Electronic Supplementary Material (ESI) for CrystEngComm

Water-mediated supramolecular architecture of Co(III)–phenanthroline complexes: Organizational control to 2D-layers and 3D-square cavities through substituted aryl carboxylate anions

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Electronic supplementary information:

1) Details of synthetic procedures, physicochemical and spectral data of complexes **1**–**8**
2) Molecular and packing diagrams of complexes **2**–**8**
3) Structural parameters of complexes **1**–**8**
4) Hydrogen bonding parameters of complexes **1**–**8**

1) Details of synthetic procedures, physicochemical and spectral data of complexes 1–8

[Co(phen)$_2$CO$_3$](3-nitrobenzoate)·4H$_2$O (1)

[Co(phen$_{)2}$CO$_3$]Cl·5H$_2$O (0.5 g, 0.8 mmol) was dissolved in 10 mL of water and to this 10 mL aqueous solution of 0.156 g (0.8 mmol) sodium salt of 3-nitrobenzoic acid was added. When the resultant solution was allowed to evaporate slowly at room temperature, reddish-pink colored crystals started appearing on next day, which were collected and dried in air (yield 88%). The complex salt decomposed at 140^{o}C. Anal. Calcd. (%) for $C_{32}H_{28}CoN_5O_{11}$: C, 53.52; H, 3.90; N, 9.76; Co, 8.22. Found (%): C, 54.30; H, 3.85; N, 9.74; Co, 8.15. IR/cm^{-1} (KBr pellet, b = broad, s = strong, m = medium, w = weak): 3434(b), 3057(w), 1665(s), 1632(s), 1569(m), 1546(w), 1518(m), 1426(s), 1391(m), 1317(w), 1224(s), 1145(m), 1011(s), 854(s), 781(w), 750(s), 718(s), 686(w), 637(w), 529(w), 478(s). ^{1}H NMR/ppm (DMSO-d$_6$): cation, [Co(phen)$_2$CO$_3$]$^+$, δ = 9.19(d, H9), 8.99(d, H7), 8.55(d, H2), 8.31(t, H8), 8.19(d, H6), 8.09(m, H5), 7.47(m, H3/4); Anion, [C$_7$H$_4$NO$_4$]$^-$, δ = 8.09(m, H4), 8.01(m, H6), 7.47(m, H5). ^{13}C NMR/ppm (DMSO-d$_6$): δ = 173.76, 164.57, 153.45, 151.15, 147.50, 141.37, 140.33, 135.02, 130.96, 129.36, 128.12, 127.80, 127.68, 126.40, 125.48, 123.47, 99.90. Solubility (H$_2$O, 25^{o}C) = 0.612 g/100 mL, K_{sp} = 7.22×10^{-5}. UV/Vis (λ_{max} (nm) (logε), H$_2$O): 218 (5.06), 272 (4.92), 352 (3.41), 511 (2.12).

[Co(phen)$_2$CO$_3$](4-nitrobenzoate)·5H$_2$O (2)

To a 10 mL solution of [Co(phen)$_2$CO$_3$]Cl·5H$_2$O (0.5 g, 0.8 mmol) in water, 10 mL solution of sodium salt of 4-nitrobenzoic acid (0.156 g, 0.8 mmol) was added. When the solution was allowed to evaporate slowly at room temperature, reddish pink colored crystals appeared after one day, which were separated from the mother liquor and dried in the air (yield 85%). The complex salt decomposed at 135^{o}C. Anal. Calcd. (%) for $C_{32}H_{30}CoN_5O_2$: C, 55.20; H, 4.07; N, 9.52; Co, 8.02. Found (%): C, 51.95; H, 4.01; N, 9.50; Co, 7.80. IR/cm^{-1} (KBr): 3360(b), 3040(w), 1663(s), 1631(s), 1580(s), 1514(s), 1427(s), 1226(s), 1146(w), 1097(m), 1013(w), 855(s), 824(m), 799(w), 748(w), 720(s), 674(w), 503(w), 480(m). ^{1}H NMR/ppm (DMSO-d$_6$): cation, [Co(phen)$_2$CO$_3$]$^+$, δ = 9.21(d, H9), 9.00(d, H7), 8.56(d, H2), 8.32(m, H8), 8.00(d, H6), 7.74(d, H5), 7.46(m, H4/3); Anion, [C$_7$H$_4$NO$_4$]$^-$, δ = 8.19(d, H3/5), 8.08(d, H 2/6). ^{13}C NMR/ppm (DMSO-d$_6$): δ = 173.5, 166.56, 153.44, 151.06, 148.64, 147.47, 147.40, 141.37, 140.34, 130.95, 130.86, 129.42, 128.13, 127.82, 127.69, 126.43, 123.28. Solubility (H$_2$O, 25^{o}C) = 1.151 g/100 mL. K_{sp} = 2.43×10^{-4}. UV/Vis (λ_{max} (nm) (logε), H$_2$O): 222 (4.93), 273 (4.88), 352 (3.31), 510 (2.08).

$[Co(phen)_2CO_3]$(2-chloro-4-nitrobenzoate)·$5H_2O$ (3)

0.5 g of $[Co(phen)_2CO_3]Cl·5H_2O$ (0.8 mmol) was dissolved in 10 mL of water in a beaker and in another beaker, 0.166 g (0.8mmol) of 2-chloro-4-nitrobenzoic acid and 0.033 g (0.8 mmol) sodium hydroxide were dissolved in 10 mL of water. Two solutions were mixed. Red colored crystals appeared after two days when resulting solution was allowed to evaporate slowly at room temperature. Crystals were collected and dried in air (yield 75%). The complex salt decomposed at 122^oC. Anal. Calcd. (%) for $C_{32}H_{29}ClCoN_5O_{12}$: C, 49.87; H, 3.77; N, 9.09; Co, 7.66. Found (%): C, 49.70; H, 3.65; N, 8.95; Co, 7.60. IR/cm^{-1} (KBr): 3370(b), 3090(w), 1664(w), 1633(s), 1587(w), 1517(s), 1429(s), 1388(w), 1346(s), 1336(m), 1224(m), 1145(m), 1093(w), 1043(w), 857(s), 825(w), 740(s), 720(s), 672(w), 654(w), 508(w), 479(m). ^1H NMR/ppm (DMSO-d_6): cation, $[Co(phen)_2CO_3]^+$, δ = 9.25(d, H9), 9.05(d, H7), 8.61(d, H2), 8.37(t, H8), 8.25(d, H6), 8.13(d, H5), 7.52(m,H3/4); Anion, $[C_7H_3NO_4Cl]^-$, δ = 8.03(d, H3), 7.52(m, H5), 7.44(d, H5). ^{13}C NMR/ppm (DMSO-d_6): δ = 174.02, 166.29, 153.51, 151.24, 147.47, 141.43, 140.39, 131.01, 130.92, 128.18, 127.87, 127.74, 127.60, 126.49, 124.81, 122.39. Solubility (H_2O, 25^oC) = 1.953 g/100 mL. K_{sp} = 6.45×10^{-4}. UV/Vis (λ_{max} (nm) (logε), H_2O): 223 (4.93), 273 (4.86), 351 (3.32), 511 (2.02).

$[Co(phen)_2CO_3]$(3-methyl-4-nitrobenzoate)·$5H_2O$ (4)

$[Co(phen)_2CO_3]Cl·5H_2O$ (0.5 g, 0.8 mmol) was dissolved in 10 mL of water in a beaker and to this, 10 mL aqueous solution of 0.168 g (0.8 mmol) sodium salt of 3-methyl-4-nitrobenzoic acid was added. When the resultant solution was allowed to evaporate slowly at room temperature, pink colored crystals started appearing after one day, which were collected and dried in air (yield 78%). The complex salt decomposed at 230^oC. Anal. Calcd. (%) for $C_{33}H_{32}CoN_5O_{12}$: C, 52.28; H, 4.27; N, 9.34; Co, 7.87. Found (%): C, 52.10; H, 4.15; N, 9.25; Co, 7.60. IR/cm^{-1} (KBr): 3354(b), 3050(w), 1663(w), 1634(s), 1571(m), 1515(s), 1428(s), 1396(w), 1342(s), 1231(s), 1145(w), 1014(w), 852(s), 791(s), 744(m), 718(s), 653(w), 562(w), 478(m). ^1H NMR/ppm (DMSO-d_6): cation, $[Co(phen)_2CO_3]^+$, δ = 9.23(d, H9), 8.99(d, H7), 8.53(d, H2), 8.34(t, H8), 8.16(d, H6), 8.03(m, H5), 7.45(m, H3,4); Anion, $[C_8H_6NO_4]^-$, δ = 7.55(m, H5,6), 7.45(m, H2), 2.23(s, $-CH_3$). ^{13}C NMR/ppm (DMSO-d_6): δ = 173.09, 166.36, 153.41, 151.23, 149.48, 147.36, 141.35, 140.82, 140.29, 133.35, 132.79, 130.88, 130.77, 128.09, 127.84, 127.66, 126.82, 126.54, 124.27, 19.20. Solubility (H_2O, 25^oC) = 1.943 g/100 mL, K_{sp} = 6.71×10^{-4}. UV/Vis (λ_{max} (nm) (logε), H_2O): 223 (4.98), 272 (4.91), 350 (3.48), 510 (2.11).

$[Co(phen)_2CO_3]$(4-chlorobenzoate)·$7H_2O$ (5)

0.5 g of $[Co(phen)_2CO_3]Cl·5H_2O$ (0.8 mmol) was dissolved in 10 mL of water in a beaker. In another beaker, 0.129 g (0.8 mmol) of 4-chlorobenzoic acid and 0.033 g (0.8 mmol) of sodium hydroxide were dissolved in 10 mL of water. On mixing the two solutions, red colored crystals started appearing after 10 days. Crystals were collected and dried in air (yield 68%). The complex salt melted at 80°C. Anal. Calcd. (%) for $C_{32}H_{34}ClCoN_4O_{12}$: C, 50.46; H, 4.47; N, 7.36; Co, 7.75. Found (%): C, 50.35; H, 4.40; N, 7.30; Co, 7.60. IR/cm^{-1} (KBr): 3352(b), 3040(w), 1661(m), 1628(s), 1559(s), 1520(w), 1430(s), 1376(s), 1236(s), 1147(w), 1013(w), 850(s), 785(s), 746(w), 719(s), 664(w), 540(w), 478(m). ^{1}H NMR/ppm (DMSO-d_6): cation, $[Co(phen)_2CO_3]^+$, δ = 9.22(d, H9), 8.94(d, H7), 8.49(d, H2), 8.30(m, H8), 8.10(d, H6), 7.98(d, H5), 7.43(m,H3/4); Anion, $[C_7H_4O_2Cl]^-$, δ = 7.43(m, H3/5), 6.98(d, H2/6). ^{13}C NMR/ppm (DMSO-d_6): δ = 166.39, 153.37, 151.19, 147.30, 147.26, 141.31, 140.27, 136.15, 130.82, 130.72, 130.15, 128.06, 127.91, 127.80, 127.61, 126.45. Solubility (H_2O, 25°C) = 3.984 g/100 mL, $K_{sp} = 2.75\times10^{-3}$. UV/Vis ($\lambda_{max}$ (nm) (logε), H_2O): 225 (4.98), 273 (4.85), 351 (3.28), 509 (2.12).

$[Co(phen)_2CO_3]$(2-iodobenzoate)·$7H_2O$ (6)

0.5 g of $[Co(phen)_2CO_3]Cl·5H_2O$ (0.8 mmol) was dissolved in 10 mL of water in a beaker and in another beaker, 0.205 g (0.8 mmol) of 2-iodobenzoic acid and 0.033 g (0.8 mmol) of sodium hydroxide were dissolved in 10 mL of water. On mixing the two solutions, red colored crystals started appearing after one week. Crystals were collected and dried in air (yield 75%). The complex salt decomposed at 205°C. Calcd. (%) for $C_{32}H_{34}CoIN_4O_{12}$: C, 45.04; H, 3.99; N, 6.57; Co, 6.92. Found (%): C, 44.80; H, 3.90; N, 6.52; Co, 6.80. IR/cm^{-1} (KBr): 3425(b), 3055(w), 1662(m), 1632(s), 1583(m), 1561(w), 1519(m), 1481(s), 1428(m), 1233(s), 1149(s), 1096(s), 1038(w), 852(s), 804(w), 758(s), 719(s), 696(w), 580(w), 481(m). ^{1}H NMR/ppm (DMSO-d_6): cation, $[Co(phen)_2CO_3]^+$, δ = 9.21(d, H9), 8.99(d, H7), 8.55(d, H2), 8.33(m, H8), 8.17(d, H6), 8.06(d, H5), 7.50(m,H3/4); Anion, $[C_7H_4O_2I]^-$, δ = 7.57(d, H6), 7.21(t, H4), 7.15(t, H5), 6.84(d, H3). ^{13}C NMR/ppm (DMSO-d_6): δ = 172.01, 168.33, 154.11, 151.85, 148.10, 148.05, 142.04, 141.02, 139.50, 131.60, 131.53, 129.99, 128.80, 128.69, 128.50, 128.35, 127.16, 126.99, 92.10. Solubility (H_2O, 25°C) = 4.212 g/100 mL. $K_{sp} = 2.44\times10^{-3}$. UV/Vis ($\lambda_{max}$ (nm) (logε), H_2O): 225 (4.90), 272 (4.76), 351 (3.18), 510 (1.97).

$[Co(phen)_2CO_3]$(2-phenoxybenzoate)·$8H_2O$ (7)

$[Co(phen)_2CO_3]Cl·5H_2O$ (0.5 g, 0.8 mmol) was dissolved in 10 mL of water and to this 10 mL aqueous solution of 0.195 g (0.8 mmol) sodium salt of 2-phenoxybenzoic acid was added. When the resultant solution was allowed to evaporate slowly at room temperature, reddish pink coloured crystals started appearing after four days, which were collected and dried in air (yield 88%). The complex salt decomposed at 83°C. Anal. Calcd. (%) for $C_{38}H_{41}CoN_4O_{14}$: C, 54.50; H, 4.90; N, 6.70; Co, 7.05. Found (%): C, 54.30; H, 4.85; N, 6.62; Co, 6.95. IR/cm^{-1} (KBr): 3434(b), 3057(w), 1665(s), 1632(s), 1569(m), 1546(w), 1518(m), 1426(s), 1391(m), 1317(w), 1224(s), 1145(m), 1011(s), 854(s), 781(w), 750(s), 718(s), 686(w), 637(w), 529(w), 478(s). ^{1}H NMR/ppm (DMSO-d_6): cation, $[Co(phen)_2CO_3]^+$, δ = 9.19(d, H9), 8.96(d, H7), 8.52(d, H2), 8.29(t, H8), 8.14(d, H6), 8.03(m, H5), 7.44(m, H3,4); Anion, $[C_{13}H_9O_3]^-$, δ = 7.36(m, H6), 7.11(m, H3/4/5), 7.03(d, H9), 6.88(m, H13), 6.71(d, H10/11/12). ^{13}C NMR/ppm (DMSO-d_6): δ = 157.31, 153.40, 151.16, 147.40, 147.35, 141.35, 140.32, 130.90, 130.82, 130.32, 129.66, 128.77, 128.12, 127.81, 127.66, 126.45, 123.94, 122.91, 119.93, 117.72 Solubility (H_2O, 25°C) = 3.201 g/100 mL, K_{sp} =1.44×10^{-3}. UV/Vis (λ_{max} (nm) (logε), H_2O): 223 (5.00), 274 (4.85), 352 (3.23), 508 (2.10).

$[Co(phen)_2CO_3]$(2-napthaleneacetate)·$7H_2O$ (8)

0.5 g of $[Co(phen)_2CO_3]Cl·5H_2O$ (0.8 mmol) was dissolved in 10 mL of water taken in a beaker and in another beaker, 0.154 g (0.8 mmol) of 2-napthaleneacetic acid and 0.033 g (0.8 mmol) of sodium hydroxide were dissolved in 10 mL of water. Upon mixing two solutions, reddish-orange colored crystal appeared after one week. Crystals were collected and dried in air (yield 65%). The complex salt decomposed at 85°C. Anal. Calcd. (%) for $C_{37}H_{39}CoN_4O_{12}$: C, 56.15; H, 4.93; N, 7.08; Co, 7.46. Found (%): C, 55.98; H, 4.90; N, 6.98; Co, 7.38. IR/cm^{-1} (KBr): 3352(b), 3040(w), 1661(m), 1628(s), 1559(s), 1520(w), 1430(s), 1376(s), 1236(s), 1147(w), 1013(w), 850(s), 785(s), 746(w), 719(s), 664(w), 540(w), 478(m). ^{1}H NMR/ppm (DMSO-d_6): cation, $[Co(phen)_2CO_3]^+$, δ = 9.18(d, H9), 8.94(d, H7), 8.48(d, H2), 8.27(m, H8), 8.12(d, H6), 8.00(d, H5), 7.39(m,H3/4); Anion, $[C_{12}H_9O_2]^-$, δ = 7.72(d, H4), 7.57(d, H11), 7.48(d, H6) 7.29(t, H5), 7.21(m, H8/9/10). ^{13}C NMR/ppm (DMSO-d_6): δ = 177.23, 166.62, 153.32, 151.10, 147.38, 147.33, 141.33, 133.22, 130.89, 130.79, 128.33, 128.06, 127.75, 127.61, 126.94, 126.36, 126.17, 125.73, 125.69, 123.73, 88.31. Solubility (H_2O, 25°C) = 0.604 g/100 mL, K_{sp} = 5.84×10^{-6}. UV/Vis (λ_{max} (nm) (logε), H_2O): 225 (5.07), 272 (4.72), 351 (3.07), 507 (2.16).

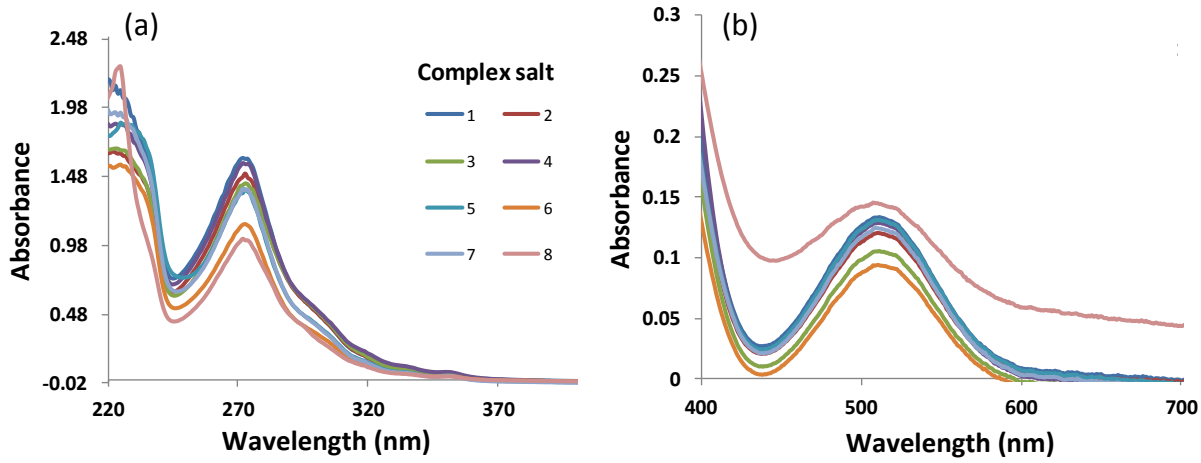
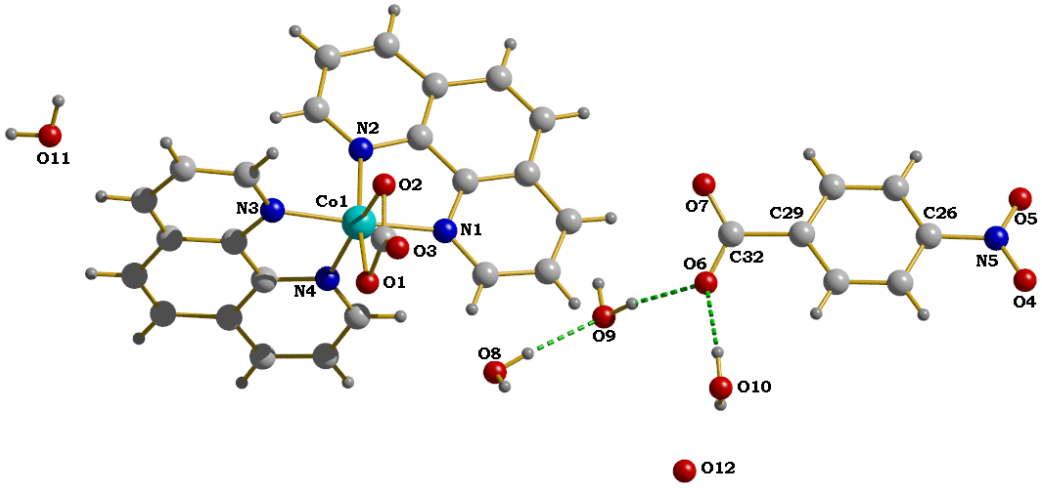
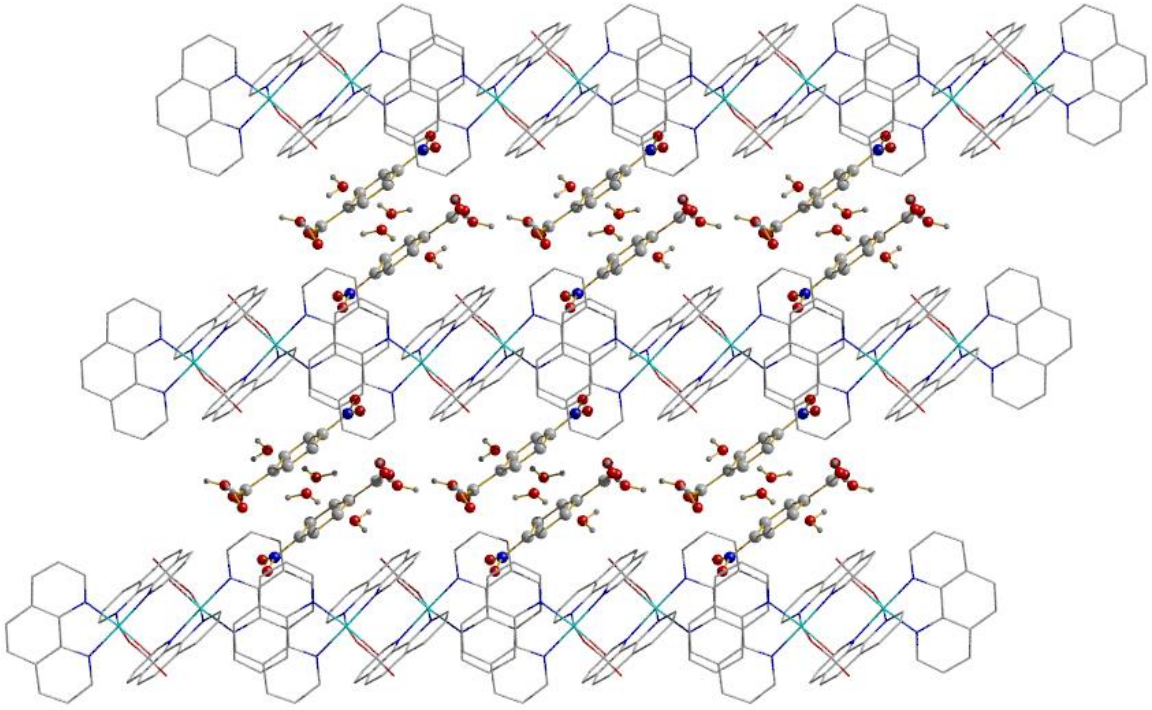


Fig. S1 (a) UV and (b) visible spectra of the $[Co(phen)_2CO_3]L{\cdot}nH_2O$ complexes in water at 25°C where L = 3-nitrobenzoate, *n* = 4, **1**; 4-nitrobenzoate, *n* = 5, **2**; 3-chloro-4-nitrobenzoate, *n* = 5, **3**; 3-methyl-4-nitrobenzoate, *n* = 5, **4**; 4-chlorobenzoate, *n* = 7, **5**; 2-iodobenzoate, *n* = 7, **6**; 3-phenoxybenzoate, *n* = 8, **7**; 2-napthaleneacetate, *n* = 7, **8**

2) Molecular and packing diagrams of complexes **2**–**8**



(a)



(b)

Fig. S2 (a) Molecular diagram of complex salt **2**. (b) Packing diagram showing the arrangement of cations and anions viewed down *c* axis where the complex cations are represented by sticks and anions and water molecules by ball and stick model.

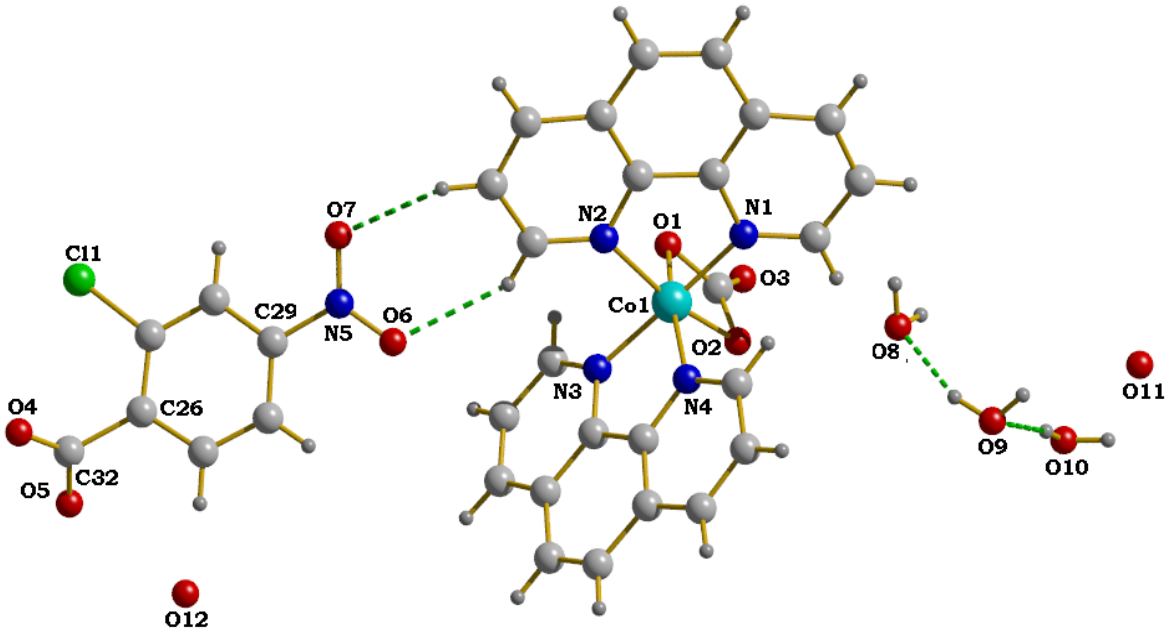
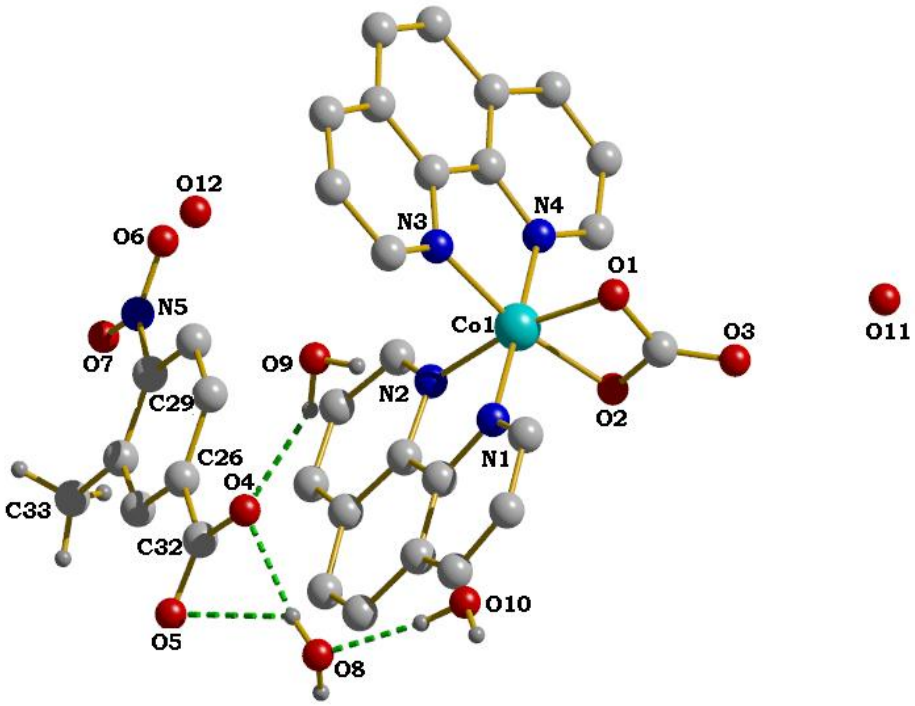
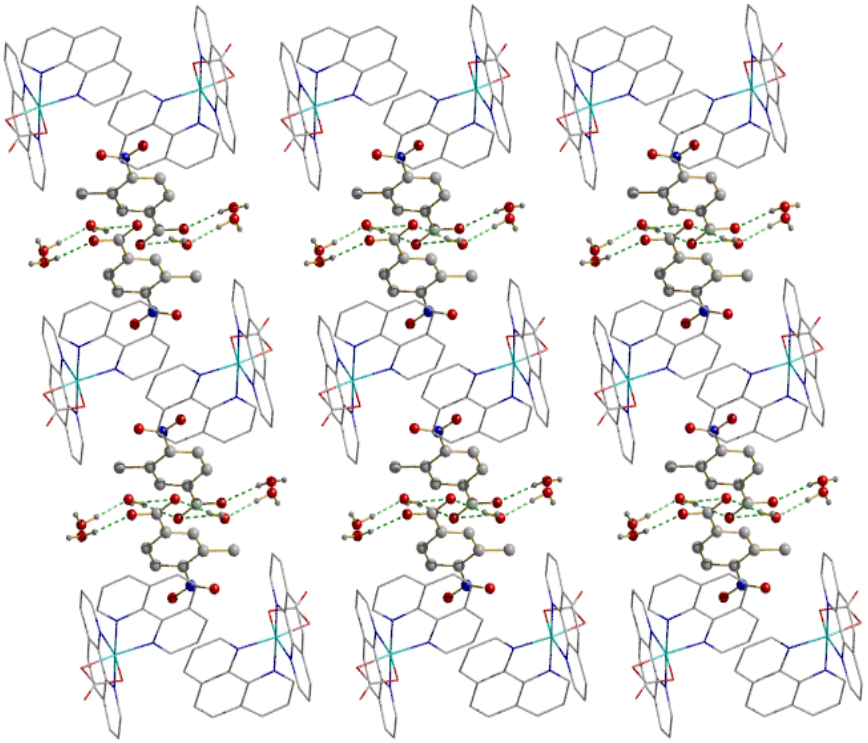


Fig. S3 Molecular diagram of complex salt **3**.

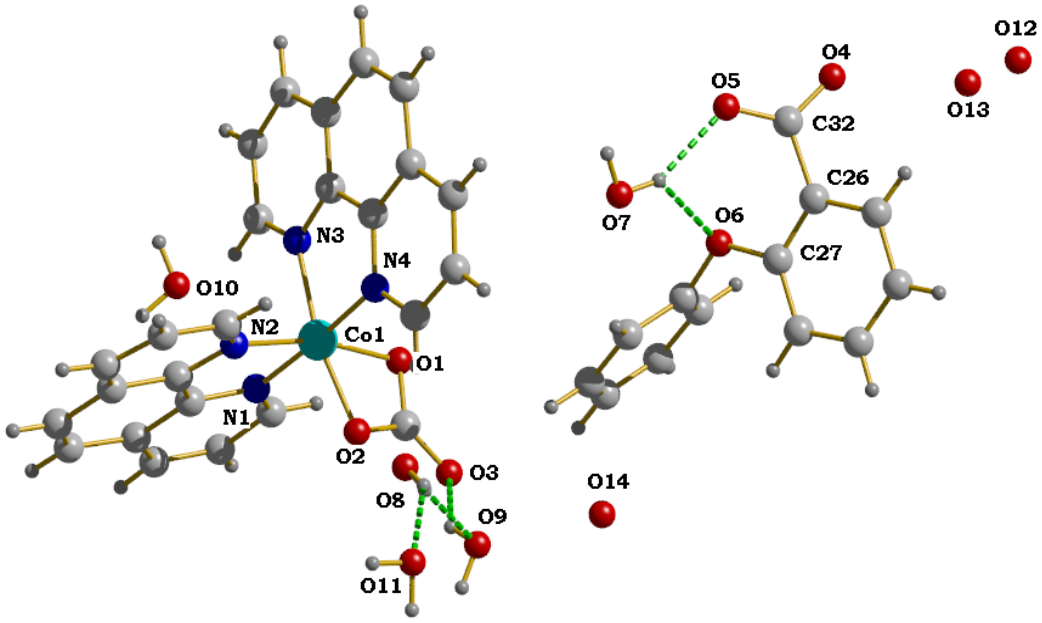


(a)

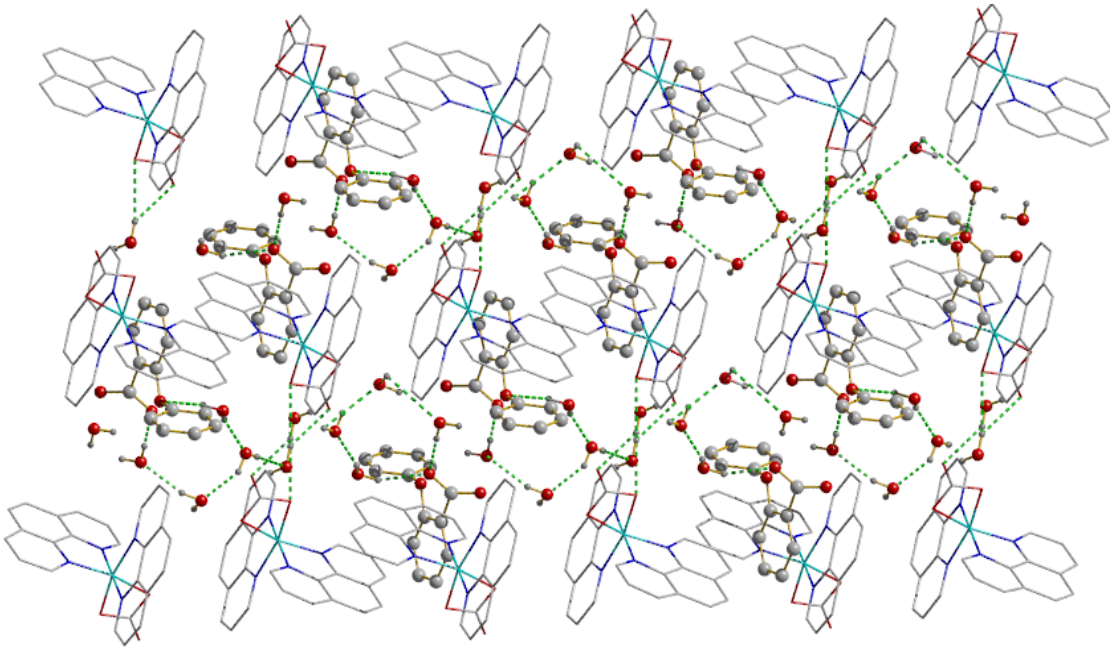


(b)

Fig. S4 (a) Molecular and (b) packing diagrams of complex salt **4**.



(a)



(b)

Fig. S5 (a) Molecular and (b) packing diagrams of complex salt **7**.

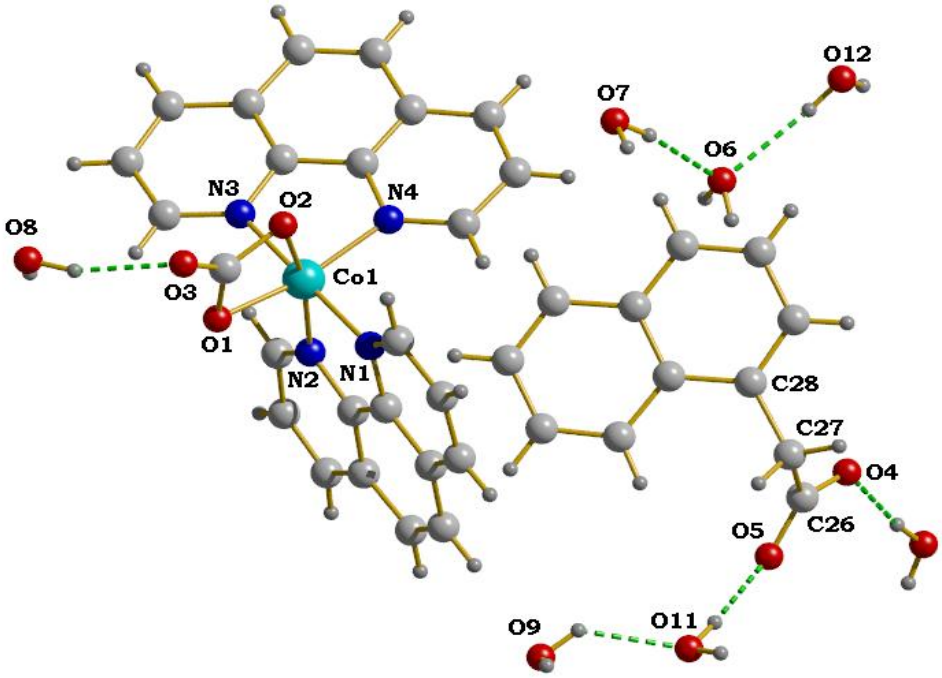


Fig. S6 Molecular diagram of complex salt **8**.

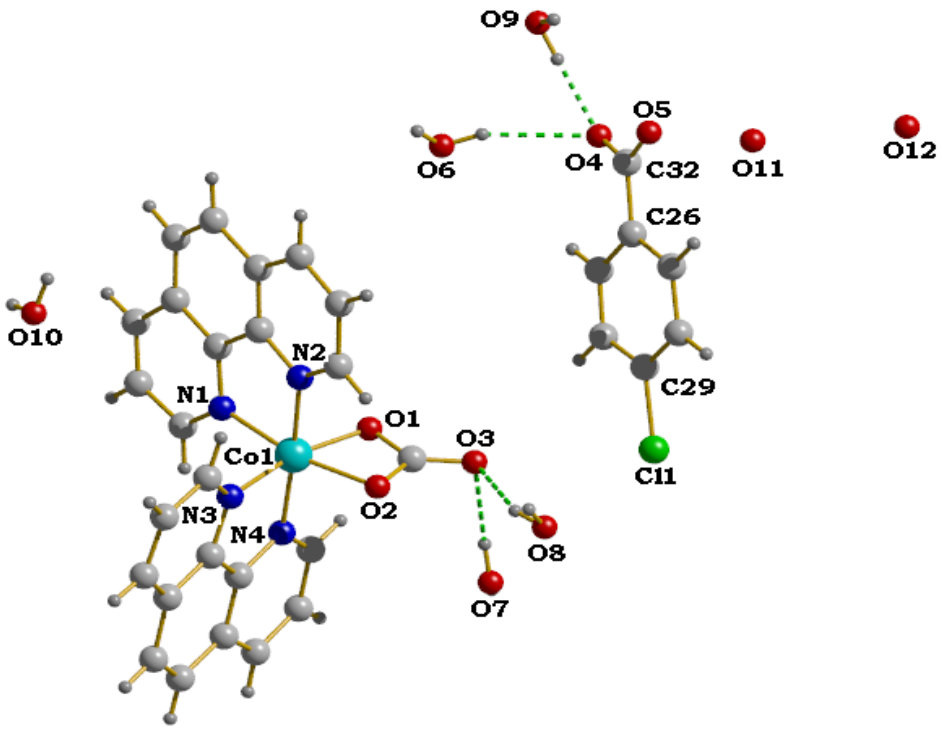


Fig. S7 Molecular diagram of complex salt **5**.

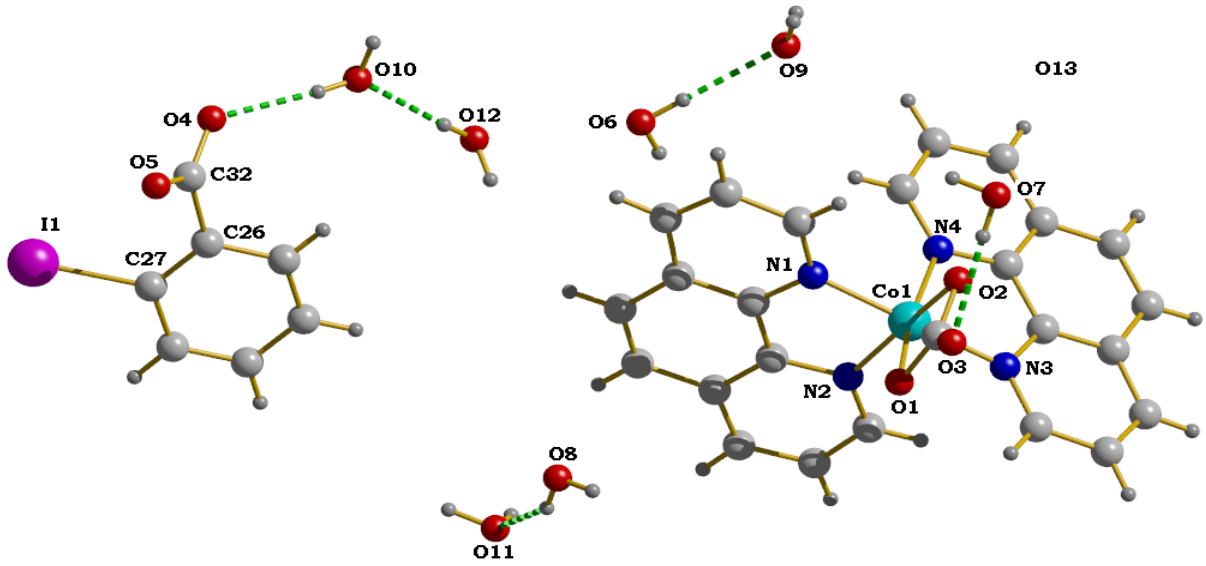


Fig. S8 Molecular diagram of complex salt **6**.

3) Structural parameters (Å, °) of complexes 1–8

Table S1 Selected bond lengths and bond angles

Complex Salt	1	2	3	4	5	6	7	8
$[Co(phen)_2CO_3]^+$								
Co–O1	1.885(3)	1.891(2)	1.890(2)	1.884(1)	1.892(2)	1.893(2)	1.890(3)	1.893(1)
Co–O2	1.896(3)	1.888(2)	1.895(2)	1.888(1)	1.890(2)	1.887(2)	1.874(3)	1.893(1)
Co–N1	1.925(3)	1.926(2)	1.937(2)	1.926(1)	1.965(3)	1.918(2)	1.931(3)	1.931(2)
Co–N2	1.964(3)	1.959(2)	1.964(2)	1.956(1)	1.922(3)	1.936(3)	1.946(3)	1.951(2)
Co–N3	1.938(3)	1.926(2)	1.964(2)	1.945(2)	1.949(3)	1.923(2)	1.957(3)	1.932(2)
Co–N4	1.902(4)	1.944(2)	1.934(2)	1.926(1)	1.935(3)	1.939(2)	1.929(3)	1.953(2)
O1–Co–O2	69.26(11)	69.27(7)	69.23(9)	69.37(6)	69.27(10)	69.26(9)	69.44(12)	69.55(6)
N1–Co–N2	83.73(13)	83.96(8)	83.73(10)	84.14(6)	84.32(14)	84.32(10)	83.83(13)	84.09(7)
N1–Co–N3	94.43(15)	176.05(8)	95.11(10)	95.40(6)	95.79(11)	176.46(10)	94.42(12)	176.98(7)
N1–Co–N4	176.86(14)	95.32(8)	176.53(9)	177.94(5)	93.57(12)	93.20(10)	176.80(12)	94.21(7)
N2–Co–N3	96.03(13)	92.15(8)	69.00(10)	91.46(6)	94.01(11)	93.42(10)	94.50(12)	93.46(7)
N2–Co–N4	94.06(13)	95.04(8)	93.04(9)	93.81(6)	177.14(11)	93.78(10)	93.93(12)	94.82(7)
N3–Co–N4	83.56(15)	84.26(8)	83.97(10)	84.44(6)	84.27(11)	84.21(10)	83.47(12)	84.23(7)
Anionic ligands								
O4–C32	1.231(6)	1.234(3)	1.201(6)	1.252(3)	1.266(6)	1.239(4)	1.241(6)	1.228(3) [a]
O5–C32	1.240(5)	1.242(3)	1.251(6)	1.241(3)	1.231(6)	1.228(4)	1.243(6)	1.230(3) [a]
C26–C32	1.509(7)	1.530(3)	1.518(6)	1.522(2)	1.499(6)	1.512(4)	1.504(7)	1.513(3) [b]
N5–C	1.459(6)	1.470(3)	1.462(4)	1.471(3)	-	-	-	-
O6–N5	1.205(6)	1.217(3)	1.220(5)	1.199(4)	-	-	-	-
O7–N5	1.202(6)	1.213(3)	1.204(5)	1.183(3)	-	-	-	-
O4–C32–O5	125.5(5)	125.5(2)	126.8(5)	125.5(2)	123.4(5)	127.0(3)	126.3(6)	123.3(2)
O4–C32–C26	118.3(5)	117.5(2)	117.5(5)	116.7(2)	117.0(5)	115.6(3)	116.4(6)	-
O5–C32–C26	116.1(5)	117.0(2)	115.7(4)	117.8(2)	119.6(5)	117.4(3)	117.0(5)	-
O7–N5–O6	122.0(6)	123.6(3)	122.9(4)	116.7(2)	-	-	-	-
O7–N5–C	119.7(5)	118.6(3)	118.9(4)	120.6(3)	-	-	-	-
O6–N5–C	118.3(6)	117.8(3)	118.2(4)	118.4(3)	-	-	-	-
C–X (X = Cl/I/O)	-	-	1.729(3)	-	1.731(5)	2.084(4)	1.384(5)	-

[a] Read C(32) as C(26). [b] Read C(32) as C(27).

4) Hydrogen bonding parameters (Å, °) of complexes 1–8

Table S2 $[Co(phen)_2CO_3]$(3-nitrobenzoate)·$4H_2O$ (**1**)

D–H•••A	*d*(D•••A)	*d*(H•••A)	∠DHA
O8–H8B•••O4	2.685(7)	1.808(4)	173.8(3)
O8–H8C•••O9	3.287(9)	2.401(7)	157.7(3)
O9–H9B•••O3 [i]	2.879(6)	2.019(3)	178.4(4)
O9–H9C•••O5	2.651(7)	1.793(4)	172.0(4)
C2–H2A•••O3 [ii]	3.205(5)	2.455(3)	137.8(3)
C9–H9A•••O2 [iii]	3.298(6)	2.618(3)	130.5(3)
C10–H10A•••O4 [iv]	3.326(6)	2.479(4)	151.6(3)
C11–H11A•••O2 [iii]	3.359(5)	2.707(2)	127.8(3)
C13–H13A•••O6 [v]	3.335(8)	2.533(6)	144.7(3)
C14–H14A•••O5 [iii]	3.124(6)	2.336(4)	142.4(3)
C21–H21A•••O3 [v]	3.395(6)	2.503(3)	160.9(3)
C22–H22A•••O1 [vi]	3.304(5)	2.505(3)	144.1(3)
C24–H24A•••O5 [vii]	3.517(7)	2.599(4)	169.3(3)

Equivalent positions: (i) x, y, z – 1; (ii) –x + 1, –y + 1, –z + 1; (iii) –x + 1, –y + 1, –z; (iv) x, y + 1, z; (v) x – 1, y, z; (vi) –x, –y + 1, –z + 1; (vii) –x + 1, –y, –z.

Table S3 $[Co(phen)_2CO_3]$(4-nitrobenzoate)·$5H_2O$ (**2**)

D–H•••A	*d*(D•••A)	*d*(H•••A)	∠DHA
O8–H8B•••O9	2.761(3)	1.938(2)	171.0(2)
O8–H8C•••O3 [i]	2.936(3)	2.128(2)	167.8(2)
O9–H9B•••O6	2.889(3)	2.044(2)	172.3(2)
O9–H9C•••O7 [ii]	2.751(3)	1.929(2)	170.3(2)
O10–H10B•••O6	2.744(4)	1.972(2)	159.1(2)
O11–H11B•••O10 [iii]	3.030(6)	2.150(4)	179.9(3)
O11–H11C•••O8 [iv]	2.762(4)	1.971(2)	154.4(2)
C3–H3A•••O6	3.328(4)	2.540(3)	142.7(2)
C3–H3A•••O7	3.309(4)	2.422(2)	159.4(2)
C10–H10A•••O2 [v]	3.254(3)	2.553(2)	132.5(2)
C12–H12A•••O4 [iii]	3.207(5)	2.475(4)	135.6(2)
C14–H14A•••O9 [iv]	3.456(4)	2.701(2)	138.8(2)
C15–H15A•••O11	3.328(5)	2.496(4)	149.0(2)
C21–H21A•••O3 [vi]	3.326(4)	2.467(2)	153.6(2)
C23–H23A•••O10 [vi]	3.330(4)	2.651(3)	130.5(2)
C24–H24A•••O8	3.286(4)	2.479(3)	145.2(2)

Equivalent positions: (i) –x, –y + 2, –z; (ii) –x, –y + 1, –z + 1; (iii) x + 1, y + 1, z; (iv) x, y + 1, z; (v) –x, –y + 2, –z + 1; (vi) x + 1, y, z. The hydrogen bonds involving disordered water molecules are discarded.

Table S4 $[Co(phen)_2CO_3]$(2-chloro-4-nitrobenzoate)·$5H_2O$ (**3**)

D–H•••A	***d*(D•••A)**	***d*(H•••A)**	**∠DHA**
O8–H8B•••O5 [i]	2.754(4)	1.927(3)	163.2(2)
O8–H8C•••O3 [ii]	2.888(3)	2.079(2)	156.5(2)
O9–H9B•••O11	2.977(8)	2.243(7)	149.2(3)
O9–H9C•••O8	2.774(5)	1.944(3)	159.0(2)
O10–H10B•••O9	2.923(5)	2.117(3)	173.0(3)
C9–H9A•••O1 [iii]	3.241(3)	2.580(2)	128.4(2)
C10–H10A•••O4 [iv]	3.314(6)	2.397(5)	168.7(2)
C11–H11A•••O1 [iii]	3.263(8)	2.496(7)	140.0(2)
C12–H12A•••O7	3.371(5)	2.662(3)	133.6(2)
C13–H13A•••O6	3.250(5)	2.427(4)	147.6(2)
C15–H15•••Cl1 [v]	3.590(4)	2.943(1)	127.8(2)
C16–H16A•••O10 [vi]	3.584(5)	2.783(4)	144.9(2)
C21–H21A•••O2 [vi]	3.427(3)	2.661(2)	140.2(2)
C22–H22A•••O3 [vii]	3.410(4)	2.553(2)	153.3(2)
C25–H25A•••O8	3.272(4)	2.544(3)	135.4(2)

Equivalent positions: (i) –x + 2, –y + 1, –z + 1; (ii) –x + 1, –y, –z + 1; (iii) –x + 1, –y + 1, –z + 1; (iv) x – 1, y, z – 1; (v) –x + 2, –y + 1, –z + 2; (vi) –x + 2, –y, –z + 1; (vii) x + 1, y, z. The hydrogen bonds involving disordered water molecules are discarded.

Table S5 $[Co(phen)_2CO_3]$(3-methyl-4-nitrobenzoate)·$5H_2O$ (**4**)

D–H•••A	***d*(D•••A)**	***d*(H•••A)**	**∠DHA**
O8–H8B•••O4	2.832(3)	1.993(2)	168.9(1)
O8–H8B•••O5	3.327(3)	2.659(2)	136.4(1)
O8–H8C•••O5 [i]	2.776(2)	1.928(2)	175.2(1)
O9–H9B•••O4	2.734(3)	1.984(2)	151.9(2)
O10–H10B•••O8	2.750(3)	1.904(2)	173.0(2)
C2–H2A•••O3 [ii]	3.336(3)	2.664(2)	129.7(1)
C3–H3A•••O10	3.329(4)	2.664(3)	129.1(1)
C3–H31A•••O9	3.430(4)	2.528(3)	163.5(2)
C10–H10A•••O5 [i]	3.457(3)	2.577(2)	158.0(1)
C12–H12A•••O6 [iii]	3.341(5)	2.528(4)	146.2(1)
C13–H13A•••O7 [iii]	3.461(5)	2.651(4)	146.0(1)
C14–H14A•••O9	3.287(3)	2.565(2)	134.8(1)
C16–H16A•••O1 [iv]	3.218(2)	2.626(1)	122.1(1)
C21–H21A •••O3 [v]	3.155(3)	2.381(1)	140.5(2)

Equivalent positions: (i) –x, –y, –z + 1; (ii) –x, –y + 1, –z; (iii) –x + 1, –y + 1, –z + 1; (iv) –x + 1, –y + 1, –z; (v) x + 1, y, z. The hydrogen bonds involving disordered water molecules are discarded.

Table S6 $[Co(phen)_2CO_3]$(2-phenoxybenzoate)·$8H_2O$ (**7**)

D–H•••A	***d*(D•••A)**	***d*(H•••A)**	**∠DHA**
O7–H7B•••O5	2.931(6)	2.139(4)	155.1(4)
O7–H7C•••O8 [i]	2.913(9)	2.131(7)	151.1(4)
O8–H8B•••O9	2.998(11)	2.138(9)	177.5(5)
O8–H8C•••O11	2.614(11)	1.911(8)	143.0(5)
O9–H9B•••O3 [ii]	3.203(9)	2.484(3)	142.7(6)
O9–H9C•••O2	3.354(8)	2.583(3)	149.8(5)
O9–H9C•••O3	2.987(8)	2.237(4)	145.6(5)
O10–H10C•••O5 [iii]	2.698(10)	1.848(5)	179.5(5)
O11–H11C•••O10 [iv]	2.898(14)	2.074(9)	155.5(8)
C3–H3A•••O4 [v]	3.409(8)	2.540(5)	155.6(3)
C4–H4A•••O5 [v]	3.384(7)	2.590(5)	143.6(3)
C13–H13A•••O7 [i]	3.314(7)	2.707(5)	123.6(3)
C14–H14A•••O10	3.255(9)	2.427(8)	148.3(3)
C15–H15A•••O5 [iii]	3.462(7)	2.611(5)	152.3(3)
C21–H21A•••O11 [i]	3.582(12)	2.676(11)	165.1(4)
C25–H25A•••O8	3.339(7)	2.547(6)	143.2(3)
C36–H36A•••O3	3.286(7)	2.550(3)	136.3(4)

Equivalent positions: (i) –x + 2, –y + 1, –z + 1; (ii) –x + 2, –y + 1, –z; (iii) –x + 2, –y + 2, –z + 1; (iv) x, y – 1, z; (v) x – 1, y, z – 1. The hydrogen bonds involving disordered water molecules are discarded.

Table S7 $[Co(phen)_2CO_3]$(2-napthaleneacetate)·$7H_2O$ (**8**)

D–H•••A	***d*(D•••A)**	***d*(H•••A)**	**∠DHA**
O6–H6B•••O11 [i]	2.825(3)	2.102(2)	150.2(2)
O6–H6C•••O5 [ii]	2.651(2)	1.798(2)	170.8(1)
O7–H7B•••O6	2.822(3)	2.003(2)	171.8(2)
O7–H7C•••O4 [i]	2.822(3)	2.012(2)	171.5(2)
O8–H8C•••O9 [iii]	2.786(3)	1.993(2)	157.0(2)
O9–H9B•••O10	2.716(4)	2.095(3)	132.4(2)
O9–H9C•••O12 [iv]	2.799(3)	1.963(2)	167.5(2)
O10–H10B•••O5	2.748(4)	1.920(2)	175.7(2)
O10–H10C•••O7 [iv]	2.849(3)	2.114(2)	148.6(2)
O11–H11B•••O4	2.720(3)	1.843(2)	172.6(1)
O11–H11C•••O7 [ii]	3.089(3)	2.331(2)	158.5(1)
O12–H12B•••O6	2.809(3)	2.042(2)	158.0(1)
O12–H12C•••O8 [v]	2.779(3)	2.017(2)	154.5(2)
C2–H2A•••O12 [vi]	3.308(3)	2.656(2)	127.8(2)
C3–H3A•••O3 [vii]	3.449(3)	2.544(2)	164.4(2)
C10–H10A•••O7 [viii]	3.340(4)	2.576(2)	139.8(2)
C14–H14A•••O6 [ix]	3.443(3)	2.531(2)	166.6(2)
C15–H15A•••O10 [x]	3.606(4)	2.704(2)	163.8(2)
C22–H22A•••O1 [iii]	3.329(3)	2.596(1)	136.1(1)
C18–H18A•••O12 [iv]	3.627(3)	2.723(2)	164.5(2)
C19–H19A•••O9	3.319(3)	2.627(2)	131.7(2)
C24–H24A•••O3 [viii]	3.216(3)	2.452(2)	139.5(1)

Equivalent positions: (i) x, y, z + 1; (ii) –x + 1, –y, –z + 1; (iii) –x, –y, –z + 1; (iv) –x + 1, y – 1/2, –z + 3/2; (v) x + 1, y, z; (vi) x – 1, –y + 1/2, z – 1/2; (vii) –x, y + 1/2, –z + 3/2; (viii) x, –y + 1/2, z – 1/2, (ix) –x + 1, –y, –z + 2; (x) x, –y – 1/2, z + 1/2.

Table S8 $[Co(phen)_2CO_3]$(4-chlorobenzoate)·$7H_2O$ (**5**)

D–H•••A	***d*(D•••A)**	***d*(H•••A)**	**∠DHA**
O6–H6B•••O4 [i]	2.862(6)	2.055(4)	152.1(3)
O6–H6C•••O3 [ii]	2.850(4)	1.966(3)	167.1(3)
O7–H7B•••O4 [iii]	3.045(8)	2.267(6)	156.1(3)
O7–H7C•••O6 [iv]	2.831(7)	2.046(4)	163.1(3)
O8–H8C•••O3 [v]	2.963(6)	2.173(3)	152.6(3)
O9–H9B•••O4 [vi]	2.629(10)	1.790(5)	177.1(6)
O10–H10B•••O6	3.024(9)	2.343(4)	143.6(5)
O10–H10C•••O8 [vii]	2.592(10)	1.831(6)	153.8(7)
C4–H4A•••O6	3.584(7)	2.689(4)	161.9(4)
C12–H12A•••O9	3.290(11)	2.688(8)	123.1(5)
C13–H13A•••O9	3.293(9)	2.678(8)	124.3(4)
C14–H14A•••O3 [viii]	3.208(5)	2.444(3)	139.5(2)
C16–H16A•••O9 [viii]	3.281(7)	2.601(7)	130.3(3)
C21–H21A•••O7	3.446(6)	2.653(4)	143.64(2)
C21–H21A•••O2 [v]	3.208(4)	2.635(2)	120.45(2)
C23–H23A•••O7	3.303(5)	2.456(4)	151.5(2)
C24–H24A•••O5 [ix]	3.483(5)	2.569(3)	167.5(3)
C31–H31A•••O1 [x]	3.305(4)	2.616(2)	131.4(3)

Equivalent positions: (i) x, y, z + 1; (ii) x – 1, y, z; (iii) –x, –y + 1, –z + 1; (iv) –x, y – 1/2, –z + 3/2; (v) –x + 1, –y + 1, –z + 2; (vi) x + 1, y, z + 1; (vii) –x, –y + 1, –z + 2, (viii) x, –y + 3/2, z + 1/2; (ix) –x, y – 1/2, –z + ½; (x) x, –y + 3/2, z – 1/2.

Table S9 $[Co(phen)_2CO_3]$(2-iodobenzoate)·$7H_2O$ (**6**)

D–H•••A	***d*(D•••A)**	***d*(H•••A)**	**∠DHA**
O6–H6B•••O9	2.940(7)	2.090(4)	179.9(4)
O6–H6C•••O7 [i]	2.872(7)	2.433(6)	113.5(4)
O7–H7B•••O3	2.991(5)	2.163(2)	175.1(4)
O7–H7C•••O8 [ii]	3.052(8)	2.239(6)	162.8(4)
O8–H8B•••O4 [iii]	2.943(7)	2.184(4)	156.2(4)
O8–H8C•••O11	2.792(6)	2.031(4)	148.6(3)
O9–H9B•••O5 [iv]	2.839(4)	2.008(3)	165.8(3)
O9–H9C•••O5 [v]	2.864(4)	2.073(3)	164.4(3)
O10–H10B•••O1 [vi]	2.891(4)	2.136(2)	143.5(3)
O10–H10C•••O4	2.749(6)	1.945(4)	162.9(3)
O11–H11B•••O6 [vii]	2.917(10)	2.049(7)	168.9(4)
O11–H11C•••O12 [vii]	2.740(6)	1.912(3)	175.0(4)
O12–H12B•••O10	2.729(6)	1.942(4)	163.8(3)
O12–H12C•••O3 [ii]	2.792(4)	1.936(2)	167.8(3)
C2–H2A•••O8 [ii]	3.299(5)	2.556(4)	137.2(3)
C3–H3A•••O4 [iv]	3.334(4)	2.527(3)	145.4(3)
C4–H4A•••O1 [ii]	3.334(5)	2.654(2)	130.5(2)
C13–H13A•••O11 [viii]	3.279(7)	2.519(5)	139.0(2)
C16–H16A•••O5 [ix]	3.530(6)	2.726(4)	145.1(2)
C16–H16A•••O9 [iii]	3.445(6)	2.615(4)	148.8(2)
C22–H22A•••O5	3.461(6)	2.631(4)	149.0(2)
C24–H24A•••O9	3.324(6)	2.705(4)	124.7(2)
C23–H23A•••O2 [x]	3.162(4)	2.467(3)	131.6(2)
C25–H25A•••O9	3.345(5)	2.738(3)	123.7(2)
C30–H30A•••O7 [ii]	3.534(8)	2.711(6)	148.0(3)

Equivalent positions: (i) x – 1, y, z; (ii) –x + 1, –y + 1, –z + 1; (iii) x, y + 1, z; (iv) –x + 1, –y, –z + 1; (v) x, y, z + 1; (vi) x, y – 1, z; (vii) –x, –y + 1, –z + 1; (viii) –x, –y + 2, –z + 1; (ix) x, y + 1, z + 1; (x) –x + 1, –y + 1, –z + 2.