Pseudo [M(II)$_7$] (M = Co, Ni and Zn) metallocalix[6]arene hosts encapsulate a range of organic guest molecules in the solid state.

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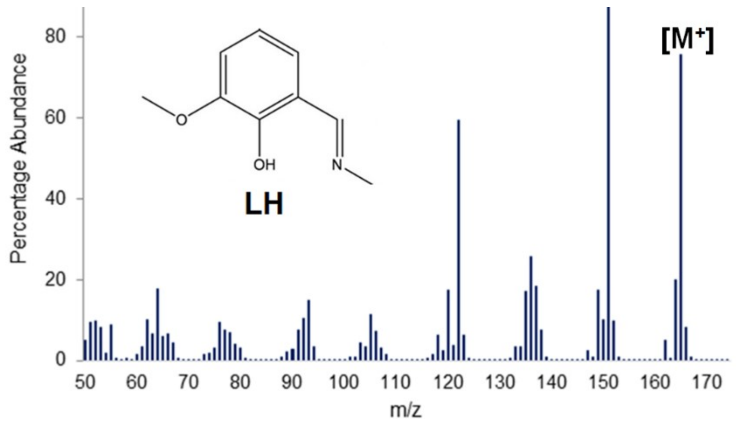
Experimental Section

Synthesis of 2-Methoxy-6-[(E)-(methylimino)methyl]phenol (LH)

Ortho-vanillin (5.0 g, 33.0 mmol) was dissolved in 50 cm^3 of methanol before 33% methylamine solution (4.1 cm^3, 33.0 mmol) was added. The resulting mixture was allowed to stir at room temperature for 4 hours, before a 100 cm^3 of brine solution was added. The product was then extracted using 3 x 40 cm^3 portions of $CHCl_3$. The combined extracts were dried over magnesium sulphate before being concentrated in vacuum, the product was allowed to dry over a 24-hour period and yielded a yellow solid (yield 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 13.86 (s, 1H), 8.32 (s, 1H), 6.91 (d, 1H, J = 7.8, 1.4 Hz), 6.86 (d, 1H, J = 7.8, 1.5 Hz), 6.79 (t, 1H, J = 7.8 Hz), 3.90 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.39, 152.32, 148.69, 122.81, 118.74, 117.79, 113.88, 56.21, 45.72. FT-IR (cm^{-1}): 2992 (w), 2941 (w), 2888 (w), 2839 (w), 2774 (w), 2117 (w), 1629 (s), 1463 (s), 1438 (m), 1410 (m), 1391 (m), 1333 (w), 1248 (s), 1165 (m), 1078 (s), 1004 (m), 960 (s), 866 (m), 835 (m), 777 (s), 733 (s), 637 (w), 619 (m), 579 (w). ESI MS: m/z (% Rel. Ab.); 165.10 (75, $\{M\}^+$), 150.15 (100, $\{M\text{-}CH_3\}^+$), 136.22 (25, $\{M\text{-}N\text{-}CH_3\}^+$), 122.20 (60, $\{M\text{-}C_2H_4N\}^+$).



*Synthesis of [(2-fur)⊂Zn(II)$_7$(OMe)$_6$(L)$_6$](NO$_3$)$_2$·3H$_2$O (**1**)*

To a solution of LH (0.14 g, 0.85 mmol) in 30 cm^3 of methanol, NaOH (0.034 g, 0.84 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (0.25 g, 0.84 mmol) were added. The solution was allowed to stir for 1 hour before 2-furaldehyde (0.70 cm^3, 8.4 mmol) was added and the solution stirred for a further 3 hours. The resultant solution was then allowed to settle for 30 minutes before filtration. X-ray quality crystals of **1** were obtained after 3 weeks in 17% yield. Elemental analysis (%) calculated for **1**: ($C_{65}H_{88}N_8O_{29}Zn_7$): C 41.02, H 4.66, N 5.89. Found: C 41.09, H 4.30, N 5.85. FT-IR (cm^{-1}): 3431 (vb), 2998 (w), 2965 (w), 2929 (m), 2828 (w), 1857 (w), 1667 (m), 1639 (s), 1602 (m), 1561 (w), 1476 (s), 1461 (s), 1436 (m), 1409 (m), 1383 (s), 1340 (b/m), 1311 (s), 1241 (m), 1222 (s), 1172 (m), 1148 (w), 1093 (m), 1077 (m), 1036 (m), 1014 (m), 966 (m), 928 (w), 881 (w), 859 (w), 829 (w), 793 (m), 747 (m). Solid state ^{13}C NMR (ppm) (spinning speed = 12 KHz) (Prominent guest peaks in bold): **177.06**, 173.70, 155.75, 151.74, 149.49, 129.80, **122.07**, 119.62, 118.22, **112.43**, 56.11, 53.25, 45.69.

*Synthesis of [(2-fur)⊂Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**2**)*

To a solution of LH (0.14 g, 0.85 mmol) in 30 cm^3 of methanol, NaOH (0.034 g, 0.84 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (0.25 g, 0.86 mmol) were added. The solution was allowed to stir for 1 hour before 2-furaldehyde (0.74 cm^3, 8.4 mmol) was added and the reaction mixture stirred for a further 3 hours. The resultant solution was then filtered to give X-ray quality crystals of **2** in 20% yield over a 3-week period. Elemental analysis (%) calculated for **2** ($C_{59}H_{70}N_8O_{26}Ni_7$): C 41.25, H 4.22, N 6.54. Found: C 41.56, H 4.22, N 6.24. FT-IR (cm^{-1}): 3411 (vb), 3122 (w), 3088 (w), 3002 (w), 2932 (m), 2815 (w), 2704 (w), 2579 (w), 2400 (w), 2036 (w), 1973 (w), 1933 (w), 1857 (w), 1669 (m), 1630 (s), 1603 (m), 1561 (m), 1552 (m), 1478 (s), 1407 (s), 1382 (s), 1354 (s), 1317 (s), 1224 (s), 1170 (m), 1149 (m), 1087 (m), 1073 (m), 1044 (m), 1018 (m), 963 (m), 928 (w), 864 (m), 829 (w), 793 (m), 748 (s), 643 (m), 627 (m), 591 (w), 555 (w), 492 (m), 438 (w), 402 (m).

*Synthesis of [(2-fur)⊂Co(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$·3H$_2$O (**3**)*

A mixture of $Co(NO_3)_2.6H_2O$ (0.25 g, 0.86 mmol) and LH (0.14 g, 0.86 mmol) were stirred in EtOH (25 cm^3) until complete dissolution of solid material was achieved. NaOH (0.034 g, 0.06 mmol) was then added effecting a colour change from purple-red to dark red-brown. 2-furaldehyde (0.71 cm^3, 8.6 mmol) was then added and the red-brown opaque solution stirred for a further 4 hours following which it was filtered to afford a purple-brown mother liquor. Purple-brown blocks of **3** were harvested both from the mother liquor and Et_2O diffused samples of the mother liquor with a combined yield of 22% after 2 weeks. Elemental analysis (%) calculated for **3** ($C_{59}H_{76}N_8O_{29}Co_7$): C 39.95, H 4.32, N 6.32. Found: C 41.18, H 3.78, N 6.27. FT-IR (cm^{-1}): 3464 (w), 2932 (w), 1671 (m), 1629 (m), 1602 (w), 1560 (w), 1474 (m), 1459 (m), 1436 (m), 1407 (w), 1339 (m), 1306 (m), 1240 (m), 1221 (s), 1171 (w), 1149 (w), 1090 (m), 1076 (m), 1054 (w), 1015 (m), 964 (m), 927 (w), 882 (w), 860 (m), 830 (w), 788 (m), 744 (s).

*Synthesis of [(3-fur)⊂Zn(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**4**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.84 mmol) were added NaOH (0.034 g, 0.84 mmol) and $Zn(NO_3)_2·6H_2O$ (0.25 g, 0.84 mmol). The resultant solution was allowed to stir for 1 hour before 3-furaldehyde (0.74 cm^3, 8.4 mmol) was added and the mixture stirred for a further 3 hours. The solution was then allowed to settle for 30 minutes before filtration. X-ray quality crystals of **4** were obtained after 3 weeks in 18% yield. Elemental analysis (%) calculated for **4**·2H_2O ($C_{59}H_{74}N_8O_{28}Zn_7$): C 39.34, H 4.14, N 6.22. Found: C 39.33, H 4.23, N 6.37. FT-IR (cm^{-1}): 3429 (vb), 2929 (m), 2829 (w), 1859 (w), 1676 (m), 1639 (s), 1602 (m), 1560 (w), 1475 (s), 1461 (s), 1436 (m), 1409 (m),1383 (s),1356 (b/m), 1311 (s), 1241 (m), 1222 (s), 1172 (m), 1149 (m), 1093 (m), 1076 (m), 1035 (m), 1013 (m), 966 (m), 860 (w), 829 (w), 795 (m), 746 (m).

*Synthesis of [(3-fur)⊂Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$·3H$_2$O (**5**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.84 mmol) were added NaOH (0.034 g, 0.84 mmol) and $Ni(NO_3)_2·6H_2O$ (0.25 g, 0.86 mmol). The solution was allowed to stir for 1 hour before 3-furaldehyde (0.74 cm^3, 8.6 mmol) was added and the reaction mixture stirred for a further 3 hours. The resultant solution was filtered and X-ray quality crystals of **5** were obtained in 10% yield over a 3-week period. Elemental analysis (%) calculated for **5** ($C_{59}H_{76}N_8O_{29}Ni_7$): C 39.99, H 4.32, N 6.32. Found: C 41.25, H 4.23, N 6.24. FT-IR (cm^{-1}): 3438 (vb), 3002 (w), 2932 (w), 2814 (w), 1676 (m), 1626 (s), 1603 (m), 1561 (w), 1550 (w), 1511 (w), 1459 (s), 1436 (m), 1407 (m), 1336 (s), 1315 (s), 1239 (m), 1222 (s), 1210 (s), 1169 (m), 1149 (m), 1086 (m), 1072 (m), 1044 (m), 1017 (m), 957 (m), 866 (m), 828 (m), 792 (m), 742 (s), 727 (m), 641 (m), 627 (m), 599 (m), 555 (m), 492 (m).

Synthesis of $[(3\text{-}fur)\subset Co(II)_7(OH)_6(L)_6](NO_3)_2\cdot 4.5H_2O$ (**6**)

A solution of $Co(NO_3)_2.6H_2O$ (0.25 g, 0.86 mmol) and LH (0.14 g, 0.86 mmol) were stirred in EtOH (25 cm^3) and placed in a glass-lined microwave reaction vessel, adopting a purple-red colour in the process. Solid NaOH (0.034 g, 0.86 mmol, 1.0 eq.) and 3-furaldehyde (0.74 cm^3, 8.6 mmol) were then added neat and the system isolated from its surroundings by capping with a Teflon seal. The solution was heated under microwave conditions (110°C, 110 psi, 200 W, 20 mins) affording a dark, red-brown solution which was filtered to afford a similarly coloured mother liquor. Et_2O diffusion of the mother liquor afforded purple-brown blocks of **6** after one week which were harvested with a combined yield of 10%. Elemental analysis (%) calculated for $C_{59}H_{70}N_8O_{26}Co_7$ (loss of waters): C 39.35, H 4.42, N 6.22. Found: C 40.53, H 4.58, N 6.63. FT-IR (cm^{-1}): 3575 (w), 2932 (w), 1678 (m), 1632 (s), 1601 (m), 1562 (w), 1512 (w), 1474 (w), 1459 (s), 1436 (m), 1407 (m), 1345 (s), 1306 (s), 1239 (m), 1221 (s), 1171 (m), 1149 (m), 1089 (m), 1078 (s), 1055 (w), 1011 (m), 968 (m), 869 (w), 858 (m), 796 (m), 744 (s).

Synthesis of $[(bzal)\subset Zn(II)_7(OMe)_6(L)_6](NO_3)_2\cdot 5H_2O$ *(7)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.84 mmol) were added NaOH (0.034 g, 0.84 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (0.25 g, 0.84 mmol). The resultant solution was allowed to stir for 1 hour before benzaldehyde (0.86 cm^3, 8.4 mmol) was added and the mixture stirred for a further 3 hours. The solution was then allowed to settle for 30 minutes before filtration. X-ray quality crystals of **7** were obtained after 3 weeks in 15% yield. Elemental analysis (%) calculated for **7** ($C_{67}H_{82}N_8O_{30}Zn_7$): C 41.54, H 4.27, N 5.78. Found: C 31.68, H 4.43, N 5.51. FT-IR (cm^{-1}): 3435 (vb), 2938 (b/w), 2825 (w), 1826 (w), 1689 (m), 1643 (s), 1599 (m), 1556 (w), 1472 (s), 1351 (b/s), 1315 (s), 1230 (m), 1221 (s), 1176 (w), 1080 (m), 1032 (m), 961 (m), 857 (m), 827 (w), 789 (m), 753 (s). Solid state ^{13}C NMR (ppm) (spinning speed = 12 KHz)

(Prominent guest peaks in bold): **193.21**, 173.14, 155.36, 149.00, **135.15**, 129.16, 118.94, 117.59, 55.53, 52.90, 45.41.

*Synthesis of [(bzal)⊂Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**8**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.86 mmol) were added NaOH (0.034 g, 0.86 mmol) and $Ni(NO_3)_2 \cdot 6H_2O$ (0.25 g, 0.86 mmol). The solution was allowed to stir for 1 hour before benzaldehyde (0.88 cm^3, 8.6 mmol) was added and the resultant mixture stirred for a further 3 hours. The solution was filtered and X-ray quality crystals of **8** were obtained after 3 weeks in 17% yield. Elemental analysis (%) calculated for **8**.2H$_2$O ($C_{61}H_{76}N_8O_{27}Ni_7$): C 41.53, H 4.34, N 6.35. Found: C 41.21, H 4.19, N 6.63. FT-IR (cm^{-1}): 3568 (w), 3439 (vb), 3003 (w), 2932 (w), 2811 (w), 1689 (m), 1626 (s), 1602 (m), 1549 (w), 1458 (s), 1437 (w), 1407 (m), 1337 (s), 1315 (s), 1239 (w), 1222 (s), 1209 (s), 1169 (m), 1148 (w), 1087 (m), 1072 (m), 1042 (m), 1017 (m), 956 (m), 864 (w), 828 (m), 792 (s), 744 (m), 727 (m), 688 (m), 643 (m), 628 (m), 606 (w), 589 (w), 556 (w), 493 (m).

*Synthesis of [(2-thio)⊂Zn(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**9**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.84 mmol) was added NaOH (0.034 g, 0.84 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.25 g, 0.84 mmol). The resultant solution was allowed to stir for 1 hour before 2-thiophenecarboxaldehyde (0.79 cm^3, 8.4 mmol) was added and the solution stirred for a further 3 hours. The solution was then filtered and X-ray quality crystals of **9** were obtained in 14% yield after 2 weeks. Elemental analysis (%) calculated for **9**.2H$_2$O ($C_{59}H_{74}N_8O_{27}S_1Zn_7$): C 39.00, H 4.11, N 6.17. Found: C 38.82, H 4.08, N 5.61. FT-IR (cm^{-1}): 3432 (vb), 3084 (w), 2999 (w), 2964 (m), 2930 (m), 2825 (m), 2792 (w), 2698 (w), 2572 (w), 2416 (w), 2165 (w), 2046 (w), 1989 (w), 1933 (w), 1858 (w), 1787 (w), 1747 (w), 1653 (s), 1638 (s), 1602 (s), 1557 (m), 1474 (s), 1461 (s), 1437 (s), 1409 (s), 1353 (s/b), 1310 (s), 1240 (s), 1222 (s), 1172 (m), 1147 (m), 1093 (m), 1077 (m), 1032 (m), 1014 (m), 965 (m), 859 (m), 829 (w), 794 (m), 746 (s), 664 (m), 631 (m), 612 (m), 584 (w), 552 (w), 474 (m), 430 (w).

*Synthesis of [(2-thio)⊂Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**10**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.86 mmol) was added NaOH (0.034 g, 0.86 mmol) and $Ni(NO_3)_2 \cdot 6H_2O$ (0.25 g, 0.86 mmol). The solution was allowed to stir for 1 hour before 2-thiophenecarboxaldehyde (0.80 cm^3, 8.6 mmol) was added and the reaction mixture stirred for a further 3 hours. The resultant solution was then filtered and X-ray quality crystals of **10** were obtained over a 3-week period (12% yield). Elemental analysis (%) calculated for **10**.4H_2O ($C_{59}H_{78}N_8O_{29}S_1Ni_7$): C 39.23, H 4.35, N 6.20. Found: C 38.85, H 3.91, N 5.65. FT-IR (cm^{-1}): 3568 (vb), 3084 (w), 3002 (w), 2932 (w), 2812 (w), 1656 (m), 1626 (s), 1603 (m), 1549 (w), 1520 (w), 1459 (s), 1437 (m), 1407 (m), 1335 (s), 1315 (s), 1239 (m), 1222 (s), 1209 (s), 1170 (m), 1148 (m), 1087 (m), 1072 (m), 1041 (m), 1017 (m), 956 (m), 863 (m), 828 (w), 792 (m), 743 (s), 727 (s), 665 (m), 641 (m), 627 (m), 605 (m), 589 (w), 555 (w), 492 (m).

*Synthesis of [(2-acetylfuran)⊂[Zn(II)$_7$(OH)$_6$(L)$_6$(NO$_3$)$_2$] (**11**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.84 mmol) was added NaOH, (0.034 g, 0.84 mmol) and $Zn(NO_3)_2.6H_2O$ (0.25 g, 0.84 mmol. The resultant solution was stirred for 1 hour before 2-acetylfuran (0.84 cm^3, 8.4 mmol) was added. The subsequent reaction mixture was stirred for a further 3 hours before being filtered. X-ray quality crystals of **11** were obtained (10%) over a three-week period. Elemental analysis (%) calculated for **11**·3H_2O ($C_{61}H_{78}N_8O_{29}Zn_7$): C 39.71, H 4.26, N 6.07. Found: C 39.54, H 4.62, N 5.72. FT-IR (cm^{-1}): 3404 (vb), 2998 (w), 2930 (b), 2824 (m), 2041 (w), 1986 (w), 1963 (w), 1667 (w), 1636 (s), 1601 (m), 1560 (w), 1435 (s), 1408 (m), 1334 (s), 1308 (s), 1240 (s), 1229 (s), 1173 (w), 1147 (m), 1092 (w), 1076 (w), 1013 (w), 967 (w), 859 (w), 828 (w), 791 (w), 743 (s), 630 (m), 612 (m), 596 (w), 584 (m), 551 (w), 473 (m), 428 (w).

*Synthesis of [(2-acetylfuran)⊂[Ni(II)$_7$(OMe)$_6$(L)$_6$](NO$_3$)$_2$·3H$_2$O (**12**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.86 mmol) was added NaOH, (0.034 g, 0.86 mmol) and $Ni(NO_3)_2.6H_2O$ (0.25 g, 0.86 mmol). The resultant solution stirred for 1 hour before 2-acetylfuran (0.86 cm^3, 8.6 mmol) was then added. The reaction mixture was stirred for a further 3 hours and allowed to settle for 30 minutes prior to being gravity filtered. X-ray quality crystals of **12** were obtained in 10% yield over a period of three weeks. Elemental analysis (%) calculated for **12** ($C_{66}H_{90}N_8O_{29}Ni_7$): C 42.38, H 4.85, N 5.99. Found: C 42.42, H 4.62, N 6.36. FT-IR (cm^{-1}): 3528 (vb), 3001 (w), 2932 (b), 2813 (m/b), 1665 (w), 1626 (s), 1602 (m), 1560 (m), 1550 (w), 1460 (s), 1437 (w), 1407 (m), 1335 (s), 1315 (s), 1239 (s), 1222 (s), 1210 (w), 1170 (m), 1148 (m), 1087 (w), 1072 (m), 1042 (m), 1017 (m), 957 (m), 915 (m), 906 (m), 882 (m), 864 (w), 829 (w), 791 (m), 744 (s), 726 (m), 641 (w), 627 (w), 591 (w), 555 (w), 491 (m), 442 (w).

*Synthesis of [(2-acetylfuran)⊂[Co(II)$_7$(OMe)$_6$(L)$_6$](NO$_3$)$_2$·7H$_2$O (**13**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.86 mmol) was added NaOH, (0.034 g, 0.86 mmol) and $Co(NO_3)_2.6H_2O$ (0.25 g, 0.86 mmol). The resultant solution stirred for 1 hour before 2-acetylfuran (0.86 cm^3, 8.6 mmol), was then added. The reaction mixture was stirred for a further 3 hours and allowed to settle for 30 minutes prior to being gravity filtered. X-ray quality crystals of **13** were obtained in 20% yield over a period of three weeks. Elemental analysis (%) calculated for **13**·3H$_2$O ($C_{66}H_{90}N_8O_{29}Co_7$): C 42.35, H 4.85, N 5.99. Found: C 42.10, H 4.75, N 5.62. FT-IR (cm^{-1}): 3546 (w), 3464 (w, b), 3003 (m), 2933 (w), 2822 (w), 2702 (w), 2655 (w), 2577 (w), 2377 (w), 2331 (w), 2044 (w), 1742 (vw), 1670 (m), 1627 (s), 1602 (m), 1563 (m), 1475 (sh), 1460 (s), 1433 (m), 1404 (s), 1343 (s), 1300 (s), 1230 (m), 1215 (s), 1168 (s), 1149 (m), 1090 (m), 1075 (s), 1030 (m), 1014 (m), 964 (m), 913 (w), 882 (m), 859 (m), 831 (s), 792 (m), 738 (s), 728 (sh), 631 (m), 619 (m), 553 (m), 477 (s).

*Synthesis of [(acetoph)⊂Zn(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**14**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.84 mmol) was added NaOH (0.034 g, 0.84 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.25 g, 0.84 mmol). The solution was stirred for 1 hour before acetophenone (0.98 cm^3, 8.4 mmol), was introduced. The resultant solution was left to stir for a further 3 hours and allowed to settle for 30 minutes prior to being gravity filtered. X-ray quality crystals of **14** were obtained in 10% yield over a three-week period. Elemental analysis (%) calculated for **14** ($C_{62}H_{74}N_8O_{25}Zn_7$): C 41.62, H 4.17, N 6.26. Found: C 41.82, H 4.58, N 6.41. FT-IR (cm^{-1}): 3404 (vb), 2937 (b), 2820 (m), 1676 (m), 1637 (s), 1600 (m), 1561 (w), 1474 (s), 1458 (s), 1435 (s), 1408 (m), 1335 (s), 1308 (s), 1271 (m), 1240 (s), 1219 (s), 1194 (w), 11714 (w), 1093 (w), 1077 (w), 1029 (m), 1012 (m), 969 (m), 859 (w), 794 (w), 745 (s), 690 (m), 631 (m), 612 (m), 585 (m), 550 (w), 473 (m).

*Synthesis of [(acetoph)⊂[Ni(II)$_7$(OMe)$_6$(L)$_6$](NO$_3$)$_2$ (**15**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.86 mmol) was added NaOH (0.034 g, 0.86 mmol) and $Ni(NO_3)_2.6H_2O$ (0.25 g, 0.86 mmol). The solution was stirred for 1 hour before acetophenone (1.00 cm^3, 8.6 mmol), was added. The resultant solution was stirred for a further 3 hours and allowed to settle for 30 minutes prior to being gravity filtered. X-ray quality crystals of **15** were obtained in 18% yield over a three-week period. Elemental analysis (%) calculated for **15** ($C_{68}H_{86}N_8O_{25}Ni_7$): C 44.72, H 4.75, N 6.14. Found: C 44.65, H 4.43, N 6.11. FT-IR (cm^{-1}): 3435 (vb), 3001 (w), 2932 (b/m), 2814 (m), 1674 (m), 1627 (s), 1602 (m), 1560 (m), 1459 (s), 1436 (m), 1408 (m), 1334 (s), 1314 (s), 1271 (w), 1240 (s), 1221 (s), 1170 (m), 1147(m), 1080 (w), 1072 (m), 1041 (m), 1017 (m), 963 (m), 864 (m), 792 (m), 744 (s), 690 (m), 642 (w), 627 (w), 588 (w), 555 (w), 491 (m), 440 (w), 406 (w).

*Synthesis of [(acetoph)⊂[Co(II)$_7$(OMe)$_6$(L)$_6$](NO$_3$)$_2$·7H$_2$O (**16**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.86 mmol) was added NaOH (0.034 g, 0.86 mmol) and $Co(NO_3)_2.6H_2O$ (0.25 g, 0.86 mmol). The solution was stirred for 1 hour before acetophenone (1.00 cm^3, 8.6 mmol) was added. The resultant solution was stirred for a further 3 hours and allowed to settle for 30 minutes prior to being gravity filtered. X-ray quality crystals of **16** were obtained in 15% yield over a three week period. Elemental analysis (%) calculated for **16** ($C_{68}H_{100}N_8O_{32}Co_7$): C 41.80, H 5.16, N 5.73. Found: C 42.03, H 4.84, N 5.92. FT-IR (cm^{-1}): 3455 (w, b), 3058 (w), 3005 (w), 2933 (m), 2816 (w), 2361 (w), 1676 (m), 1625 (s), 1600 (m), 1559 (m), 1474 (sh), 1458 (s), 1435 (m), 1407 (s), 1330 (s), 1304 (s), 1271 (m), 1240 (m), 1217 (s), 1170 (s), 1145 (m), 1088 (m), 1073 (s), 1009 (m), 964 (m), 857 (m), 828 (s), 791 (m), 742 (s,b), 728 (sh), 691 (m), 629 (m), 617 (m), 584 (m), 555 (m), 479 (s).

*Synthesis of [(1-indanone)⊂[Zn(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**17**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.84 mmol) was added NaOH (0.034 g, 0.84 mmol) and $Zn(NO_3)_2.6H_2O$ (0.25 g, 0.84 mmol). The solution was stirred for 1 hour before 1-indanone (1.11 g, 8.4 mmol) was added. The resultant solution was stirred for a further 3 hours and allowed to settle for 30 minutes prior to being gravity filtered. X-ray quality crystals of **17** were obtained in 18% yield over a four-week period. Elemental analysis (%) calculated for **17**·2H$_2$O ($C_{63}H_{78}N_8O_{27}Zn_7$): C 41.19, H 4.28, N 6.10. Found: C 41.25, H 4.13, N 6.31. FT-IR (cm^{-1}): 3427 (vb), 3005 (w), 2973 (w), 2934 (w), 2832 (w), 2816 (w), 1705 (m), 1689 (sh), 1634 (s), 1601 (m), 1559 (m), 1468 (sh), 1459 (s), 1434 (m), 1408 (s), 1367 (s), 1332 (s), 1308 (s), 1240 (s), 1220 (s), 1173 (s), 1091 (s), 1077 (s), 1026 (sh), 1012 (s), 967 (m), 859 (m), 828 (w), 791 (m), 742 (s), 630 (m), 613 (m), 585 (m), 553 (m).

*Synthesis of [(1-indanone)⊂[Ni(II)$_7$(OH)$_6$(L)$_6$(NO$_3$)$_2$] (**18**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.84 mmol) was added NaOH (0.034 g, 0.86 mmol) and $Ni(NO_3)_2.6H_2O$ (0.25 g, 0.86 mmol). The solution was stirred for 1 hour before 1-indanone (1.14 g, 8.6 mmol) was added. The resultant solution was stirred for a further 4 hours and allowed to settle for 30 minutes prior to being gravity filtered. X-ray quality crystals of **18** were obtained in 18% yield over a four-week period. Elemental analysis (%) calculated for

18·H_2O ($C_{63}H_{76}N_8O_{26}Ni_7$): C 42.70, H 4.32, N 6.32. Found: C 42.67, H 4.33, N 6.12. FT-IR (cm^{-1}): 3438 (vb), 3003 (w), 2931 (w), 2833 (w), 2813 (w), 2364 (vw), 1699 (m), 1628 (s), 1603 (m), 1583 (m), 1548 (m), 1462 (sh), 1436 (m), 1410 (s), 1367 (s), 1332 (sh), 1314 (s), 1240 (w), 1222 (s), 1209 (s), 1169 (s), 1085 (s), 1073 (s), 1044 (m), 1026 (s), 1018 (s), 963 (s), 865 (m), 828 (w), 793 (m), 742 (s), 730 (sh), 642 (m), 626 (m), 613 (m), 591 (m), 554 (m), 491 (m).

*Synthesis of [(coumarin)⊂[Zn(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**19**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.84 mmol) was added NaOH (0.034 g, 0.84 mmol) and $Zn(NO_3)_2.6H_2O$ (0.25 g, 0.84 mmol). The solution was stirred for 1 hour before coumarin (1.23 g, 8.4 mmol) was added. The resultant solution was stirred for a further 3 hours and allowed to settle for 30 minutes prior to being gravity filtered. X-ray quality crystals of **19** were obtained in 18% yield over a four-week period. Elemental analysis (%) calculated for **19**·3H_2O ($C_{63}H_{78}N_8O_{29}Zn_7$): C 40.49, H 4.21, N 6.00. Found: C 40.25, H 4.41, N 5.99. FT-IR (cm^{-1}): 3405 (vb), 3005 (w), 2297 (w), 2968 (w), 2931 (w), 2829 (w), 1754 (vw), 1719 (m), 1707 (m), 1634 (s), 1601 (m), 1560 (m), 1475 (sh), 1458 (s), 1436 (m), 1407 (s), 1364 (sh), 1334 (s), 1307 (s), 1240 (s), 1220 (s), 1193 (sh), 1173 (s), 1146 (m), 1120 (m), 1091 (s), 1077 (s), 1024 (sh), 1011 (s), 965 (m), 932 (w), 887 (w), 859 (m), 828 (m), 794 (m), 7425 (s), 630 (m), 610 (m), 583 (m), 553 (m), 526 (m), 473 (s), 428 (m).

*Synthesis of [(coumarin)⊂[Ni(II)$_7$(OH)$_6$(L)$_6$(NO$_3$)$_2$·3H$_2$O (**20**)*

To a 30 cm^3 methanolic solution of LH (0.14 g, 0.84 mmol) was added NaOH (0.034 g, 0.86 mmol) and $Ni(NO_3)_2.6H_2O$ (0.25 g, 0.86 mmol). The solution was stirred for 1 hour before coumarin (1.26 cm^3, 8.6 mmol) was added. The resultant solution was stirred for a further 3 hours and allowed to settle for 30 minutes prior to being gravity filtered. X-ray quality crystals of **20** were obtained in 18% yield over a four-week period. Elemental analysis (%) calculated for **20**·($C_{63}H_{78}N_8O_{29}Ni_7$): C 41.53, H 4.31, N 6.15. Found: C 41.77, H 4.13, N 6.33. FT-IR (cm^{-1}): 2928 (w), 2815 (w), 2358 (w), 2331 (w), 1750 (vw), 1714 (sh), 1700 (s), 1685 (sh), 1670 (m), 1625 (s), 1602 (m), 1558 (m), 1541 (m), 1520 (m), 1506 (m), 1473 (s), 1453 (s), 1437 (m), 1397 (s), 1360 (m), 1340 (s), 1315 (s), 1278 (m), 1257 (m), 1239 (m), 1223 (s), 1169 (s), 1149 (m), 1120 (m), 1089 (m), 1073 (m), 1040 (m), 1017 (m), 929 (m), 865 (m), 829 (s), 792 (m), 744 (s), 728 (sh), 685 (w), 642 (w), 627 (m), 607 (m), 587 (m), 525 (m).

Table S1 FT-IR νCO stretching frequencies obtained from the encapsulated and free-form aldehyde / ketone guest molecules measured in the free-form compared to when encapsulated within [M_7] (M = Zn(II), Ni(II) and Co(II)) pseudo metallocalix[6]arene host materials.

Host-guest complex	**νC=O stretch (encapsulated / free form) (cm^{-1})**
[(2-fur)⊂Zn(II)$_7$] (**1**)	1667 / 1668
[(2-fur)⊂Ni(II)$_7$] (**2**)	1669 / 1668
[(2-fur)⊂Co(II)$_7$] (**3**)	1671 / 1668
[(3-fur)⊂Zn(II)$_7$] (**4**)	1676 / 1677
[(3-fur)⊂Ni(II)$_7$] (**5**)	1676/ 1677
[(3-fur)⊂Co(II)$_7$] (**6**)	1678 / 1677
[(bzal)⊂Zn(II)$_7$] (**7**)	1689 / 1697
[(bzal)⊂Ni(II)$_7$] (**8**)	1689 / 1697
[(2-thio)⊂Zn(II)$_7$] (**9**)	1653 / 1668
[(2-thio)⊂Ni(II)$_7$] (**10**)	1656 / 1668
[(2-acetylfuran)⊂[Zn(II)$_7$] (**11**)	1667 / 1671
[(2-acetylfuran)⊂[Ni(II)$_7$] (**12**)	1665 / 1671
[(2-acetylfuran)⊂[Co(II)$_7$] (**13**)	1670 / 1671
[(acetoph)⊂Zn(II)$_7$] (**14**)	1676 / 1680
[(acetoph)⊂[Ni(II)$_7$] (**15**)	1674 / 1680
[(acetoph)⊂Co(II)$_7$] (**16**)	1676 / 1680
[(1-indanone)⊂Zn(II)$_7$] (**17**)	1705 (sh 1689) / 1700
[(1-indanone)⊂Ni(II)$_7$] (**18**)	1699/ 1700
[(coumarin)⊂Zn(II)$_7$] (**19**)	1707 and 1719/ 1697 and 1670
[(coumarin)⊂Ni(II)$_7$] (**20**)	1714 (sh) and 1700 / 1697 and 1670

Table S2 Crystallographic data obtained from complexes **1**, **3** and **5**.

	1·3H_2O	**3**·3H_2O	**5**·3H_2O
Formula[a]	$C_{65}H_{88}N_8O_{29}Zn_7$	$C_{59}H_{76}N_8O_{29}Co_7$	$C_{59}H_{76}N_8O_{29}Ni_7$
M_W	1903.08	1773.81	1772.13
Crystal System	Trigonal	Trigonal	Trigonal
Space group	P-3c1	P-3c1	P-3c1
a/Å	14.064(2)	14.100(2)	13.8183(5)
b/Å	14.064(2)	14.100(2)	13.8183(5)
c/Å	23.056(5)	22.702(5)	23.1848(14)
α/°	90	90	90
β/°	90	90	90
γ/°	120	120	120
V/Å^3	3949.3(14)	3908.7(11)	3833.9(4)
Z	2	2	2
T/K	150(2)	150(2)	150(2)
λ^b/Å	0.71073	0.71073	0.71073
D_c/g cm^{-3}	1.474	1.380	1.405
μ(Mo-Ka)/ mm^{-1}	2.162	1.518	1.752
Meas./indep.(R_{int}) refl.	7622 / 2416 (0.0660)	2388 / 1897 (0.0409)	7199 / 2344 (0.0337)
wR2 (all data)^c	0.1656	0.2461	0.2398
$R1^{d,e}$	0.0582	0.0784	0.0793
Goodness of fit on F^2	1.055	1.149	1.125

[a] Includes guest molecules.[b] Mo-Kα radiation, graphite monochromator. [c] $wR2= [\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$. [d]For observed data. [e] $R1= \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

Table S3 Crystallographic data obtained from complexes **6**, **7** and **12**.

	6·4.5H_2O	**7**·5H_2O	**12**·3H_2O
Formula[a]	$C_{59}H_{79}N_8O_{30.5}Co_7$	$C_{67}H_{82}N_8O_{30}Zn_7$	$C_{60}H_{78}N_8O_{24}Ni_7$
M_W	1800.83	1937.05	1870.31
Crystal System	Trigonal	Trigonal	Trigonal
Space group	P-3c1	P-3c1	P-3c1
a/Å	14.098(2)	14.010	13.811(2)
b/Å	14.098(2)	14.010	13.811(2)
c/Å	22.706(5)	23.002	23.235(2)
α/°	90	90	90
β/°	90	90	90
γ/°	120	120	120
V/Å^3	3909.5(11)	3909.9	3838.35(6)
Z	2	2	2
T/K	150(2)	173(2)	100(2)
λ^b/Å	0.71073	0.6889	0.71073
D_c/g cm^{-3}	1.380	1.489	1.476
μ(Mo-Ka)/ mm^{-1}	1.518	2.184	1.754
Meas./indep.(R_{int}) refl.	2388 / 1561 (0.0760)	82320 / 6611	66489 / 2358 (0.0330)
wR2 (all data)[c]	0.2955	(0.0470)	0.2240
$R1^{d,e}$	0.0953	0.1373	0.0753
Goodness of fit on F^2	1.188	0.0416 1.069	1.113

[a] Includes guest molecules.[b] Mo-Kα radiation, graphite monochromator. [c] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|^2]^{1/2}$. [d]For observed data. [e] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

Table S4 Crystallographic data obtained from complexes **13**, **16** and **20**.

	13 $7H_2O$	**16**·$7H_2O$	**20**·$3H_2O$
Formula[a]	$C_{66}H_{98}N_8O_{33}Co_7$	$C_{62}H_{100}N_8O_{32}Co_7$	$C_{54}H_{78}N_8O_{29}Ni_7$
M_W	1944.05	1954.09	1822.19
Crystal System	Trigonal	Trigonal	Trigonal
Space group	P-3c1	P-3c1	P-3c1
a/Å	14.053(2)	14.143(2)	13.82410(10)
b/Å	14.053(2)	14.143(2)	13.82410(10)
c/Å	23.008(2)	22.940(3)	23.4073(4)
α/°	90	90	90
β/°	90	90	90
γ/°	120	120	120
V/Å^3	3934.91(5)	3973.90(5)	3873.96(9)
Z	2	2	2
T/K	100(2)	100(2)	100(2)
λ^b/Å	1.54184	1.54184	0.71073
D_c/g cm^{-3}	1.441	1.427	1.391
μ(Mo-Ka)/ mm^{-1}	11.890	11.733	1.734
Meas./indep.(R_{int}) refl.	2416/2385 (0.0355)	2439/2343 (0.0409)	29716 / 2379 (0.0688)
wR2 (all data)^c	0.1486	0.1658	0.1923
$R1^{d,e}$	0.0482	0.0594	0.0575
Goodness of fit on F^2	1.122	1.110	1.132

^{a} Includes guest molecules.^{b} Mo-Kα radiation, graphite monochromator. ^{c} $wR2= [\Sigma w(|F_o^2|- |F_c^2|)^2/ \Sigma w|F_o^2|^2]^{1/2}$. ^{d}For observed data. ^{e} $R1= \Sigma||F_o|- |F_c||/ \Sigma|F_o|$.

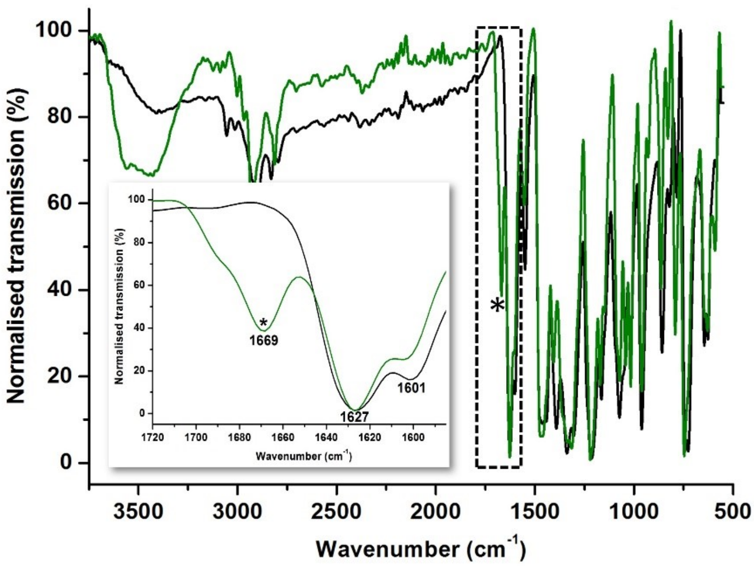


Figure S1 FT-IR spectra overlay of $[(MeOH)_2{\subset}Ni(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 2-furaldehyde accommodated complex $[(2\text{-fur}){\subset}Ni(II)_7(OMe)_6(L)_6](NO_3)_2{\cdot}3H_2O$ (**2**; green line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the 2-furaldehyde guests in **2**.

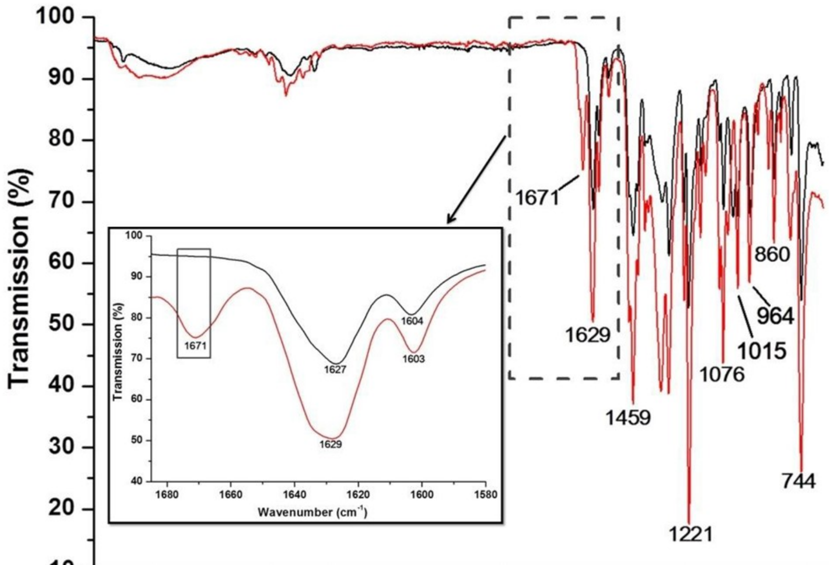


Figure S2 FT-IR spectra overlay of $[(MeOH)_2{\subset}Co(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 2-furaldehyde accommodated complex $[(2\text{-fur}){\subset}Co(II)_7(OH)_6(L)_6](NO_3)_2{\cdot}3H_2O$ (**3**) (red line). (Inset) Expansion of the 1685-1580 cm^{-1} region of the spectra highlighting the C=O aldehyde stretches (*) of the 2-furaldehyde guests in **3**.

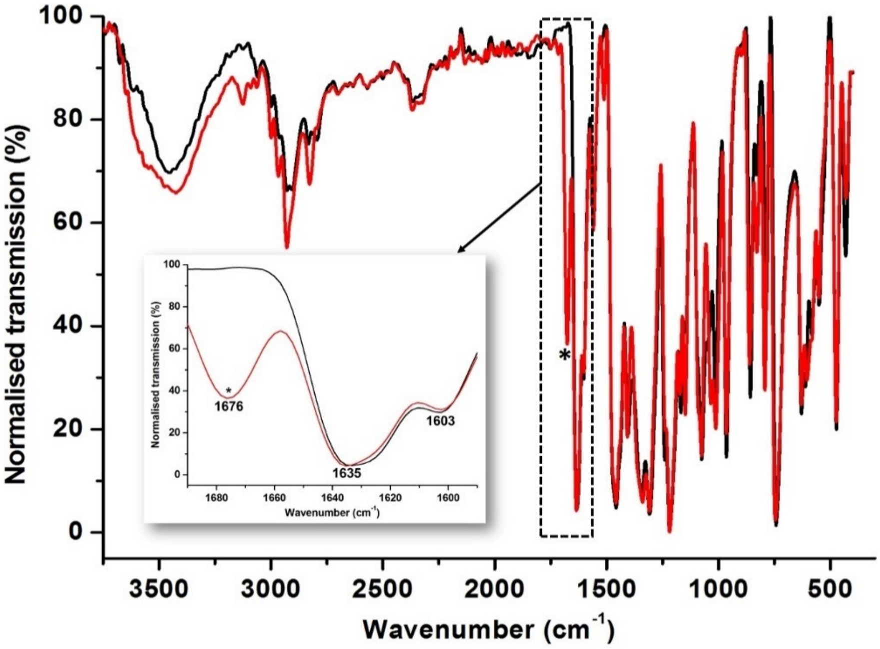


Figure S3 FT-IR spectra overlay of $[(MeOH)_2\subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 3-furaldehyde accommodated complex $[(3\text{-fur})\subset Zn(II)_7(OMe)_6(L)_6](NO_3)_2$ (**4**; red line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the 3-furaldehyde guests in **4**.

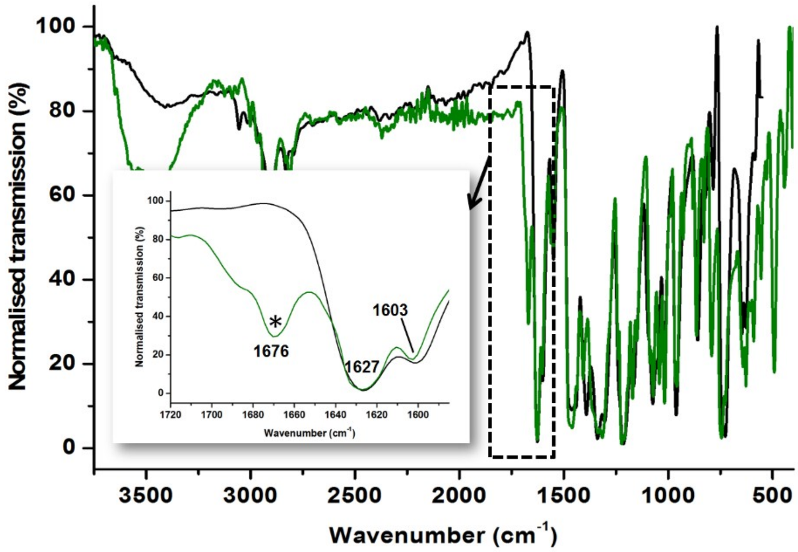


Figure S4 FT-IR spectra overlay of $[(MeOH)_2\subset Ni(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 3-furaldehyde accommodated complex $[(3\text{-fur})\subset Ni(II)_7(OMe)_6(L)_6](NO_3)_2\cdot 3H_2O$ (**5**; green line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the 3-furaldehyde guests in **5**.

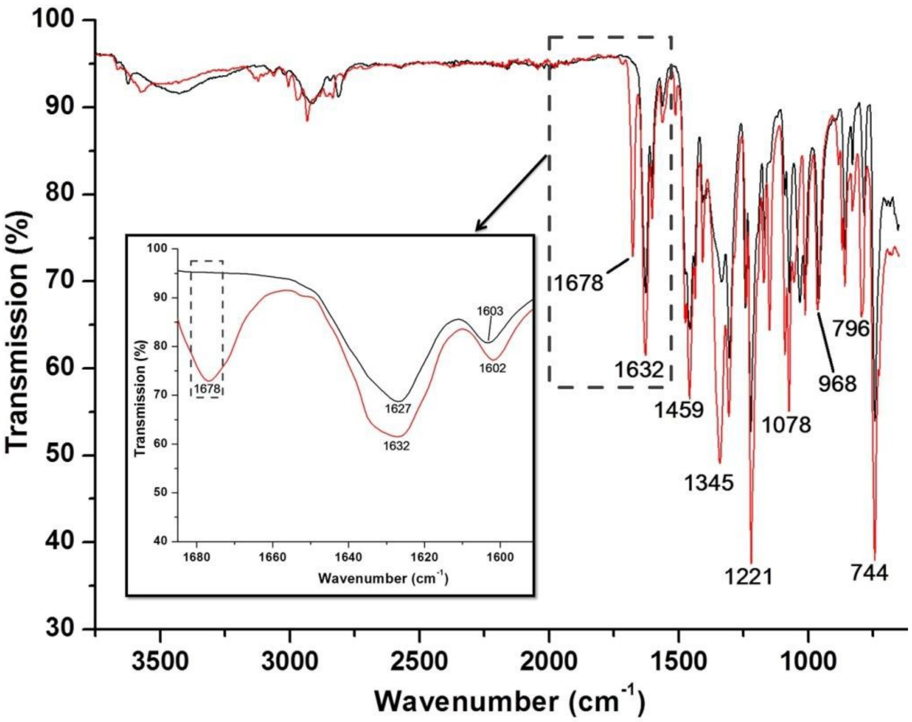


Figure S5 FT-IR spectra overlay of $[(MeOH)_2{\subset}Co(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 3-furaldehyde accommodated complex $[(3\text{-fur}){\subset}Co(II)_7(OH)_6(L)_6](NO_3)_2{\cdot}4.5H_2O$ (**6**) (red line). (Inset) Expansion of the 1685-1580 cm^{-1} region of the spectra highlighting the C=O aldehyde stretches (*) of the 3-furaldehyde guests in **6**.

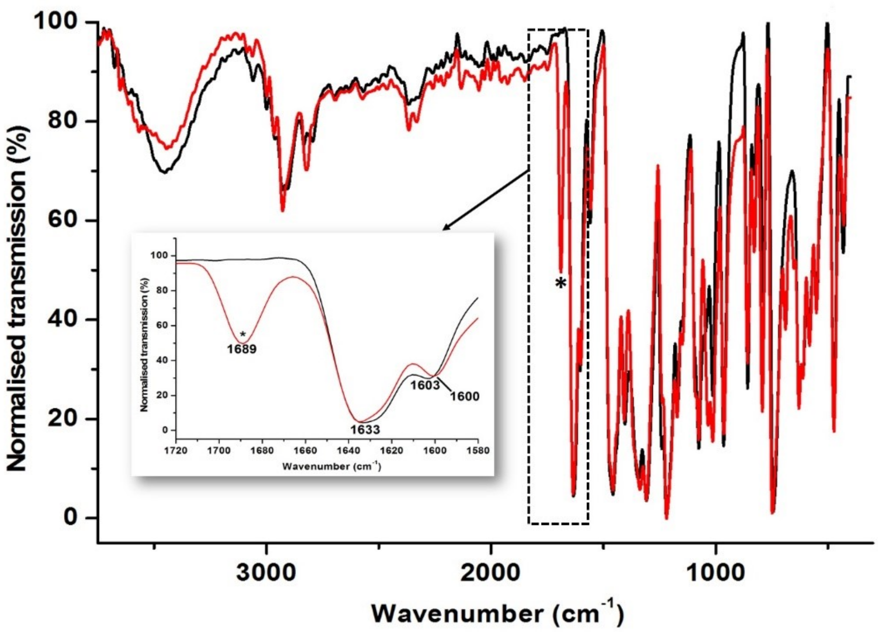


Figure S6 FT-IR spectra overlay of $[(MeOH)_2{\subset}Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the benzaldehyde accommodated complex $[(bzal){\subset}Zn(II)_7(OMe)_6(L)_6](NO_3)_2{\cdot}5H_2O$ (**7**; red line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the benzaldehyde guests in **7**.

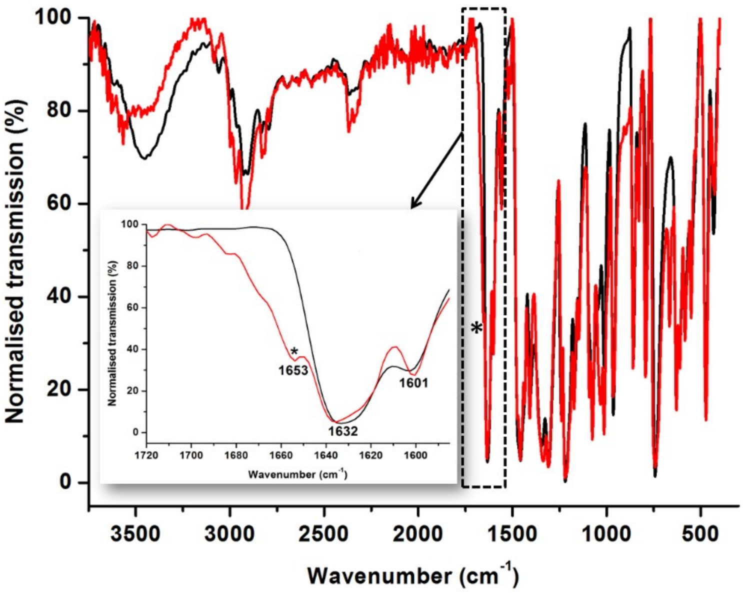


Figure S7 FT-IR spectra overlay of $[(MeOH)_2 \subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 2-thiophenecarboxaldehyde accommodated complex $[(2\text{-thio}) \subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (**9**; red line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the 2-thiophenecarboxaldehyde guests in **9**.

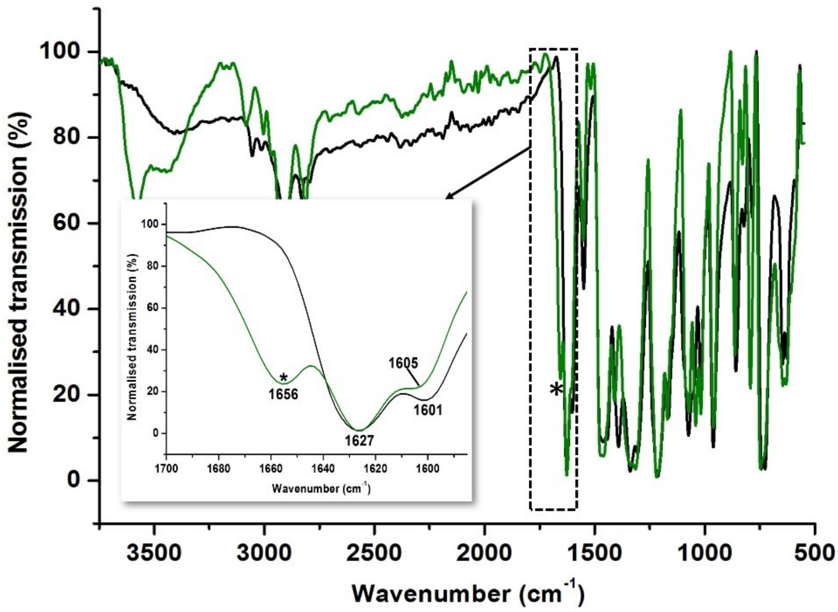


Figure S8 FT-IR spectra overlay of $[(MeOH)_2 \subset Ni(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 2-thiophenecarboxaldehyde accommodated complex $[(2\text{-thio}) \subset Ni(II)_7(OH)_6(L)_6](NO_3)_2$ (**10**; green line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the thiophenecarboxaldehyde guests in **10**.

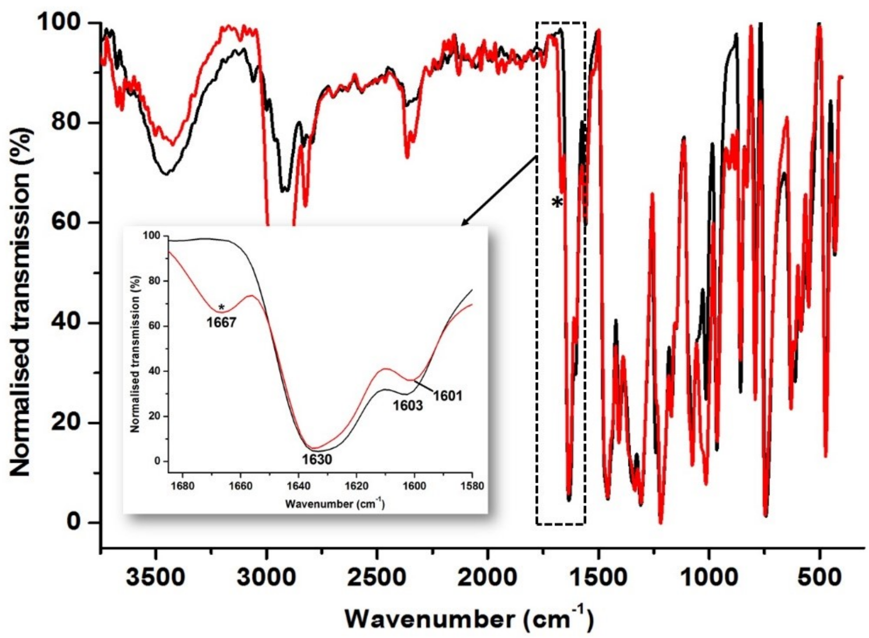


Figure S9 FT-IR spectra overlay of $[(MeOH)_2\subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 2-acetylfuran accommodated complex $[(2\text{-acetylfuran})\subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (**11**; red line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the 2-acetylfuran guests in **11**.

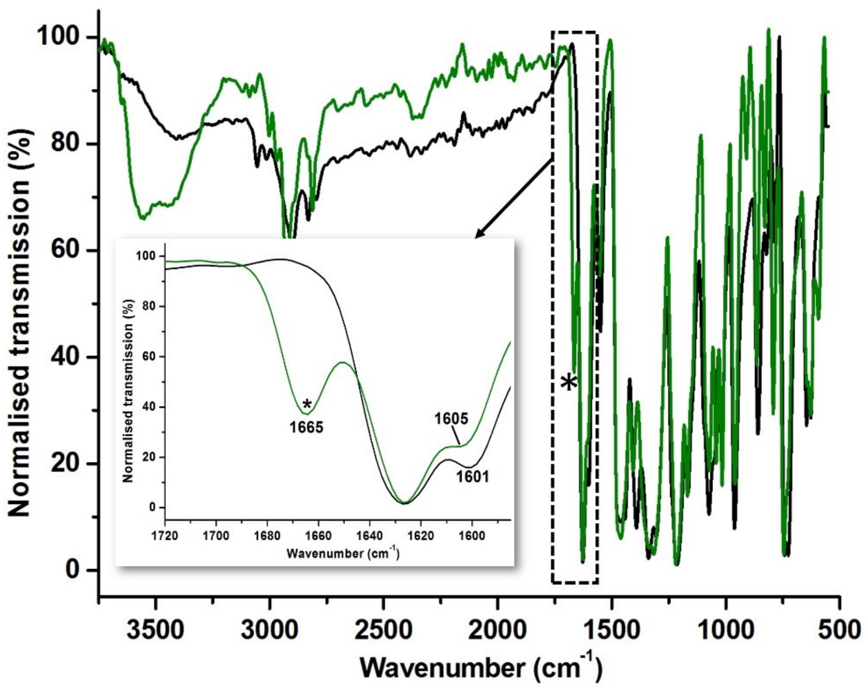


Figure S10 FT-IR spectra overlay of $[(MeOH)_2\subset Ni(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 2-acetylfuran accommodated complex $[(2\text{-acetylfuran})\subset Ni(II)_7(OMe)_6(L)_6](NO_3)_2\cdot 3H_2O$ (**12**; green line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the 2-acetylfuran guests in **12**.

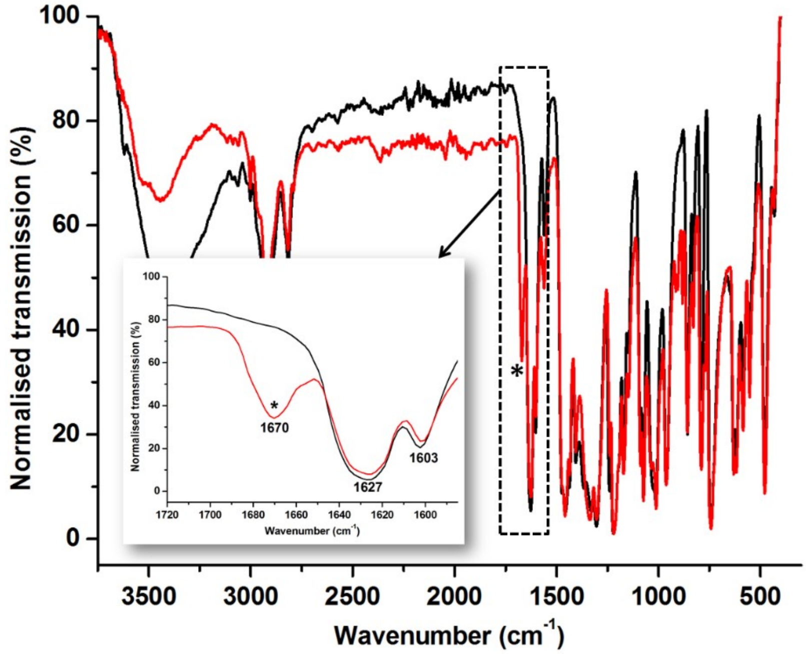


Figure S11 FT-IR spectra overlay of $[(MeOH)_2\subset Co(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 2-acetylfuran accommodated complex $[(2\text{-acetylfuran})\subset Co(II)_7(OMe)_6(L)_6](NO_3)_2\cdot 7H_2O$ (**13**; red line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the 2-acetylfuran guests in **13**.

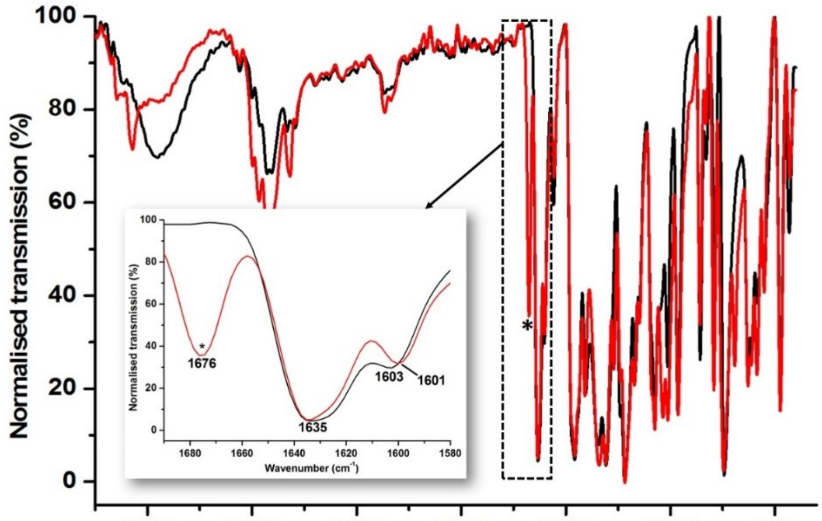


Figure S12 FT-IR spectra overlay of $[(MeOH)_2\subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the acetophenone accommodated complex $[(\text{acetophenone})\subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (**14**; red line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the acetophenone guests in **14**.

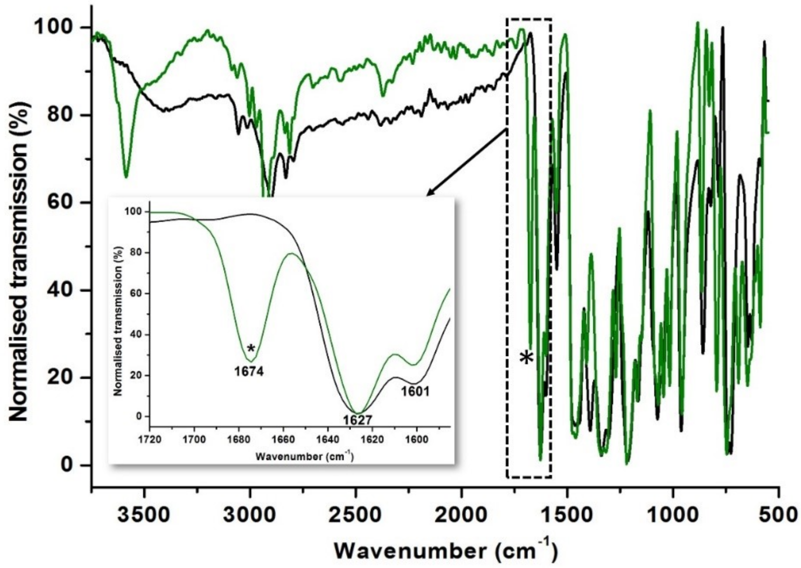


Figure S13 FT-IR spectra overlay of $[(MeOH)_2{\subset}Ni(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the acetophenone accommodated complex $[(acetophenone){\subset}Ni(II)_7(OMe)_6(L)_6](NO_3)_2$ (**15**; green line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the acetophenone guests in **15**.

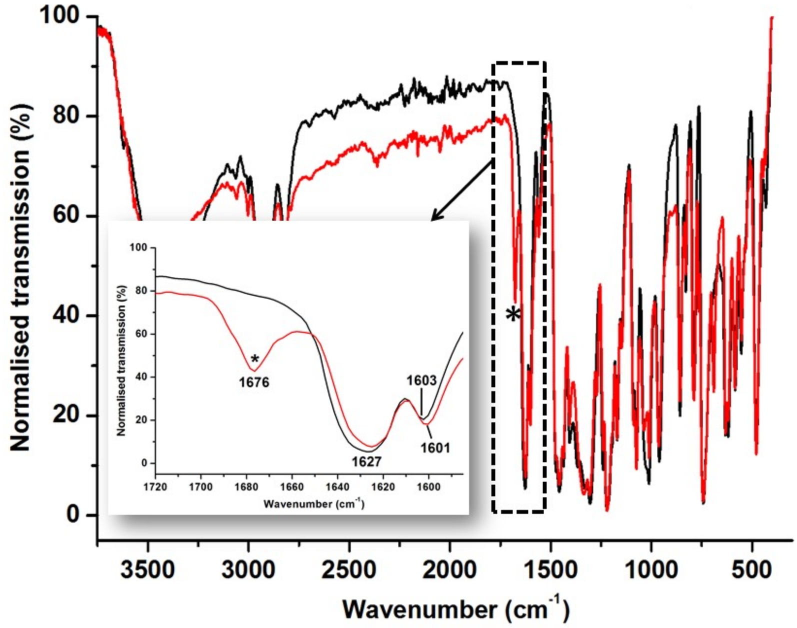


Figure S14 FT-IR spectra overlay of $[(MeOH)_2{\subset}Co(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the acetophenone accommodated complex $[(acetoph){\subset}Co(II)_7(OMe)_6(L)_6](NO_3)_2{\cdot}7H_2O$ (**16**; red line). (Inset) Expansion of the 1720-1585 cm^{-1} region of the spectra highlighting the CO aldehyde stretch (*) of the acetophenone guests in **16**.

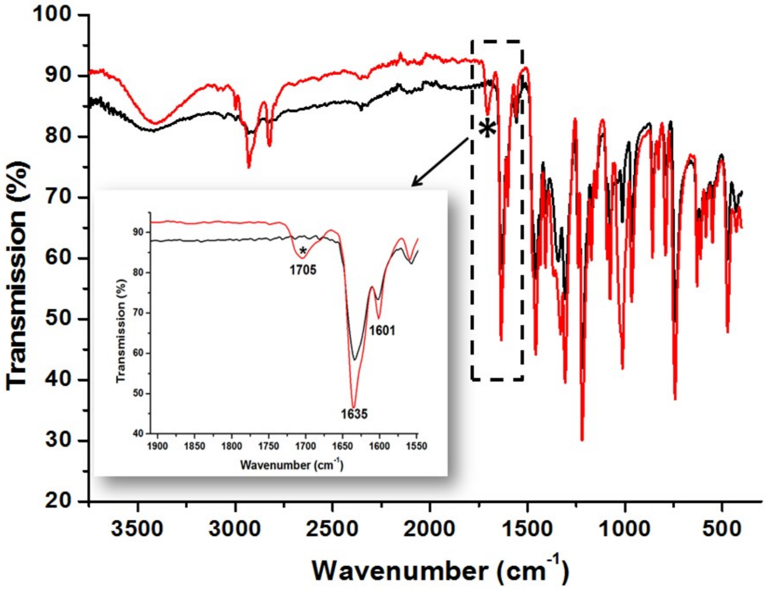


Figure S15 FT-IR spectra overlay of $[(MeOH)_2\subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the 1-indanone accommodated complex $[(\text{1-indanone})\subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (**17**; red line). (Inset) Expansion of the 1550-1900 cm^{-1} region of the spectrum highlighting the CO aldehyde stretch (*) of the 1-indanone guests in **17**.

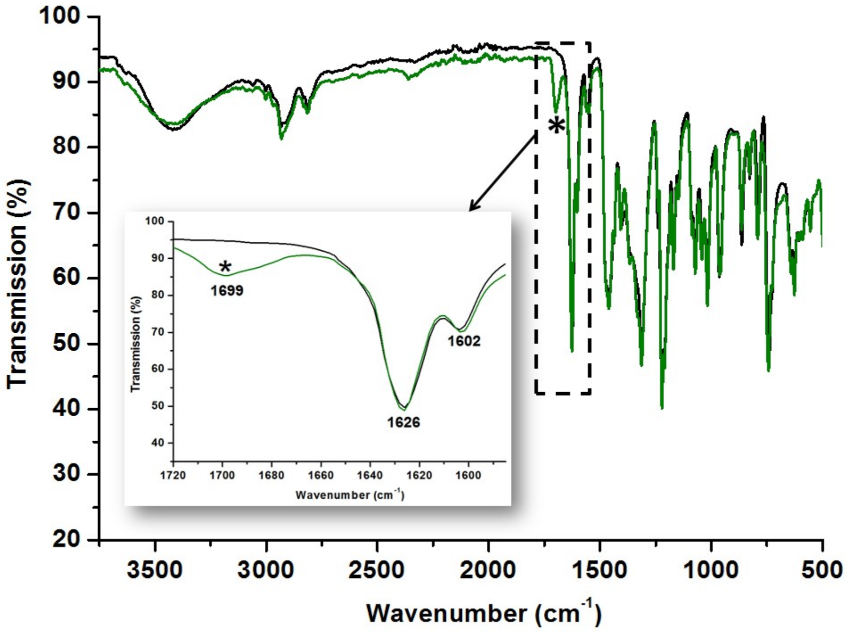


Figure S16 FT-IR spectra overlay of $[(MeOH)_2\subset Ni(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the coumarin accommodated complex $[(\text{1-indanone})\subset Ni(II)_7(OH)_6(L)_6](NO_3)_2$ (**18**; green line). (Inset) Expansion of the 1575-1900 cm^{-1} region of the spectrum highlighting the CO aldehyde stretch (*) of the 1-indanone guests in **18**.

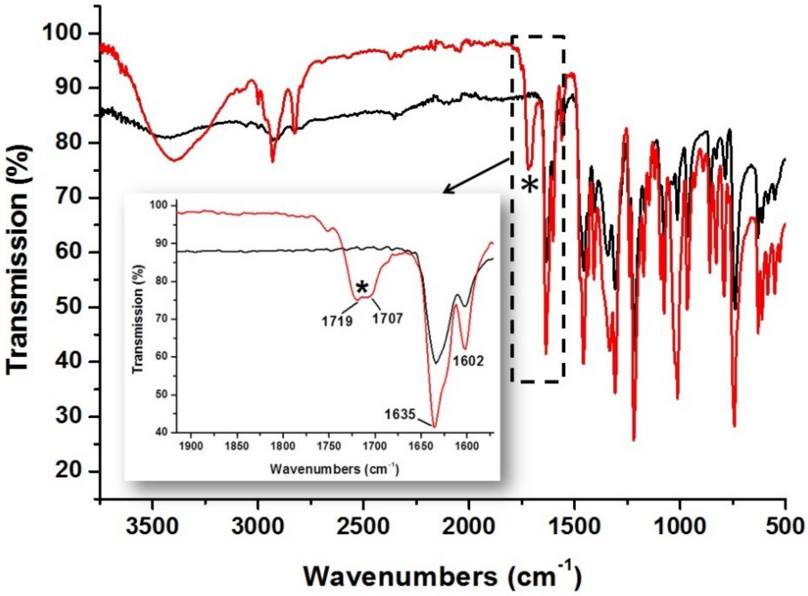


Figure S17 FT-IR spectra overlay of $[(MeOH)_2{\subset}Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the coumarin accommodated complex $[(coumarin){\subset}Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (**19**; red line). (Inset) Expansion of the 1575-1900 cm^{-1} region of the spectrum highlighting the CO aldehyde stretch (*) of the coumarin guests in **19**.

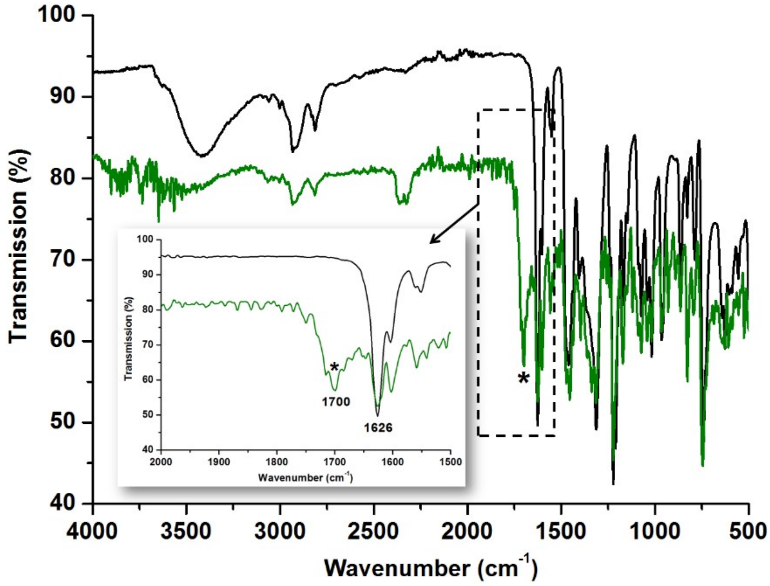


Figure S18 FT-IR spectra overlay of $[(MeOH)_2{\subset}Ni(II)_7(OH)_6(L)_6](NO_3)_2$ (black line) and the coumarin accommodated complex $[(coumarin){\subset}Ni(II)_7(OH)_6(L)_6](NO_3)_2{\cdot}3H_2O$ (**20**; green line). (Inset) Expansion of the CO aldehyde stretch region (*) of the coumarin guests in **20**.

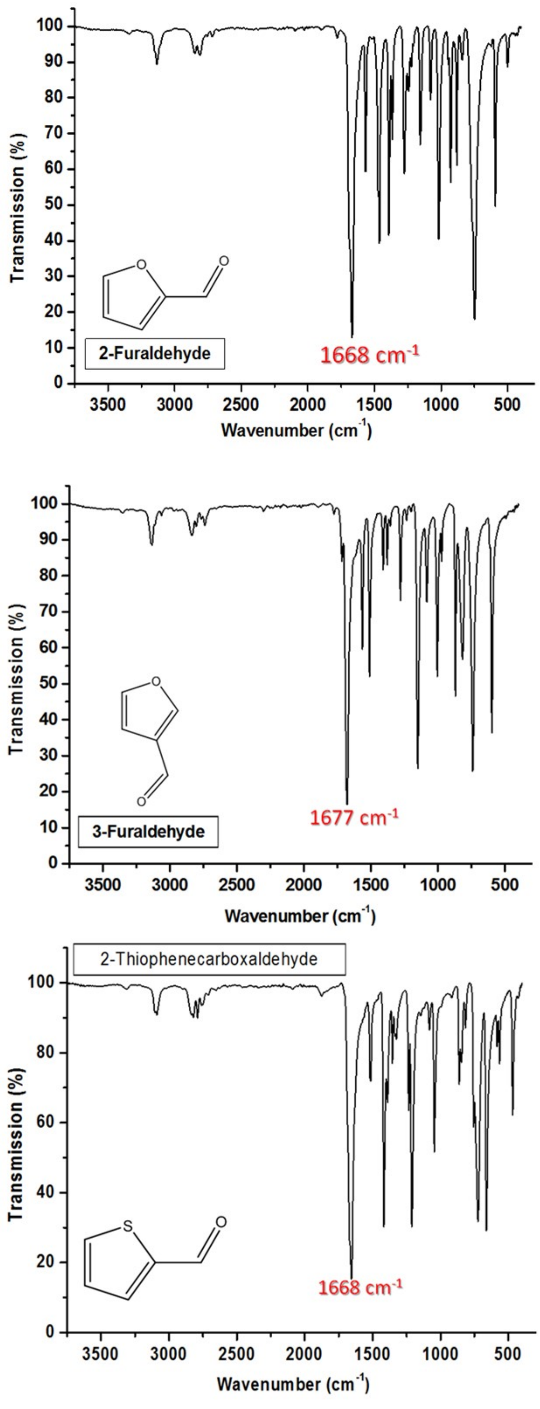


Figure S19 FT-IR spectra of the guest molecules 2-furaldehyde (top), 3-furaldehyde (middle), 2-thiophenecarboxaldehyde (bottom) used in this work. The νC=O stretch resonance is highlighted in each case.

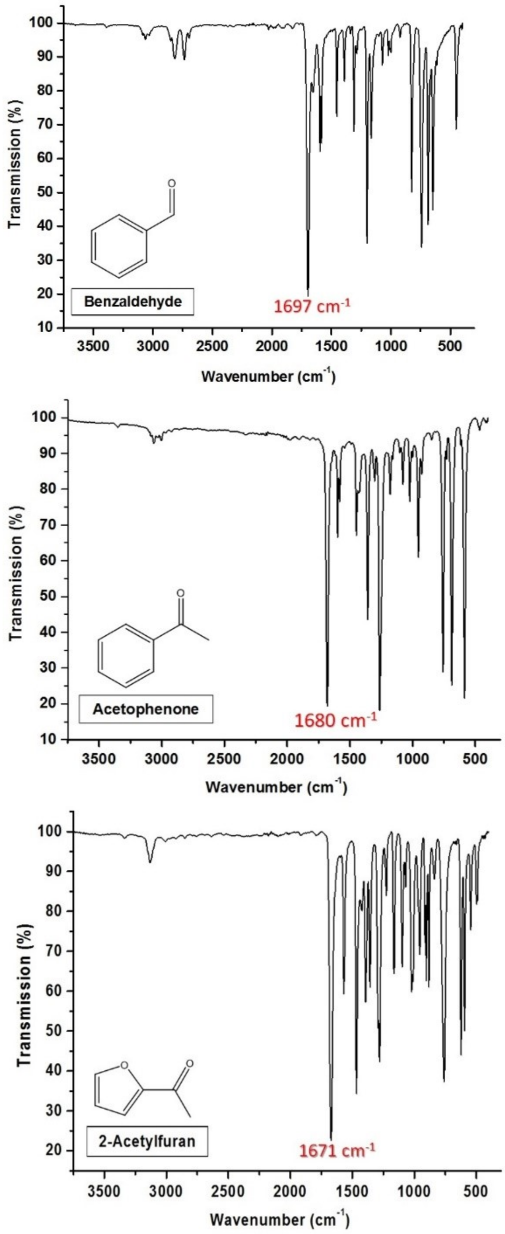
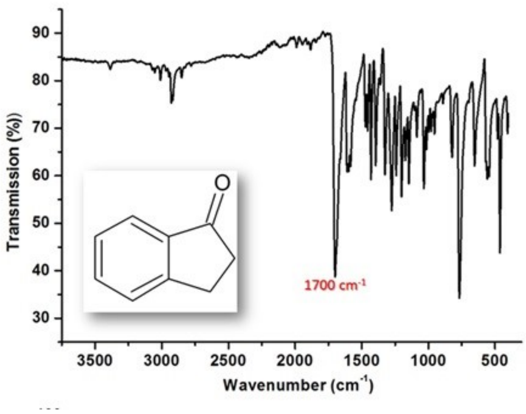


Figure S20 FT-IR spectra for the guest molecules benzaldehyde (top), acetophenone (middle) and 2-acetylfuran (bottom) used in this work. The νC=O stretch resonance is highlighted in each case.



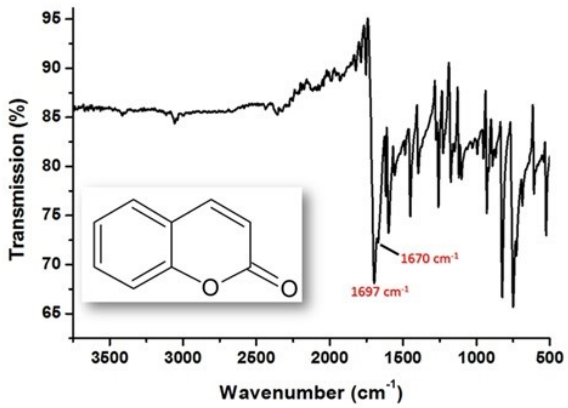


Figure S21 FT-IR spectra of the guest molecules 1-indanone (left) and coumarin (right) used in this work. The ν C=O stretch resonance(s) is highlighted in each case.

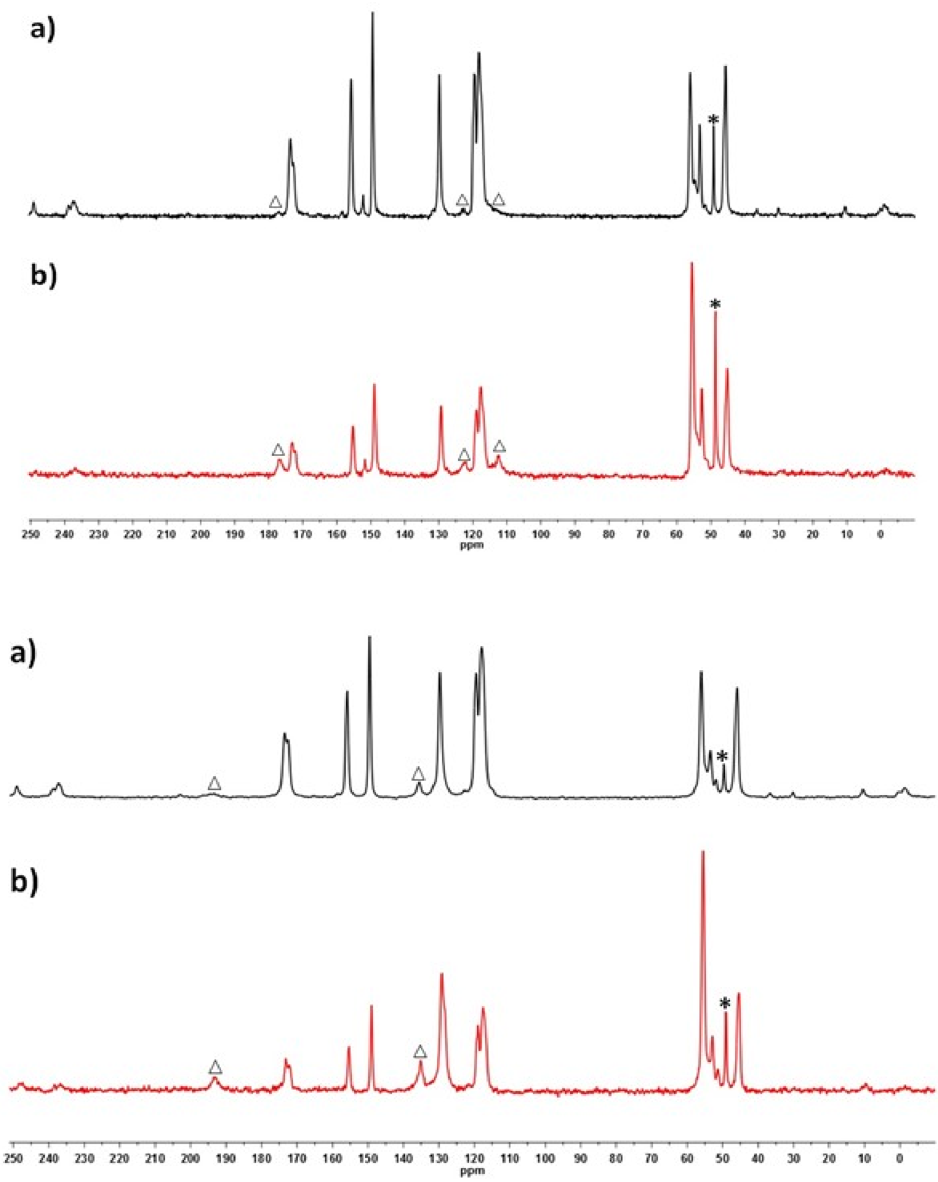


Figure S22 (Top) (a) Room temperature ^{13}C CP/MAS NMR spectrum of [(2-fur)⊂Zn(II)$_7$] (**1**) recorded at a spinning speed of 12 KHz. Triangles (Δ) trace the ^{13}C signals of 2-furaldehyde guest. (b) ^{13}C CP/MAS short-recycle, direct excitation spectrum of [(2-fur)⊂Zn(II)$_7$] (**1**) recorded at a spinning speed of 12 KHz at room temperature. (Bottom) (a) Room temperature ^{13}C CP/MAS NMR spectrum of [(bzal)⊂Zn(II)$_7$] (**7**) recorded at a spinning speed of 12 KHz. Triangles (Δ) trace the ^{13}C signals of benzaldehyde guest. (b) ^{13}C CP/MAS NMR short-recycle, direct excitation spectrum of [(bzal)⊂Zn(II)$_7$] (**7**) recorded at a spinning speed of 12 KHz at room temperature. Star (*) symbols represent trace methanol.

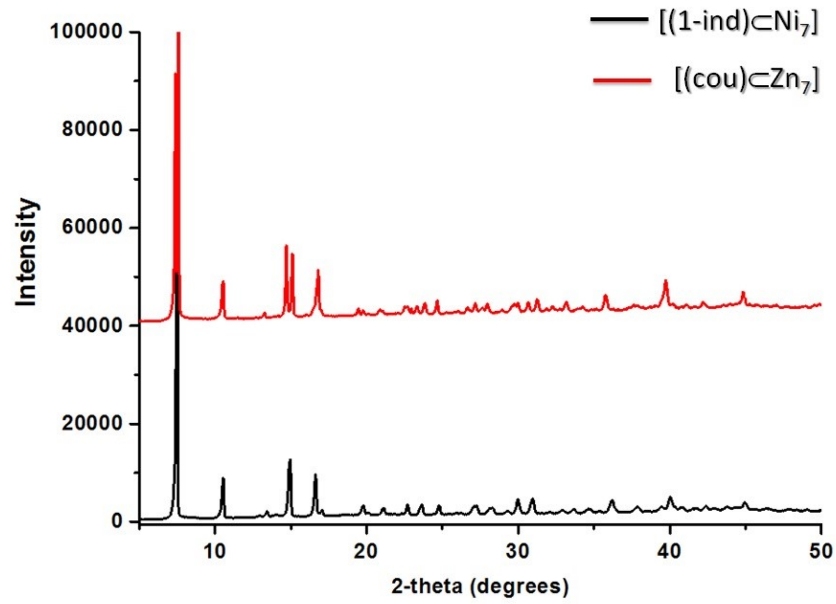


Figure S23 Powder X-ray diffraction data obtained from polycrystalline samples of [(1-indanone)⊂Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**18**; black line) and [(coumarin)⊂Zn(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**19**; red line).

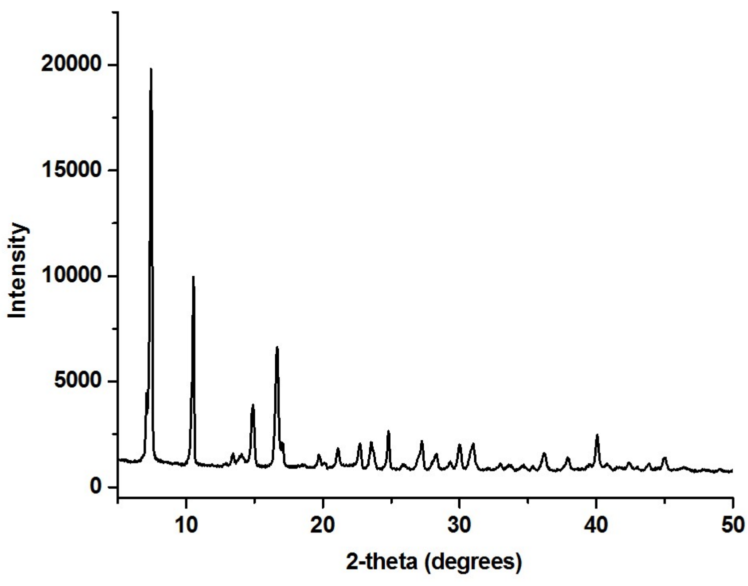


Figure 24 Powder X-ray diffraction data obtained from polycrystalline samples of [(coumarin)⊂Ni(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**20**).

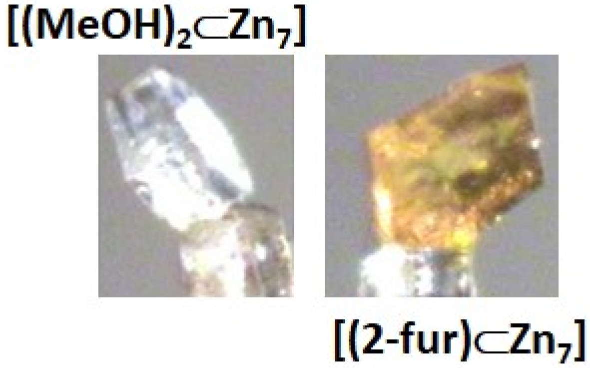


Figure S25 The single crystals of $[(MeOH)_2\subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ and $[(2\text{-}fur)\subset Zn(II)_7(OH)_6(L)_6](NO_3)_2$ (**1**) used for their X-ray diffraction collections, highlighting the colour difference upon guest encapsulation.

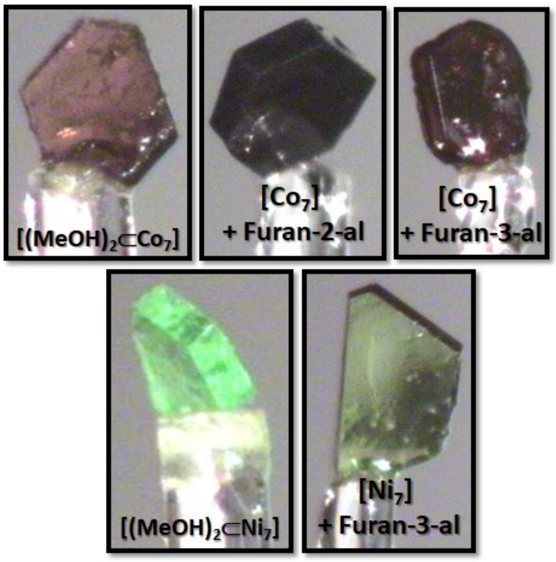


Figure S26 (Top) The single crystals of $[(MeOH)_2\subset Co(II)_7(II)_7(OH)_6(L)_6](NO_3)_2$, $[(2\text{-}fur)\subset Co(II)_7(OH)_6(L)_6](NO_3)_2\cdot 3H_2O$ (**3**) and $[(3\text{-}fur)\subset Co(II)_7(OH)_6(L)_6](NO_3)_2\cdot 4.5H_2O$ (**6**) used for their X-ray diffraction collections. (Bottom) Another example of guest influence on crystal colour using the complexes $[(MeOH)_2\subset Ni(II)_7(OH)_6(L)_6](NO_3)_2$ and $[(3\text{-}fur)\subset Ni(II)_7(OH)_6(L)_6](NO_3)_2\cdot 3H_2O$ (**5**).

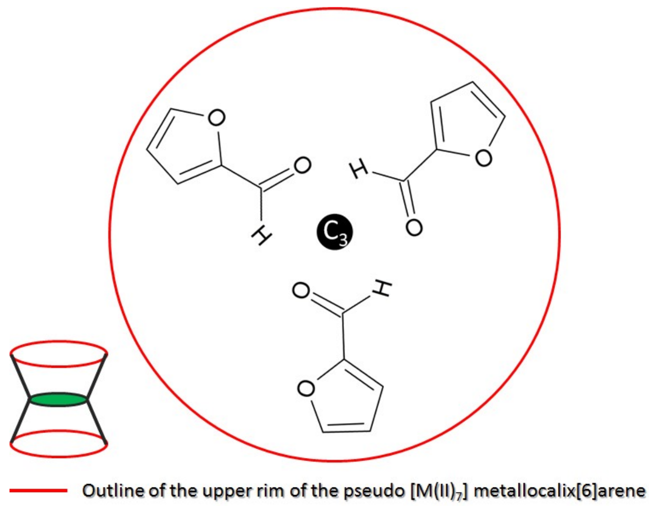
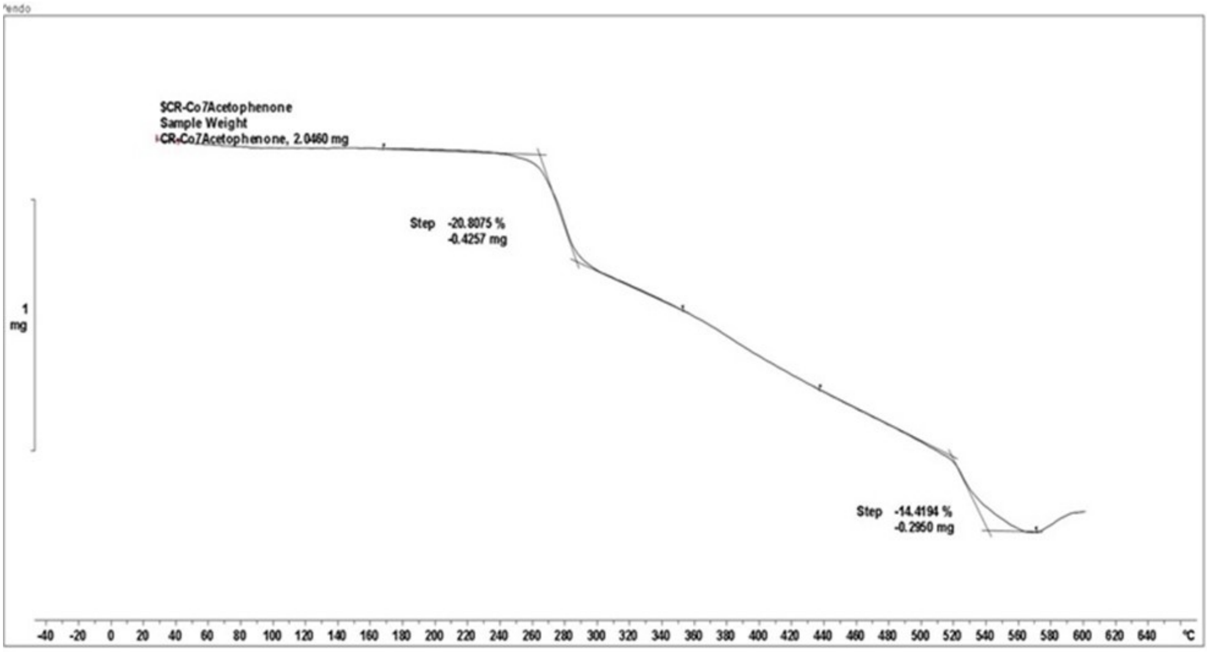


Figure 27 Schematic showing a guest 2-furaldehyde unit disordered over three sites related by a C_3 rotation axis lying central and perpendicular to the $\{M(II)_7\}$ plane. We propose this is the case for all inclusion complexes discussed in this work.

Table S5 Bond Valence Sum (BVS) analysis on complexes **3**, **6**, **13** and **16**.

*[(2-fur)⊂Co(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$·3H$_2$O (**3**)*	
Atom label	***Metal oxidation state from BVS analysis***
Co1	2.01
Co2	2.09
*[(3-fur)⊂Co(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$·4.5H$_2$O (**6**)*	
Atom label	***Metal oxidation state from BVS analysis***
Co1	*2.00*
Co2	*2.02*
*[(2-acetylfuran)⊂[Co(II)$_7$(OMe)$_6$(L)$_6$](NO$_3$)$_2$·7H$_2$O (**13**)*	
Atom label	***Metal oxidation state from BVS analysis***
Co1	*1.93*
Co2	*2.02*
*[(acetoph)⊂[Co(II)$_7$(OMe)$_6$(L)$_6$](NO$_3$)$_2$·7H$_2$O (**16**)*	
Atom label	***Metal oxidation state from BVS analysis***
Co1	*1.92*
Co2	*2.02*



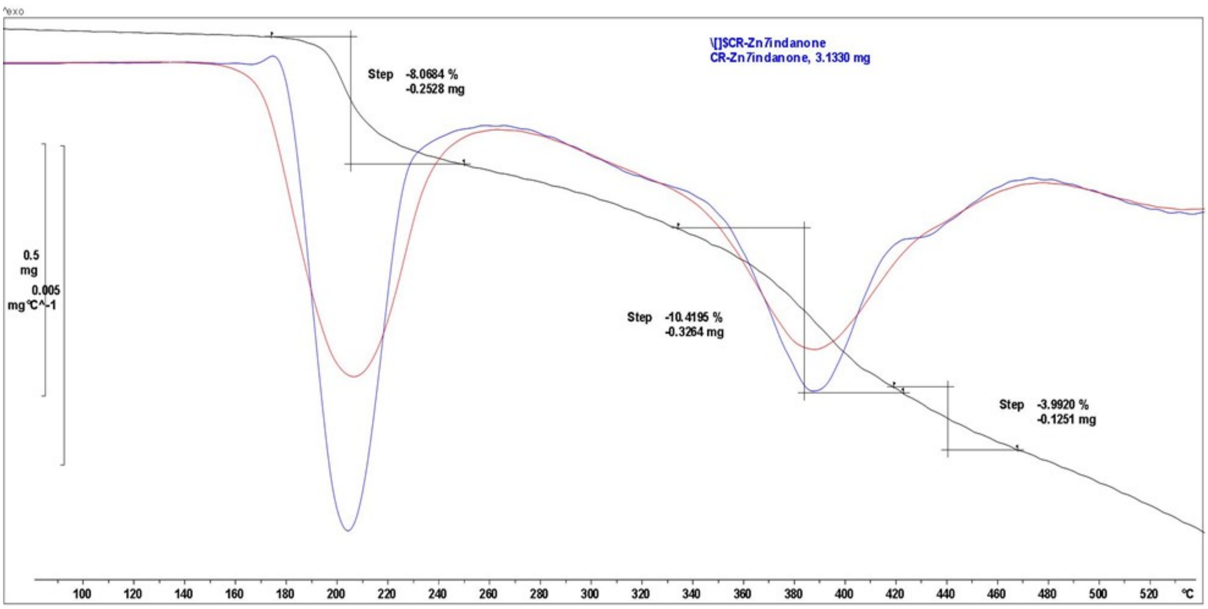


Figure S28 TGA curves (mass loss vs. temperature) obtained upon analysis of the complexes [(acetoph)⊂[Co(II)$_7$(OMe)$_6$(L)$_6$](NO$_3$)$_2$·7H$_2$O (**16**, top) and [(1-indanone)⊂[Zn(II)$_7$(OH)$_6$(L)$_6$](NO$_3$)$_2$ (**17**, bottom).

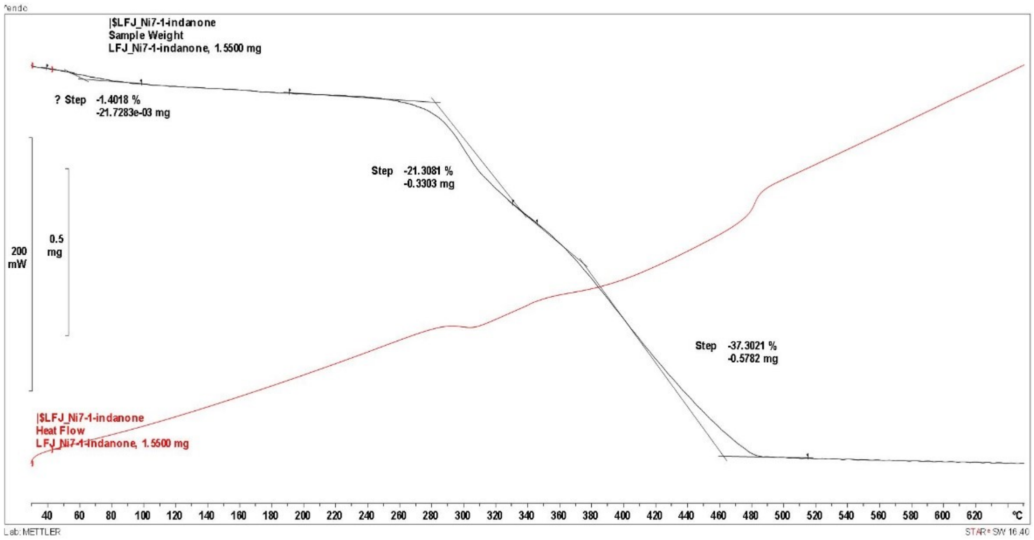
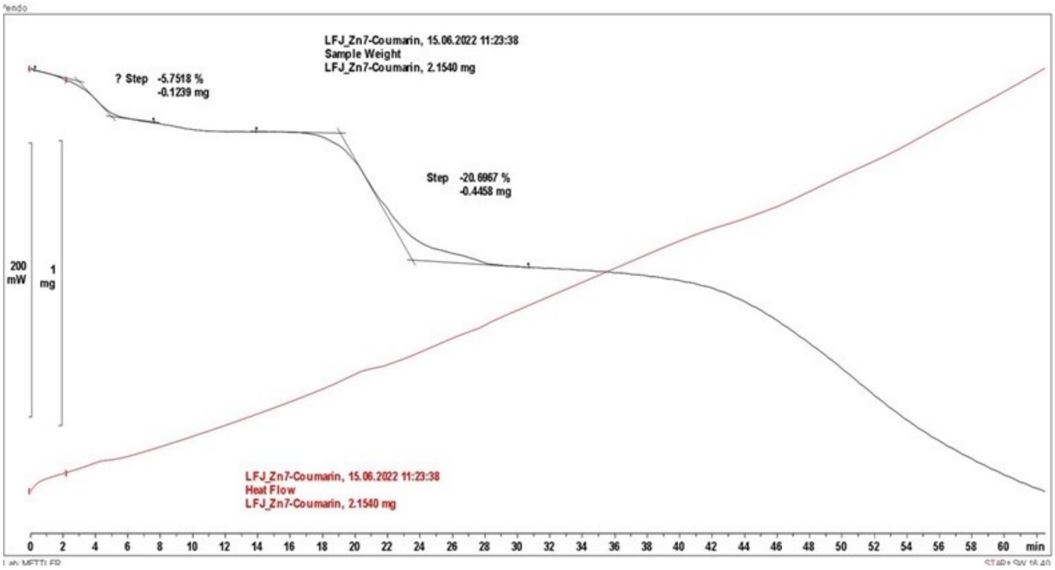


Figure S29 TGA curve (mass loss vs. temperature) obtained upon analysis of the complex [(1-indanone)⊂[Ni(II)$_7$(OH)$_6$(L)$_6$(NO$_3$)$_2$] (**18**).



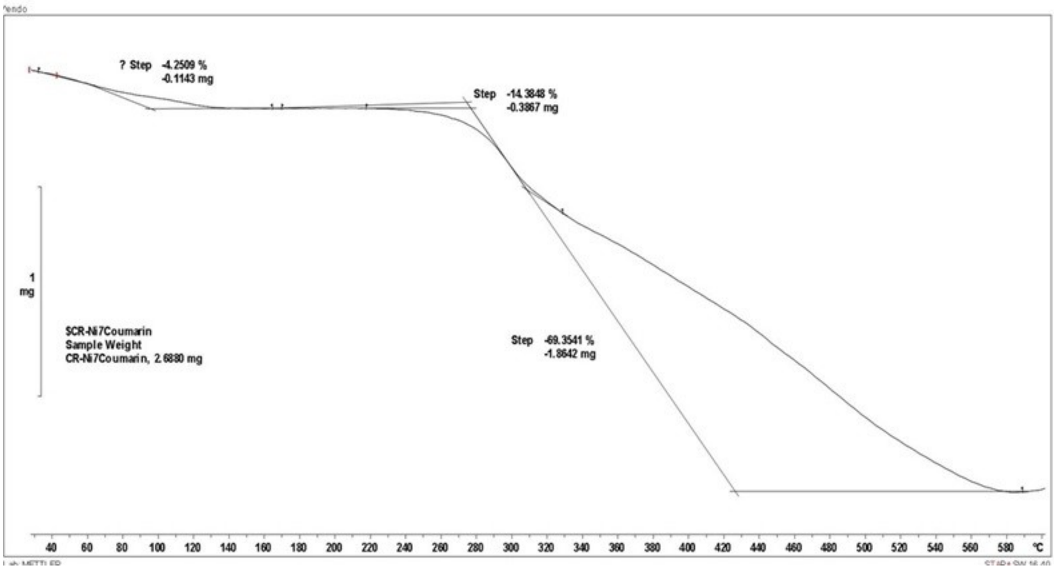


Figure S30 TGA curves (mass loss vs. temperature) obtained upon analysis of the complexes [(coumarin)⊂[Zn(II)$_7$(OH)$_6$(L)$_6$(NO$_3$)$_2$] (**19**, top) and [(coumarin)⊂[Ni(II)$_7$(OH)$_6$(L)$_6$(NO$_3$)$_2$·3H$_2$O (**20**, bottom).