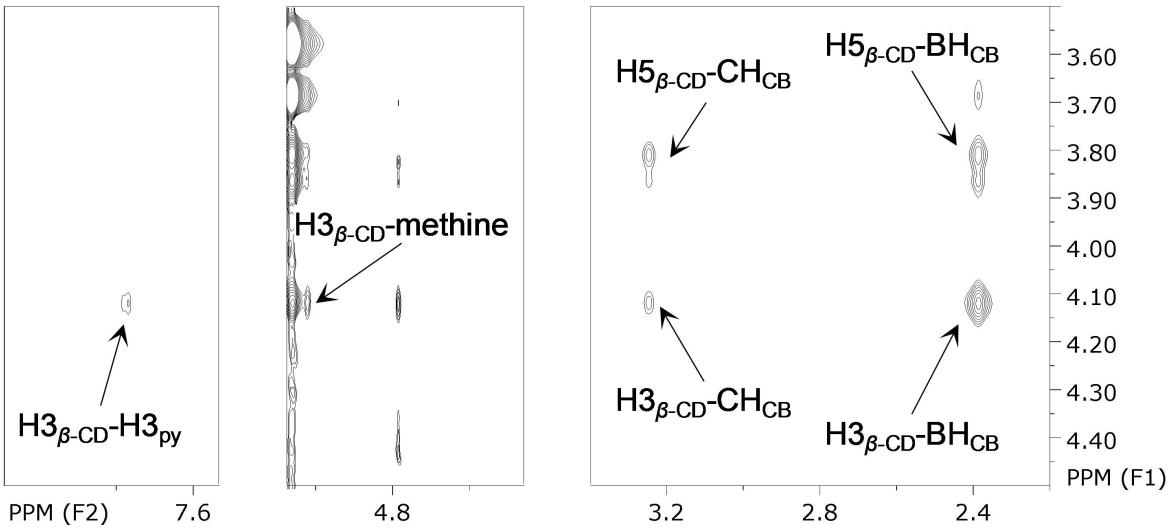


Figure S2. Expansions of a $^{1}H\{^{11}B\}$ ROESY spectrum of *S*-**1**·*β*-CD·2NO_3 in D_2O at 300 K, showing the ROE's between the interior protons of *β*-CD ($H3_{\beta\text{-CD}}$ and $H5_{\beta\text{-CD}}$) and the carboranyl ligand protons of metal complex (BH_{CB}, CH_{CB} the $H3_{py}$ and methine).

Molecular modelling

Molecular modelling was performed using HyperChem 7.5.[7] The d(GTCGAC)$_2$ nucleotides and β-CD residues were downloaded as residue templates from the database, and literature parameters for the platinum bonds[8] and carborane bonds[9] were added to the (Amber99) force-field, and were minimized to a root-mean-square gradient of 0.002 kJ (Å mol)$^{-1}$. Point charges were entered manually to reflect charge distributions from estimates of similar platinum(II) complexes,[10] the Pauli exclusion principle and AM1 single point calculations of the aliphatic ligands.

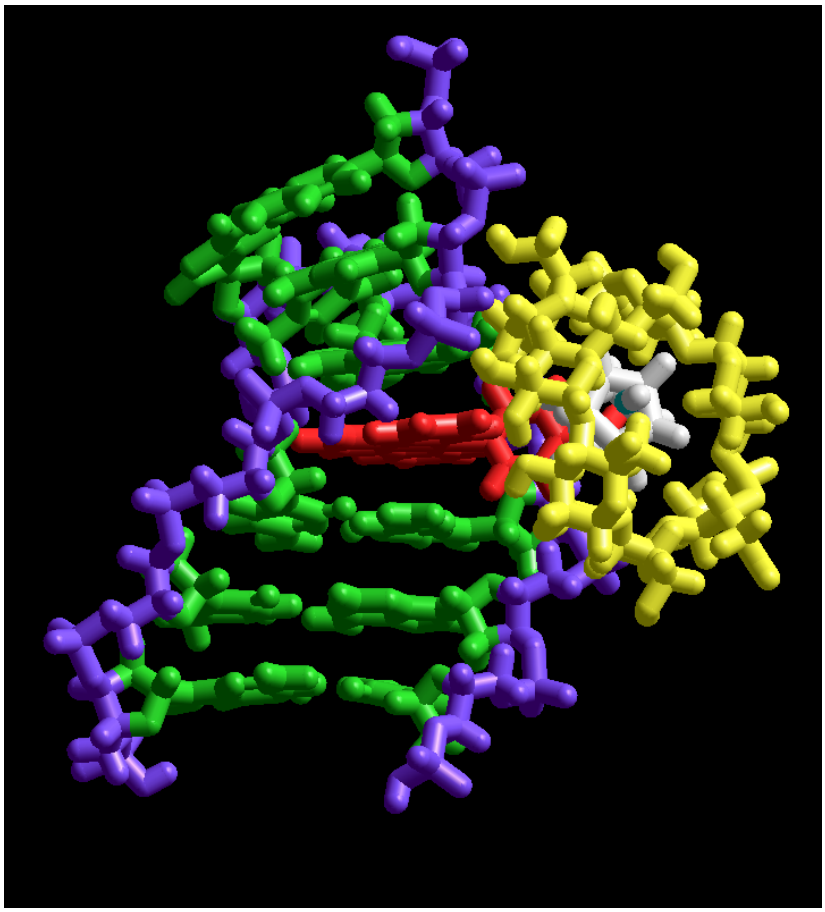


Figure S3. Model showing the ternary structure with intercalation from the minor groove. The d(GTCGAC)$_2$ residues are depicted in green and the phosphate/ribose backbones in purple. The platinum(II)-terpy complex is depicted in red, the carborane cage is white, and the β-CD is yellow.

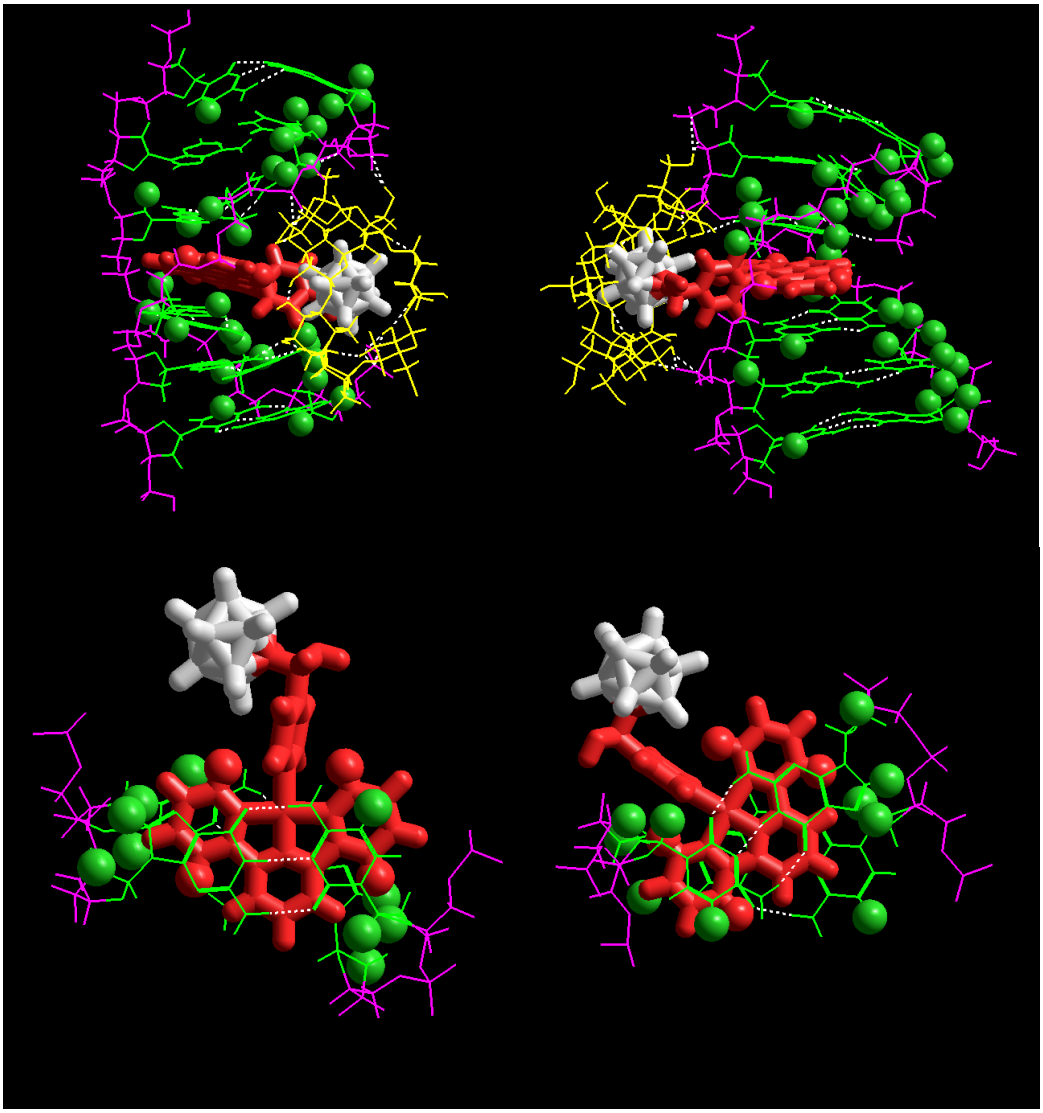


Figure S4. The major groove model is depicted in the left panels and the minor groove model in the right panels. Using the colour scheme of **Figure S3**, d(GTCGAC)$_2$ and β-CD residues are depicted as sticks and the metal complex is depicted as tubes, however, protons demonstrating the largest changes in chemical shift of each species are depicted as spheres. In the top panels, hydrogen bonds are indicated by dotted lines. In the bottom panels, only the DNA residues forming the putative intercalation site are depicted.

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