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New conjugates of cobalt bis(dicarbollide) with chlorophyll *a* derivatives

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Experimental

Absorption spectra were recorded on a Jasco - UV 7800 spectrophotometer in $CHCl_3$. ^1H NMR spectra were recorded on Bruker Avance 400 and Bruker DPX-300 spectrometers. IR spectra were measured on Bruker Equinox 55 in KBr pellets. Column chromatography was carried out on 40/60 silica gel (Merk). Preparative TLC was performed on silica gel 60 (Merck) using 200 x 200 x 1 mm plates. Analytical TLC was carried out on Kieselgel 60 F245 plates (Merck).

3a: ^1H NMR (acetone-d_6 + CF_3COOH + D_2O, ppm): 4.07 (2H, s, CH_{carb}), 3.98 (2H, s, CH_{carb}), 3.82 (2H, m, CH_2O), 3.71 (2H, m, CH_2O), 3.68 (2H, m, CH_2O), 3.62 (2H, m, CH_2N^+), 3.58 (2H, m, CH_2N^+), 3.41 (2H, m, CH_2N^+). ^{11}B NMR (acetone-d_6, ppm): 24.0 (1B, s), 5.9 (1B, d), 0.3 (1B, d), -2.5 (1B, d), -4.7 (2B, d), -6.8 (4B, d), -8.7 (2B, d), -17.2 (2B, d), -20.2 (2B, d), -22.3 (1B, d), -28.6 (1B, d).

3b: ^1H NMR (acetone-d_6 + CF_3COOH + D_2O, ppm): 4.09 (2H, s, CH_{carb}), 4.00 (2H, s, CH_{carb}), 3.97 (2H, m, CH_2O), 3.88 (2H, t, CH_2O), 3.71 (2H, t, CH_2O), 3.62 (2H, m, CH_2N^+), 3.41 (4H, m, CH_2N^+), 2.06 (4H, m, $NCH_2(CH_2)_2CH_2N$). ^{11}B NMR (acetone-d_6, ppm): 25.1 (1B, s), 7.6 (1B, d), 1.2 (1B, d), -1.8 (1B, d), -4.3 (2B, d), -6.0 (4B, d), -8.5 (2B, d), -16.5 (2B, d), -19.6 (2B, d), -21.7 (1B, d), -28.0 (1B, d).

3c: ^1H NMR (acetone-d_6 + CF_3COOH + D_2O, ppm): 4.07 (2H, s, CH_{carb}), 3.97 (2H, s, CH_{carb}), 3.88 (2H, m, CH_2O), 3.73 (2H, m, CH_2O), 3.62 (2H, m, CH_2O), 3.45 (2H, m, CH_2N^+), 3.32 (2H, m, CH_2N^+), 3.17 (2H, m, CH_2N^+), 1.88 (4H, m, $NCH_2CH_2(CH_2)_2CH_2CH_2N$), 1.50 (4H, m, $NCH_2CH_2(CH_2)_2CH_2CH_2N$). ^{11}B NMR (acetone-d_6, ppm): 23.2 (1B, s), 3.9 (1B, d), 0.36 (1B, d), -2.45 (1B, d), -4.4 (2B, d), -7.4 (6B, d), -17.3 (2B, d), -20.4 (3B, d), -28.5 (1B, d).

5a: ^{1}H NMR (acetone-d_6, ppm): 9.80 (1H, s, 5-*H*), 9.72 (1H, s, 10-*H*), 9.11 (1H, s, 20-*H*), 8.90 (1H, t, 13^2 -N*H*), 8.23 (1H, dd, 3^1-*H*), 6.42 (1H, d, E-3^2-*H*), 6.15 (1H, d, Z-3^2-*H*), 5.61 (1H, d, 15^1-CH_2), 5.43 (1H, d, 15^1-CH_2), 4.68 (1H, q, 18-*H*), 4.58 (1H, q, 17-*H*), 4.29 (4H, s, CH_{carb}), 4.11-3.90 (4H, m, OCH_2CH_2O), 3.85-3.70 (4H, m, 13^3-NCH_2CH_2N), 3.71 (3H, s, 15^2-COOCH_3), 3.61 (3H, s, 12-CH_3), 3.58 (3H, s, 17^3-COOCH_3), 3.53 (3H, s, 2-CH_3), 3.48 (6H, m, NCH_2CH_2O + 8^1-CH_2), 3.29 (3H, s, 7-CH_3), 2.74 (1H, m, 17^1-CH_2), 2.36-2.25 (3H, m, 17^2-CH_2 + 17^1-CH_2), 1.73 (3H, d, 18-CH_3), 1.69 (3H, t, 8^2-CH_3), -1.47 (1H, N*H*), -1.71 (1H, N*H*). UV ($CHCl_3$, nm): 400, 526, 609, 664. IR (KBr, cm^{-1}): 2547 (B-H), 1730 (C=O ester), 1642 (amide-I), 1538 (amide-II). MS-ESI (m/z): 1075 (M^-).

5b: ^{1}H NMR ($CDCl_3$, ppm): 9.65 (1H, s, 5-*H*), 9.55 (1H, s, 10-*H*), 9.08 (1H, s, 20-*H*), 7.94 (1H, dd, 3^1-*H*), 6.52 (1H, s, 13^{2-}–N*H*), 6.24 (1H, d, E-3^2-*H*), 6.03 (1H, d, Z-3^2-*H*), 5.34 (1H, d, 15^1-CH_2), 5.19 (1H, d, 15^1-CH_2), 4.48 (1H, g, 18-*H*,), 4.35 (1H, d, 17-*H*), 3.80 (4H, m, CH_{carb}), 3.80 (4H, m, OCH_2CH_2O), 3.74-3.58 (13H, m, 15^2-COOCH_3 + NCH_2CH_2O + NHCH_2CH$_2$CH$_2$CH_2N + 8^1-CH_2) 3.57 (3H, s, 12-CH_3), 3.47 (3H, s, 17^3-COOCH_3), 3.43 (3H, s, 2-CH_3), 3.25 (3H, s, 7-C_{H3}), 2.53 (1H, m, 17^1-CH_2), 2.30-2.10 (3H, m, 17^1-CH_2, 17^2-CH_2), 2.0-1.9 (4H, m, 13^2-NHCH$_2$CH_2CH_2CH$_2$N) 1.73 (6H, m, 18-CH_3, 8^2-CH_3), -1.64 (1H, s, N*H*), -1.82 (1H, s, N*H*). UV ($CHCl_3$, nm): 401, 525, 608, 662. IR (KBr, cm^{-1}): 2539 (B-H), 1734 (C=O ester), 1648 (amide-I), 1541 (amide-II). MS-ESI (m/z): 1103 (M^-).

5c: ^{1}H NMR (acetone-d_6, ppm): 9.77 (1H, s, 5-*H*), 9.75 (1H, s, 10-*H*), 9.19 (1H, s, 20-*H*), 8.23 (1H, dd, 3^1-*H*), 8.09 (1H, s, 13^2 -N*H*), 6.39 (1H, d, E-3^2-*H*), 6.12 (1H, d, Z-3^2-*H*), 5.60 (1H, d, 15^1-CH_2), 5.33 (1H, d, 15^1-CH_2), 4.70 (1H, q, 18-*H*), 4.53 (1H, d, 17-*H*), 4.09 (2H, s., CH_{carb}), 3.99 (2H, s, CH_{carb}), 3.80-3.58 (20H, OCH_2CH_2O + 15^2-COOCH_3 + NCH_2CH_2O + NHCH_2(CH$_2$CH$_2$)$_2$CH_2N + 8^1-CH_2 + 12-CH_3), 3.53 (3H, s, 17^3-COOCH_3), 3.48 (3H, s, 2-CH_3), 3.27 (3H, s, 7-CH_3), 2.73 (1H, m, 17^1-CH_2), 2.30 (3H, m, 17^1-CH_2, 17^2-CH_2), 1.75 (3H, d, 18-CH_3), 1.65 (3H, t, 8^2-CH$_3$), 1.61 (8H, m, NHCH$_2$C(CH_2CH$_2$)$_2$CH$_2$N), -1.88 (1H, s, N*H*), -2.10 (1H, s, N). UV ($CHCl_3$, nm): 400, 526, 608, 665. IR (KBr, cm^{-1}): 2550 (B-H), 1730 (C=O ester), 1693 (amide-I), 1541 (amide-II). MS-ESI (m/z): 1131 (M^-).

5d: UV ($CHCl_3$, nm): 423, 510, 564, 633. Co/Zn ratio: found 0.97, calculated 1.00.

6a: ^{1}H NMR ($CDCl_3$, ppm): 9.62 (1H, s, 5-*H*), 9.55 (1H, s, 10-*H*), 8.78 (1H, s, 20-*H*), 8.01 (1H, dd, 3^1-*H*), 7.73 (1H, 13^2 -N*H*), 6.31 (1H, d, E-3^2-*H*), 6.13 (1H, d, Z-3^2-*H*), 5.35 (1H, d, 15^1-CH_2), 5.14 (1H, d, 15^1-CH_2), 4.45 (1H, q, 18-*H*), 4.39 (1H, q, 17-*H*), 3.90 (4H, s, CH_{carb}), 3.80 (4H, s, CH_{carb}), 3.77 (3H, s, 15^2-COOCH_3), 3.72 (10H, m, OCH_2CH_2O + 8^1-CH_2), 3.60 (12H, m, NCH_2CH_2O + 13^3-NCH_2CH_2N), 3.56 (3H, s, 12-CH_3), 3.50 (3H, s, 17^3-COOCH_3), 3.46 (3H, s,

2-CH_3), 3.25 (3H, s, 7-CH_3), 3.10-2.95 (8H, m, *i*-Pr$_2$EtNH$^+$), 2.56 (2H, m, 17^1-CH_2), 2.20 (2H, m, 17^2-CH_2), 1.69 (3H, d, 18-CH_3), 1.67 (3H, t, 8^2-CH_3), 1.20 (30H, m, *i*-Pr$_2$EtNH$^+$), -1.52 (1H, s, N*H*), -1.64 (1H, s, N*H*). UV (CHCl$_3$, nm): 398, 524, 609, 665. IR (KBr, cm^{-1}): 2549 (B-H), 1733 (C=O ester), 1640 (amide-I), 1539 (amide-II). MS-ESI (m/*z*): 1488 (M$^-$).

6b: ^{1}H NMR (CDCl$_3$, ppm): 9.83 (1H, s, 5-*H*), 9.69 (1H, s, 10-*H*), 9.08 (1H, s, 20-*H*), 8.59 (1H, s, 13^2-N*H*), 8.18 (1H, dd, 3^1-*H*), 6.40 (1H, d, E-3^2-*H*), 6.13 (1H, d, Z-3^2-*H*), 5.63 (1H, d, 15^1-CH_2), 5.42 (1H, d, 15^1-CH_2), 4.65 (1H, q, 18-*H*), 4.57 (1H, d, 17-*H*), 4.20 (8H, s, CH_{carb}), 3.80-3.70 (19H, OCH_2CH_2O + 15^2-COOCH_3 + NCH_2CH_2O), 3.70-3.62 (6H, m, 13^2-NHCH_2CH$_2$CH$_2$CH_2N + 8^1-CH_2), 3.62 (3H, s, 12-CH_3), 3.60 (3H, s, 17^3-COOCH_3), 3.50 (3H, s, 2-CH_3), 3.29 (3H, s, 7-CH_3), 3.22-3.18 (8H, m, *i*-Pr$_2$EtNH$^+$), 2.68 (1H, m, 17^1-CH_2), 2.30 (3H, m, 17^1-CH_2, 17^2-CH_2), 2.0 (4H, m, 13^2-NHCH$_2$CH_2CH_2CH$_2$N), 1.73 (6H, m, 18-CH_3, 8^2-CH_3), 1.35 (30H, m, *i*-Pr$_2$EtNH$^+$), -1.51 (1H, s, N*H*), -1.77 (1H, s, N*H*). UV (CHCl$_3$, nm): 400, 527, 610, 665. IR (KBr, cm^{-1}): 2544 (B-H), 1730 (C=O ester), 1645 (amide-I), 1544 (amide-II). MS-ESI (m/z): 1516 (M$^-$).

6c: ^{1}H NMR (CDCl$_3$, ppm): 9.83 (1H, s, 5-*H*), 9.69 (1H, s, 10-*H*), 9.08 (1H, s, 20-*H*), 8.59 (1H, s, 13^2 -N*H*), 8.18 (1H, dd, 3^1-*H*), 6.40 (1H, d, E-3^2-*H*), 6.13 (1H, d, Z-3^2-*H*), 5.17 (1H, d, 15^1-CH_2), 4.90 (1H, d, 15^1-CH_2), 4.65 (1H, q, 18-*H*), 4.57 (1H, d, 17-*H*), 4.00 (8H, s, CH$_{carb}$), 3.80 (8H, m, OCH_2CH_2O), 3.77 (3H, s, 15^2-COOCH_3), 3.74 (8H, m, NCH_2CH_2O), 3.70-3.62 (6H, m, 13^2-NHCH_2(CH$_2$CH$_2$)$_2$CH_2N + 8^1-CH_2) 3.62 (3H, s, 12-CH_3), 3.60 (3H, s, 17^3-COOCH_3), 3.50 (3H, s, 2-CH_3), 3.29 (3H, s, 7-CH_3), 3.20-3.10 (8H, m, *i*-Pr$_2$EtNH$^+$), 2.68 (1H, m, 17^1-CH_2), 2.30 (3H, m, 17^1-CH_2, 17^2-CH_2), 2.00 (8H, m, 13^2-NHCH$_2$(CH_2CH_2)$_2$CH$_2$N), 1.73 (6H, m, 18-CH_3, 8^2-CH_3), 1.35 (30H, m, *i*-Pr$_2$EtNH$^+$), -1.51 (1H, s, N*H*), -1.77 (1H, s, N*H*). UV (CHCl$_3$, nm): 401, 522, 609, 663. IR (KBr, cm^{-1}): 2550 (B-H), 1737 (C=O ester), 1643 (amide-I), 1549 (amide-II). MS-ESI (m/z): 1544 (M$^-$).

6d: UV (CHCl$_3$, nm): 421, 507, 566, 635. Co/Zn ratio: found 2.06, calculated 2.00.

9: UV (CHCl$_3$, nm): 419, 545, 640, 707. MS (MALDI) (m/z): 621 (M$^+$).

10: ^{1}H NMR (CDCl$_3$, ppm): 9.48 (1H, s, 5-*H*), 9.25 (1H, s, 10-*H*), 8.51 (1H, s, 20-*H*), 7.83 (1H, dd, *J* = 18 Hz, *J* =12 Hz, 3^1-*H*), 6.27 (1H, d, *J* = 18 Hz, E-3^2-*H*), 6.15 (1H, d, *J* = 12 Hz, Z-3^2-*H*), 5.21 (1H, d, *J* = 9 Hz, 17-*H*), 4.82 (2H, m, NCH_2CH$_2$NH$_2^+$), 4.34 (1H, q, *J* = 7 Hz, 18-*H*), 3.89 (2H, m, NCH$_2$CH_2NH$_2^+$), 3.73 (4H, s, CH_{carb}), 3.65 (4H, м, OCH_2CH_2O), 3.64 (2H, m., 8^1-CH_2), 3.61 (3H, s, 12-CH_3), 3.60 (4H, m, H$_2$N$^+$CH_2CH_2O), 3.55 (3H, s, 17^3-COOCH_3), 3.31 (3H, s, 2-CH_3), 3.10 (3H, s, 7-CH_3), 2.73 (1H, m, 17^1-CH_2), 2.43 (2H, m, 17^1-CH_2 + 17^2-CH_2), 1.93

(1H, m, 17^2-CH_2), 1.74 (3H, d, J = 7 Hz, 18-CH_3), 1.64 (3H, t, J = 8 Hz, 8^2-CH_3), 0.37 (1H, s, N*H*), 0.24 (1H, s, N*H*). UV ($CHCl_3$, nm): 415, 546, 634, 706.

11: ^{1}H NMR (acetone-d_6, ppm): 9.65 (1H, s, 5-*H*), 9.11 (1H, s, 10-*H*), 8,76 (1H, s, 20-*H*), 5.37 (1H, m, 17-*H*), 4.50 (1H, m, 18-*H*), 4.10 (8H, m, OCH_2CH_2O), 4.04 (4H, s, CH_{carb}), 3.95 (3H, q, 3^1-CH_3), 3.88 (4H, s, CH_{carb}), 3.79 (3H, s, 12^1 -CH_3); 3.67 (8H, m, NCH_2CH_2O), 3.52 (3H, s, 17^5-CH_3), 3.22 (3H, s, 2^1-CH_3), 3.0-2.8 (11H, m, 7-CH_3 + *i*-Pr_2EtNH^+), 2.74 (1H, m, 17^1-*H*), 2.47 (2H, s, 17^2-*H* + 17^1-*H*), 2.00 (1H, m, 17^2-*H*), 1.84 (3H, d, 18-CH_3), 1.62 (3H, t, J = 7 Гц, 3^2-CH_3), 1.55 (3H, t, J = 7.5 Hz, 8^2-CH_3), 1.35 (30H, m, *i*-Pr_2EtNH^+), 0.14 (1H, s, N*H*), -0.10 (1H, s, N*H*). UV ($CHCl_3$, nm): 421, 547, 640, 702. MS-MALDI (m/z): 1411 (M^{2-}), 1434 (M^{2-} + Na^+).

12: ^{1}H NMR ($CDCl_3$, ppm): 9.31 (1H, s, 5-*H*), 9.14 (1H, s, 10-*H*), 8.49 (1H, s, 20-*H*), 7.77 (1H, dd, J = 18 Hz, 12 Hz, 3^1-*H*), 6.19 (1H, d, J = 18 Hz, E-3^2-*H*), 6.08 (1H, d, J = 12 Hz, Z-3^2-*H*), 5.15 (1H, d, J = 9 Hz, 17-*H*), 4.73 (2H, t, NCH_2CH$_2$N), 4.25 (1H, q, J = 7 Hz, 18-*H*), 3.95 (2H, m., NCH$_2$CH_2N), 3.87 (8H, s, CH_{carb}), 3.75 (8H, m, OCH_2CH_2O), 3.64 (2H, m., 8^1-CH_2), 3.60 (3H, s, 12-CH_3), 3.55 (8H, m, NCH_2CH_2O), 3.43 (3H, s, 17^3-COOCH_3), 3.24 (3H, s, 2-CH_3), 3.15 - 3.0 (8H, m, *i*-Pr_2EtNH^+), 2.97 (3H, s, 7-CH_3), 2.57 (1H, m, 17^1-CH_2), 2.25 (3H, m, 17^1-CH_2 + 17^2-CH_2), 1.72 (3H, d, J = 7 Hz, 18-CH_3), 1.48 (3H, t, J = 8 Hz, 8^2-CH_3), 0.85 (30H, m, *i*-Pr_2EtNH^+), 0.11 (1H, s, N*H*), 0.09 (1H, s, N*H*). UV ($CHCl_3$, nm): 419, 545, 640, 707.