Supplementary Material (ESI) for Chemical Communications


# Electronic Supplementary Information

# Unique hydrocarbon adsorption in a highly porous metal-organic framework made of extended aliphatic ligands

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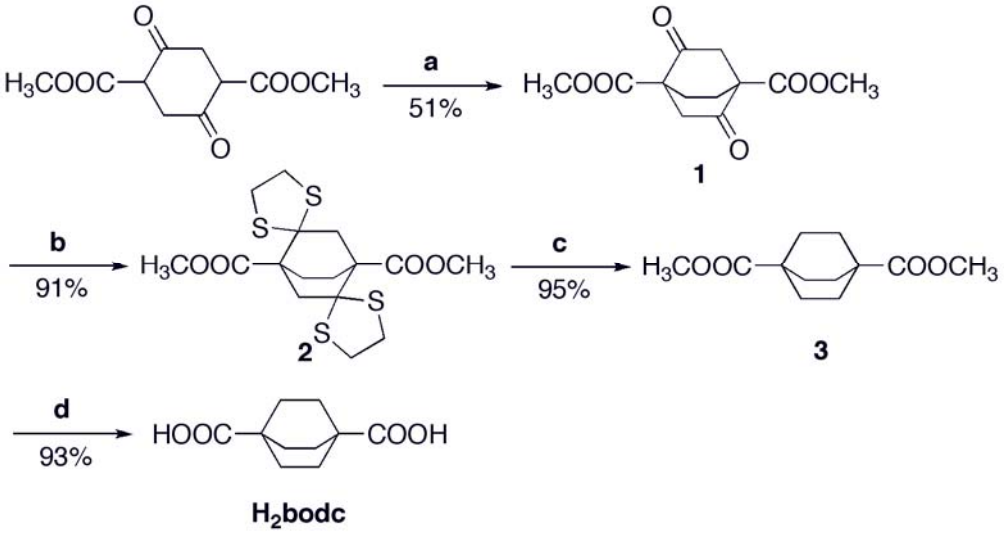
**Experimental.**

**General.** All chemicals except **1**, **2**, **3** and $H_2$bodc were purchased from Fisher Scientific or VWR and used without further purification unless stated otherwise. $^1$H and $^{13}$C NMR spectra were collected at room temperature on a Varian Mercury 200 MHz spectrometer. Tetramethylsilane (TMS) was used as internal reference. Thermogravimetric analysis data were collected on a TA Q50 Thermogravimetric Analyzer with a temperature ramping rate of 5 °C/min from room temperature to 600 °C under nitrogen gas flow. Powder X-ray diffraction patterns were recorded on a Rigaku D/M-2200T automated diffractometer (Ultima+) using Cu Kα radiation ($\lambda$ = 1.5406 Å). Graphite monochromator was used and the generator power settings are at 40 kV and 40 mA. Data were collected between a $2\theta$ of 3-50° with a step size of 0.02° at a scanning speed of 2.0 deg./min. Elemental microanalysis was carried out by an independent service provider, QTI, Whitehouse, NJ.

Heating a pink solution of $H_2$bodc (20.0 mg), ted (11.7 mg) and $Co(NO_3)_2{\cdot}6H_2O$ (29.9 mg) in DMF (3 mL, w/ 1 drop of conc. $HNO_3$ added) at 100 ºC for 4 days afforded block-like purple-blue/brown dichroic crystals of **2**. One of the crystals was selected and sealed in a fine-focus capillary tube due to its instability in air. Single-crystal X-ray diffraction data of **2** were collected at 296 K on a Bruker-AXS smart APEX I CCD diffractometer with graphite-monochromated Mo Kα Radiation ($\lambda$ = 0.71073 Å). A total of 45273 reflections were collected (5539 unique, $R$(int) = 0.0363) between a $\theta$ of 1.71° to 28.28°. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ using the Bruker SHELXTL package. See the end of the file for the selected crystallographic information as an appendix.

**Scheme S1**: **Synthesis of bicyclo[2.2.2]octane-1,4-dicarboxylic acid ($H_2$bodc).**[a]




[a] (a) NaH, DME, reflux; $BrC_2H_4Br$, reflux; (b) $HSC_2H_4SH$, $BF_3$ etherate, 0 °C to rt; (c) Raney Ni, EtOH, reflux; (d) NaOH, EtOH/$H_2O$, reflux; HCl.

**Synthesis of 1.** Into a magnetically stirred suspension of dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate (99+%, 11.453g, 50.0 mmol, pumped under vacuum at 85 ˚C for overnight before use) in dimethoxy ethane (DME, anhydrous, 99%, 100 mL) was sodium hydride (60% dispersion in mineral oil, 4.420 g, 110.5 mmol) added portion-wise under argon protection. After the bubbling subdued, the mixture was heated to reflux for 3 hrs, during which time a purple pink suspension was formed. After distilling almost all DME, 1,2-dibromoethane (99%, 175 mL, mmol, purged with argon for 10 min before use) was transferred *via cannula* into the reaction flask and the mixture was then heated at refluxing temperature for another 3 days. After the yellow suspension cooled to rt, 1,2-dibromoethane was removed in vacuo to afford a yellow solid. Chloroform (100 mL) and water (100 mL) were added and the mixture transferred into a separatory funnel. The water layer was cut out and the organic layer was rinsed with sodium hydroxide (1% in water, 100 mL × 5), water (100 mL × 5) and sodium chloride (saturated aqueous solution, 100 mL) before it was dried over anhydrous magnesium sulfate. After treating the sodium hydroxide wash with concentrated hydrochloric acid, 1.093 g of the starting material, dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate (confirmed by TLC), was

recovered. The dried chloroform solution was filtered and chloroform removed on a rotary evaporator to afford a light yellow, crysltalline solid (9.103 g, 79% yield based on the converted dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate). After recrystallization in 95% ethanol, colorless block-like crystals were obtained (5.900 g, 51% yield).

$^{1}$H NMR (200 MHz, $CDCl_3$): 2.06-2.23 (m, 2H), 2.42-2.60 (m, 2H), 5.47 (d, 2H, *J* = 19.4 Hz), 3.03-3.14 (dd, *J* = 2.8 Hz and 19.4 Hz), 3.80 (s, 6H). $^{13}$C NMR (50 MHz, $CDCl_3$): 24.64, 41.94, 52.95, 57.55, 169.22, 203.63.

**Synthesis of 2.** Under argon protection, boron trifluoride diethyl etherate (99%, 3.0 mL) was injected into a 50 mL three-neck round bottom flask containing chloroform (anhydrous, 15 mL). The flask was then chilled in an ice-water bath and a chloroform (10 mL) solution of 1,2-ethaneditiol (98+%, 3.4 mL, 39.7 mmol) and 1 (2.506 g, 9.9 mmol) was added slowly. When the addition was complete, the ice-water bath was removed and the mixture stirred at rt for another 3 hrs. After transferring the mixture into a separatory funnel, additional chloroform (30 mL) was added and the organic layer extracted with sodium hydroxide (2 M in water, 75 mL × 3), water (75 mL × 2) and sodium chloride (saturated aqueous solution, 75 mL). The organic layer was then dried over anhydrous magnesium sulfate for 15 min before it was filtered and removed in vacuo. The product, 2, was obtained as colorless needles (3.654 g, 91% yield based on **1**). **2** was shown by NMR to be essentially pure and was used for the following synthesis without further purification.

$^{1}$H NMR (200 MHz, $CDCl_3$): 1.88-2.05 (m, 2H), 2.42-2.62 (m, 2H), 2.83-3.10 (m, 6H), 3.25-3.41 (m, 6H), 3.66 (s, 6H). $^{13}$C NMR (50 MHz, $CDCl_3$): 26.57, 39.54, 40.70, 51.32, 52.29, 70.13, 173.04.

**Synthesis of 3.**Into a 500 mL three-neck round bottom flask (flushed with argon for 5 min) was added wet Raney Nickel (activated, 35 g). Ethanol (absolute, 50 mL × 3) was used to rinse off water carefully. Absolute ethanol (150 mL) and 3 (5.040 g, 12.4 mmol) were then added and the mixture heated to reflux for one day. Fresh Raney Nickel (27 g, rinsed with absolute ethanol three times under argon) and ethanol (absolute, 100 mL) were added and the mixture was refluxed for another 45 hrs. The mixture was cooled to rt and filtered through Celite® 545. After removing ethanol on a rotary evaporator, the greenish solid/oil mixture was extracted with chloroform (25 mL × 2). The colorless

chloroform solution was dried over anhydrous magnesium sulfate for 15 min. Upon removal of chloroform in vacuo, colorless crystalline solid, 3, was obtained (2.680 g, 95% yield based on **2**).

$^{1}$H NMR (200 MHz, $CDCl_3$): 1.79 (s, 12H), 3.63 (3, 6H). $^{13}$C NMR (50 MHz, $CDCl_3$): 27.95, 38.83, 51.92, 178.04.

**Synthesis of $H_2$bodc.** A mixture of **3** (2.640 g, 11.7 mmol) and potassium hydroxide (3.60 g, 85%, 54.6 mmol) in ethanol (95%, 75 mL) and water (30 mL) was heated to reflux for overnight (18 hrs). The mixture was then added into ice/water (150 mL) and acidified with concentrated hydrochloric acid. The white precipitate, **$H_2$bodc**, was filtered and dried under vacuum (2.152 g, 93% yield based on **3**). NMR showed that **$H_2$bodc** was essentially pure and therefore, was used without further purification.

Melting point (uncorrected): 393-395 °C w/ decomposition (lit.[1] >360 °C). $^{1}$H NMR (200 MHz, $CD_3OD$):1.81 (s, 12H). $^{13}$C NMR (50 MHz, $CD_3OD$): 29.10, 39.72, 181.53.

**Hydrogen Adsorption.** The low temperature high-resolution gas adsorption-desorption measurements were performed using an automated micropore gas analyzer, Autosorb-1-MP (Quantachrome Instruments). The hydrogen sorption isotherms were collected in a relative pressure range from $10^{-4}$ to 1 atm at 77K and 87K. The initial outgassing process for each sample was carried out under vacuum at 373K for 15~16 hours. About 87 mg of degassed sample was used for gas sorption studies and the weight of the sample was recorded and the PXRD patterns were taken before and after outgassing to confirm the removal of all guest molecules and the structural integrity. The outgassing procedure was repeated on the same sample between experiments for 0.5~1 hour. A total analysis time was ca. 9~10 hours for hydrogen sorption. Ultra high purity of compressed $H_2$ gas (UHP 5.0) and argon gas (UHP 5.0) were used for analysis. The pore properties including pore volume, pore size, and surface area were analyzed using Autosorb v1.50 software. The high pressure hydrogen isotherm experiments were conducted on a high pressure vapor analyzer, HPVA-100, from the VTI corporation. The pressures of manifold and the sample cell were monitored by two electronic Bourdon gauge-type transducers (Mensor), separately. The transducers could read the pressure to

1500 psi with 0.010% accuracy. The high vacuum (~$10^{-6}$ mbar) was controlled by turbomolecular pump from Pfeiffer in both units. Ultra high purity He (UHP 5.0) was used to determine dead space of the sample cell and ultra high purity $H_2$ (UHP 5.0) was used for analysis, respectively. The outgassing procedure was the same as low pressure experiment but ~411 mg of activated samples were used for high pressure measurements. The cryogenic temperatures were controlled using liquid argon for 87K and liquid nitrogen for 77K as baths, respectively. The constant room temperature was controlled by computer-controlled water bath from Polyscience.

**Hydrocarbon Adsorption.** All The hydrocarbon sorption studies were conducted on a computer-controlled DuPont Model 990 TGA. The hydrocarbon partial pressure was varied by changing the blending ratios of hydrocarbon-saturated nitrogen and pure nitrogen gas streams. The freshly made sample was activated at 150 °C. All hydrocarbons were of 99% or higher purity.

**Figures.**

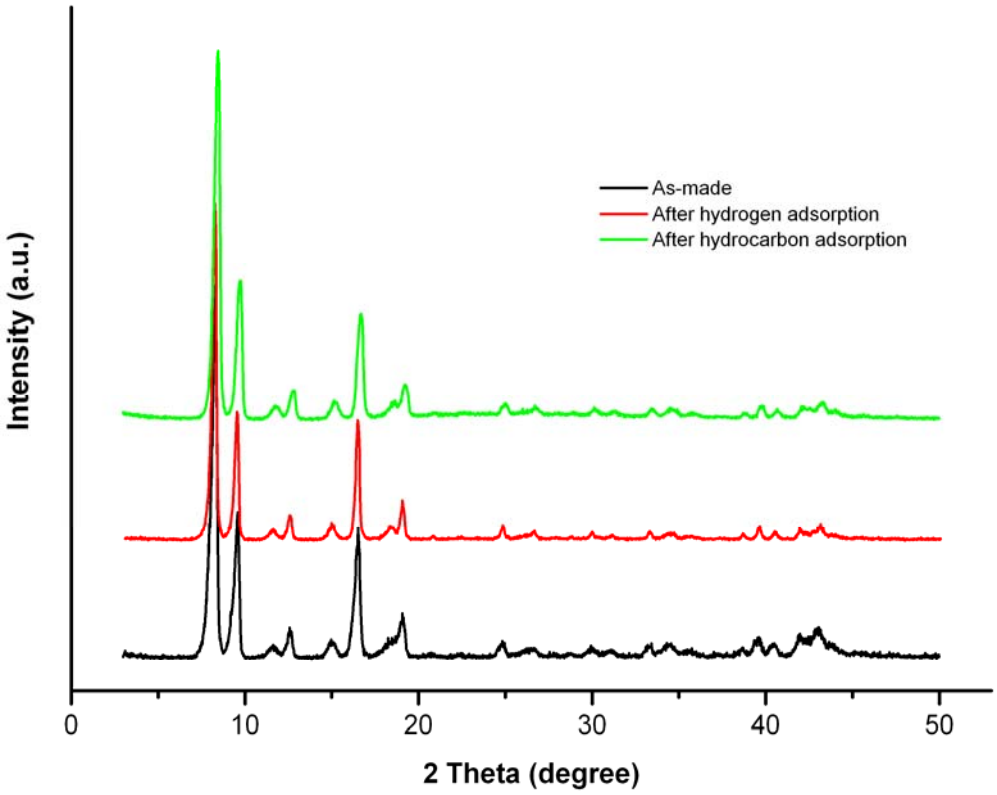



Figure S1. X-ray powder diffraction patterns of the as-made [Ni(bodc)(ted)$_{0.5}$] (black), after high pressure hydrogen adsorption/desorption (red), and after hydrocarbon adsorption/desorption (green) studies.

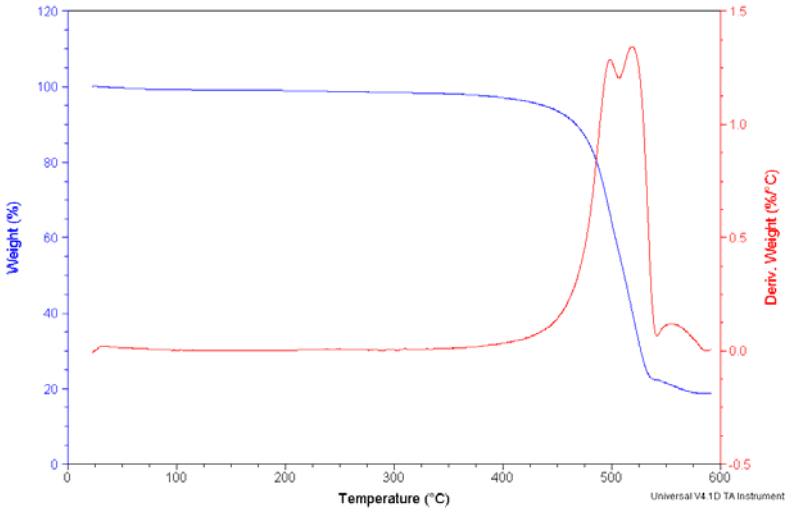



Figure S2. Thermogravimetric analysis curve for an as-made [Ni(bodc)(ted)$_{0.5}$] under nitrogen atmosphere.

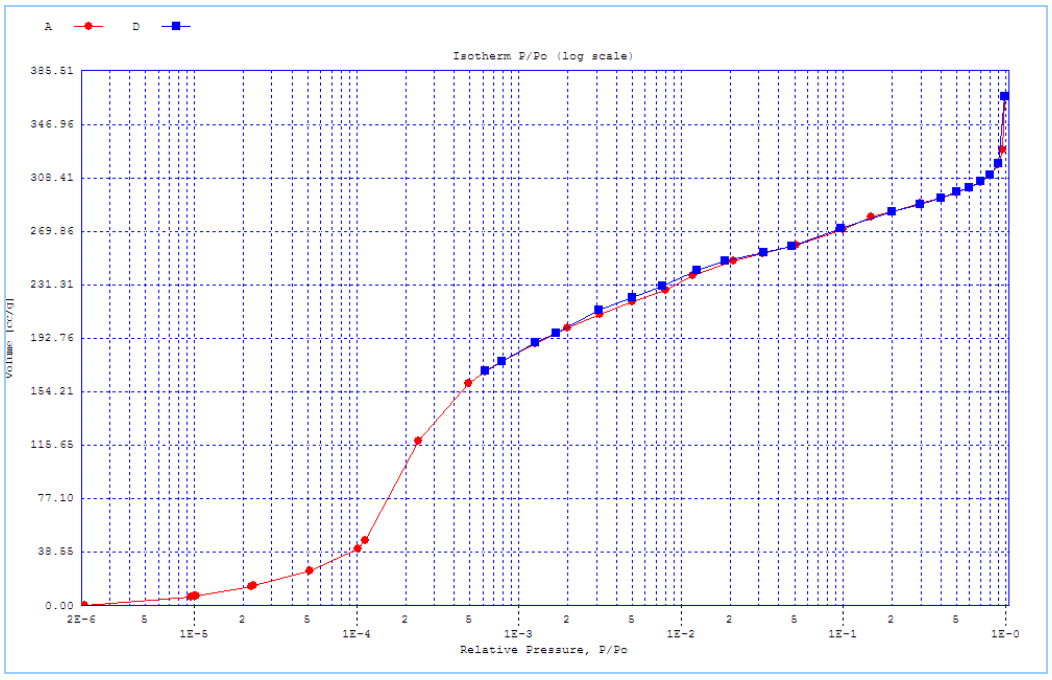



Figure S3. The argon (Ar) adsorption-desorption isotherms for [Ni(bodc)(ted)$_{0.5}$] at 87K.

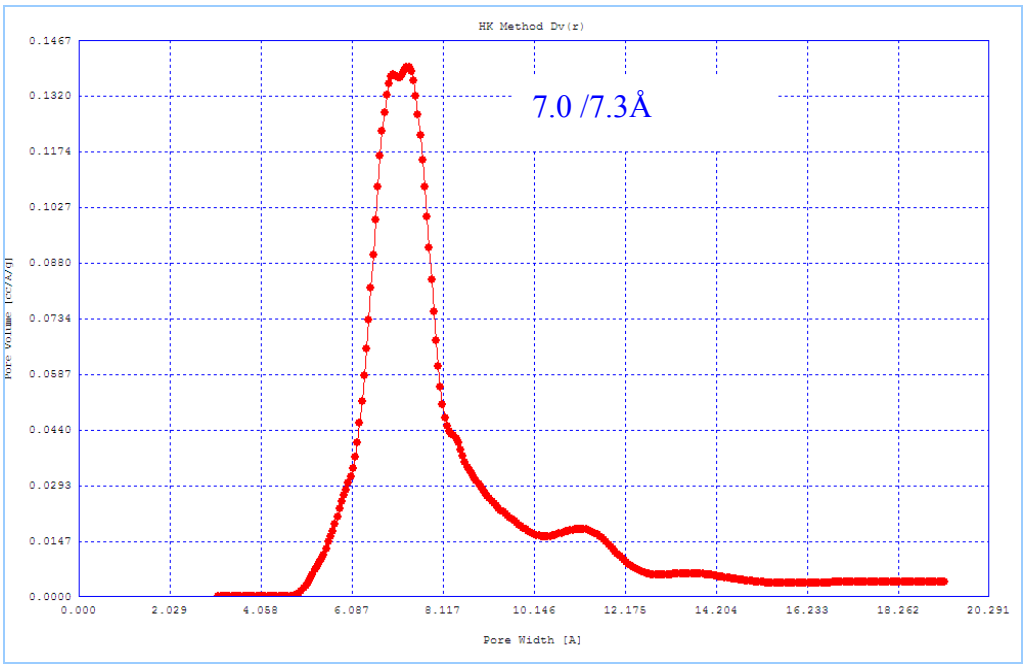



Figure S4. The H-K pore size distribution based on the Ar adsorption-desorption data at 87K.

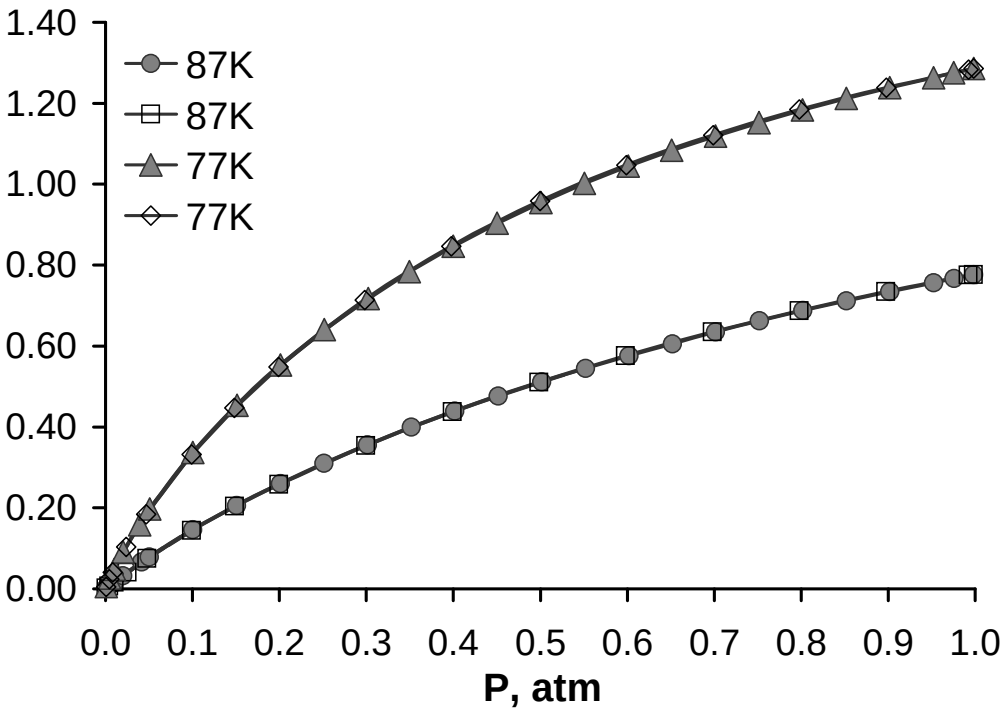


Figure S5. Hydrogen adsorption (filled) and desorption (open) isotherms for [Ni(bodc)(ted)$_{0.5}$] at 77K and 87K.

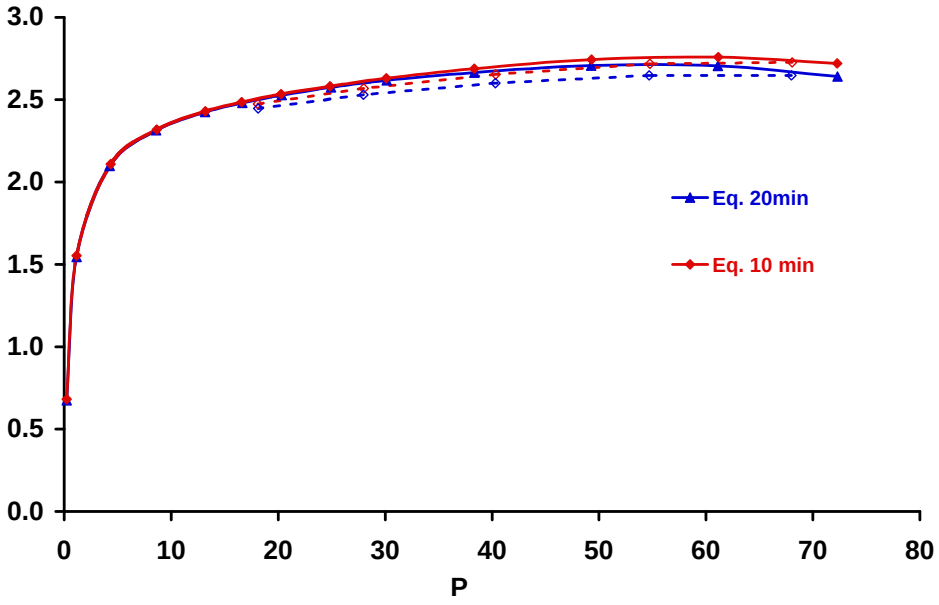



Figure S6. High pressure hydrogen adsorption (filled symbol) and desorption (open symbol) isotherms for [Ni(bodc)(ted)$_{0.5}$] at 77K. Red and blue colors indicate different equilibrium time in the measurements.

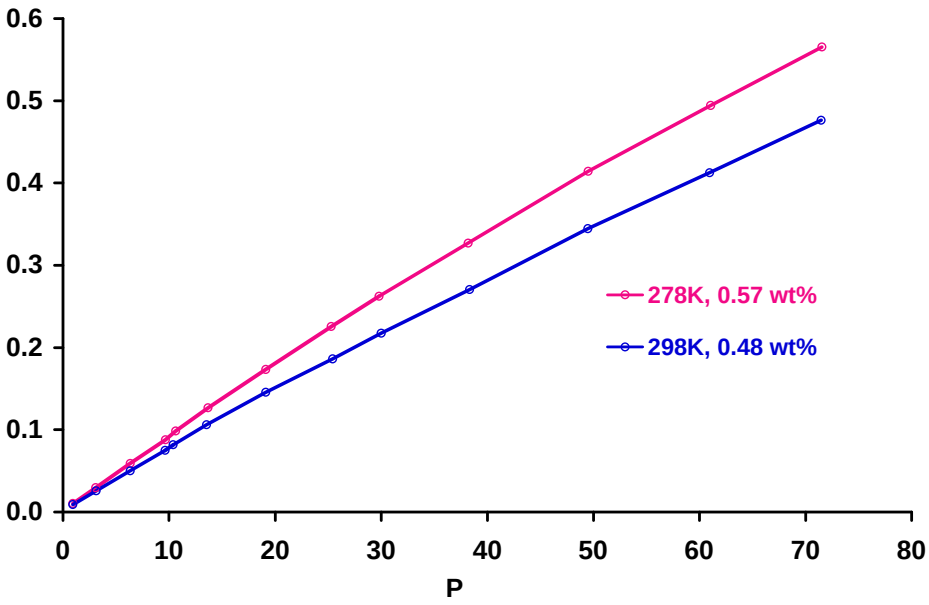



Figure S7. High pressure hydrogen adsorption isotherms for [Ni(bodc)(ted)$_{0.5}$] at 278 and 298 K.

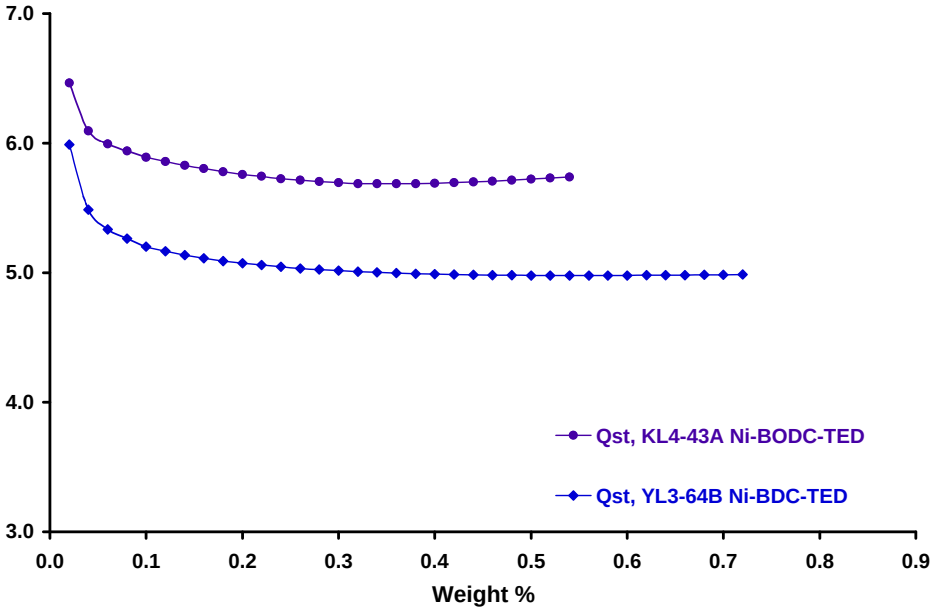



Figure S8. Calculated isosteric heats of hydrogen adsorption, $Q_{st}$, for [Ni(bodc)(ted)$_{0.5}$] (top) and [Ni(bdc)(ted)$_{0.5}$]$^{*}$ (bottom) based on the 77 and 87 K isotherms. *Isostructural to the recently published [Zn(bdc)(ted)$_{0.5}$].[2]

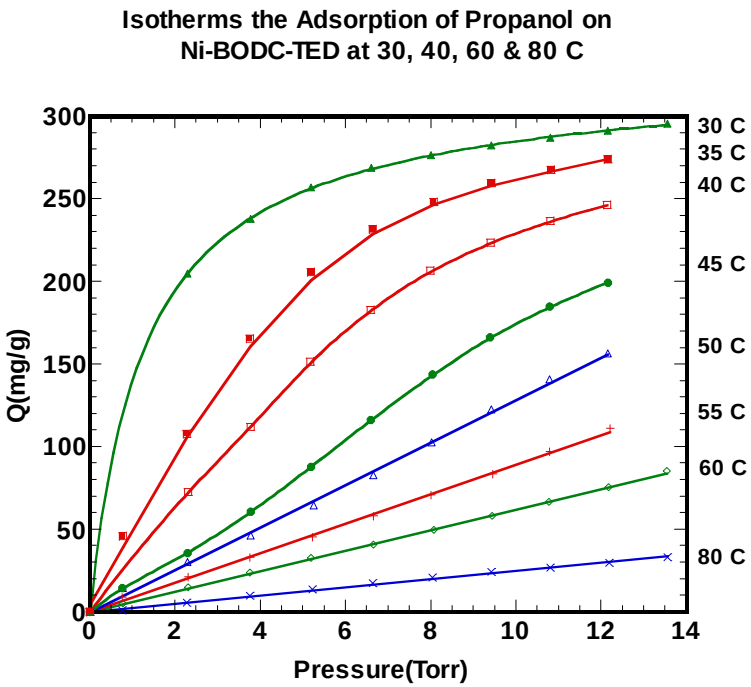



Figure S9. 1-Propanol adsorption isotherms for [Ni(bodc)(ted)$_{0.5}$].

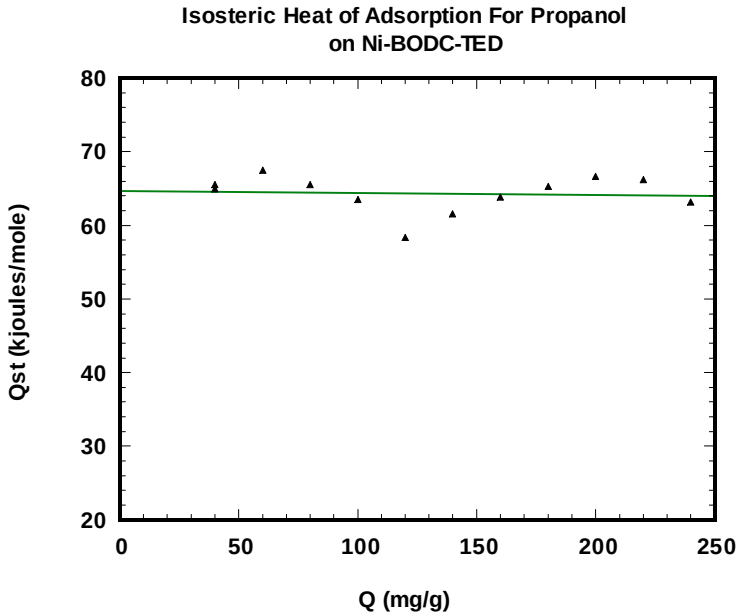



Figure S10. Isosteric heats of adsorption of 1-propanol for [Ni(bodc)(ted)$_{0.5}$].

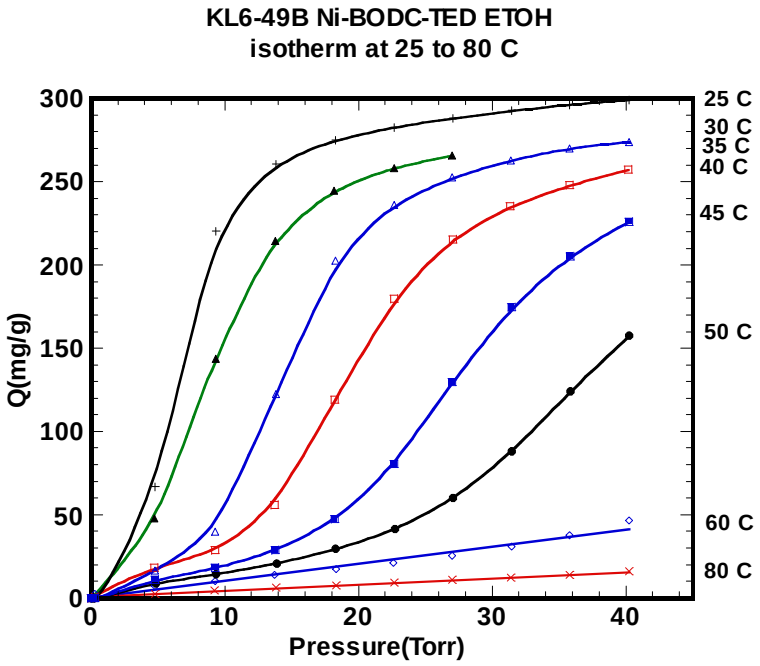



Figure S11. Ethanol adsorption isotherms for [Ni(bodc)(ted)$_{0.5}$].

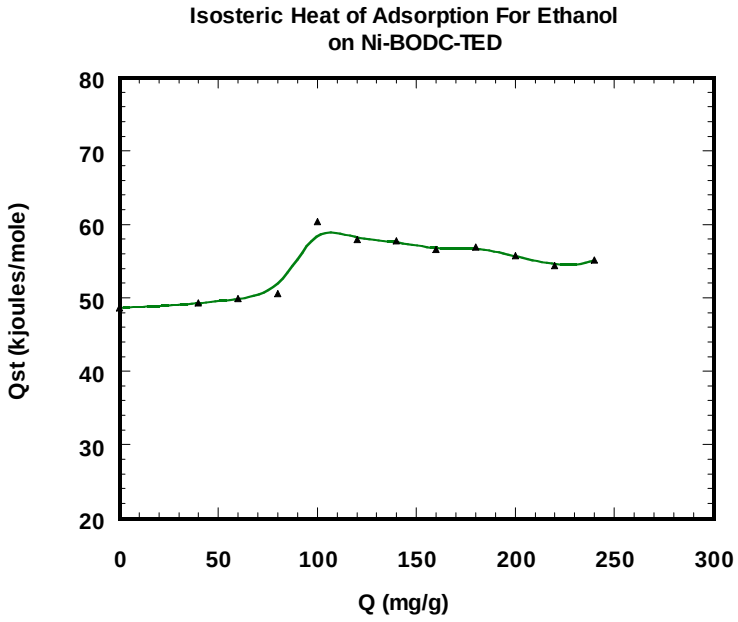



Figure S12. Isosteric heats of adsorption of ethanol for [Ni(bodc)(ted)$_{0.5}$].

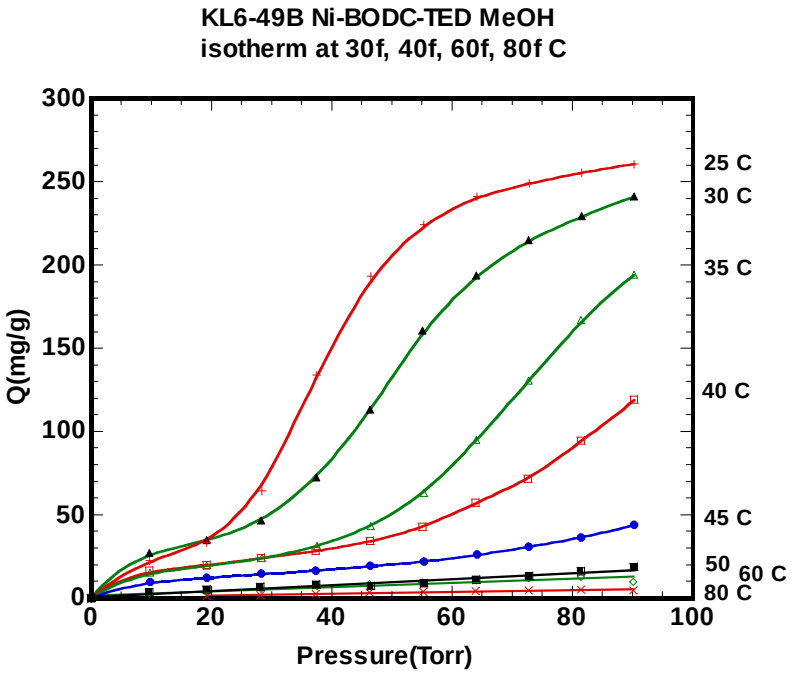



Figure S13. Methanol adsorption isotherms for [Ni(bodc)(ted)$_{0.5}$].

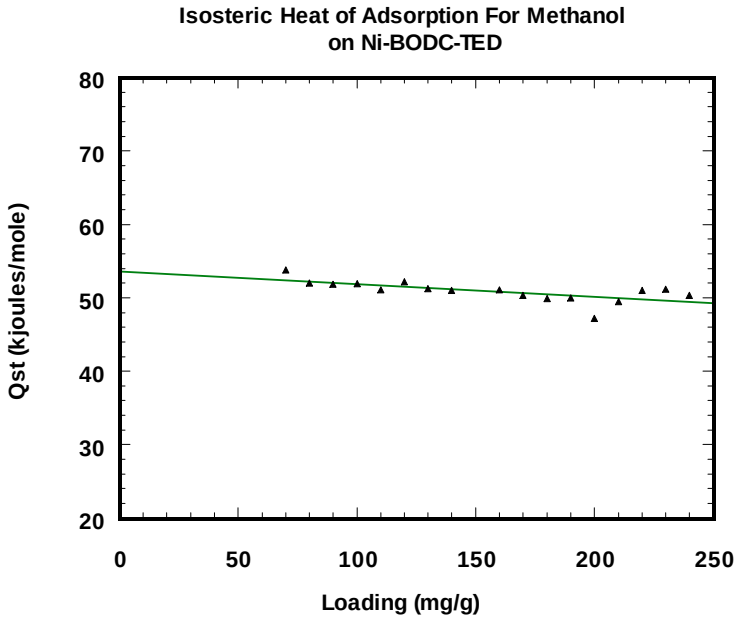



Figure S14. Isosteric heats of adsorption of methanol for [Ni(bodc)(ted)$_{0.5}$].

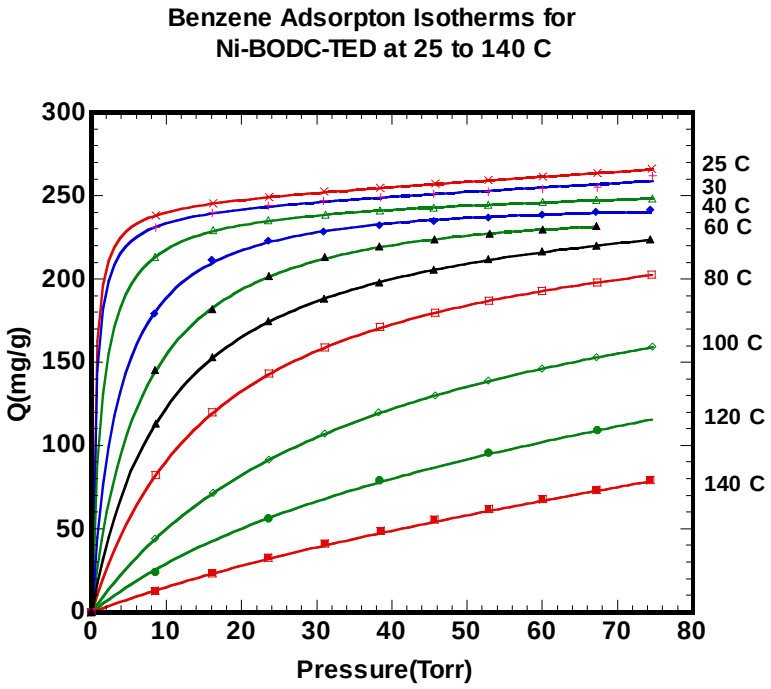



Figure S15. Benzene adsorption isotherms for [Ni(bodc)(ted)$_{0.5}$].

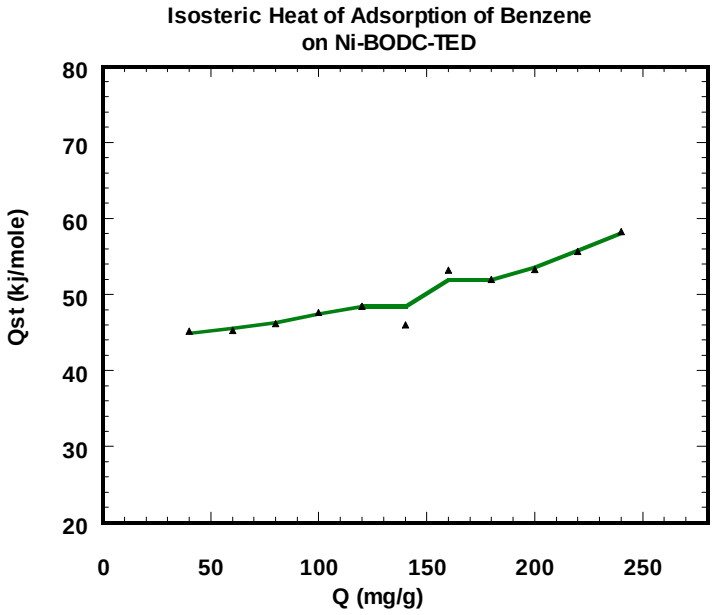



Figure S16. Isosteric heats of adsorption of benzene for [Ni(bodc)(ted)$_{0.5}$].

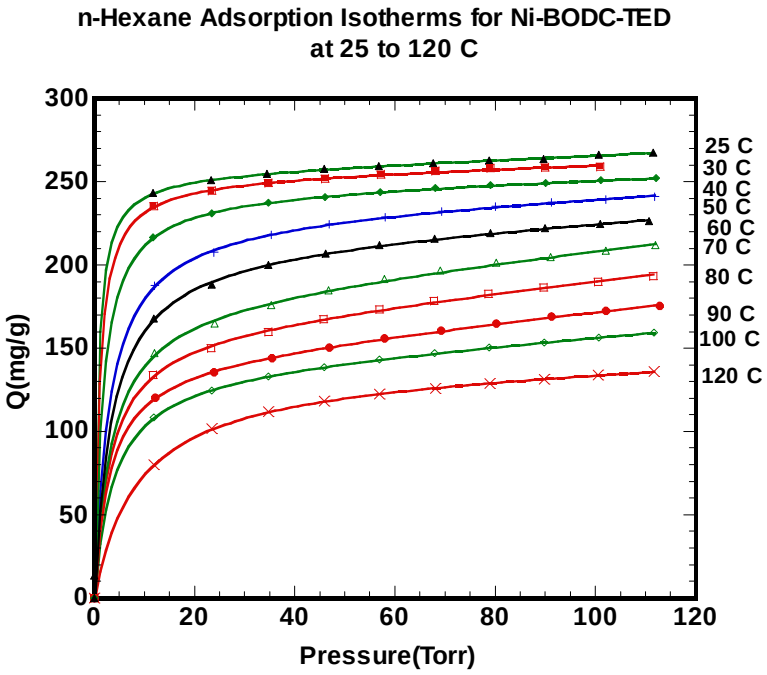



Figure S17. n-Hexane adsorption isotherms for [Ni(bodc)(ted)$_{0.5}$].

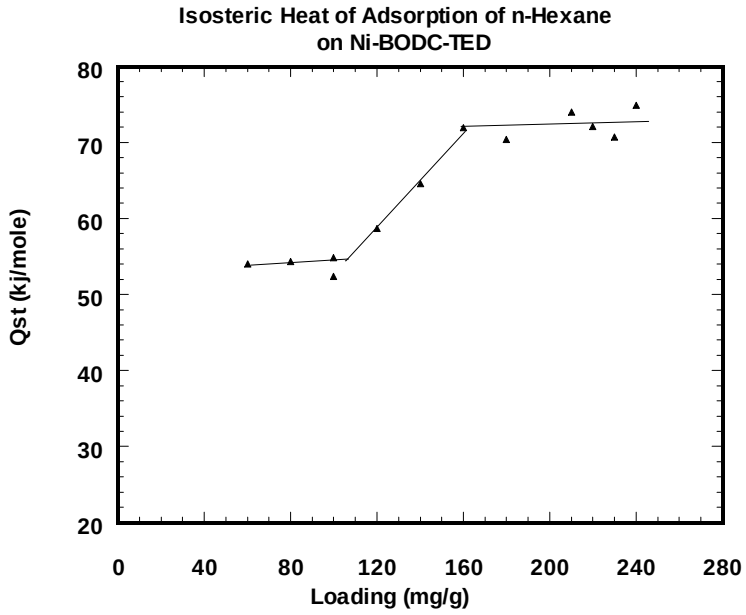



Figure S18. Isosteric heats of adsorption of n-hexane for [Ni(bodc)(ted)$_{0.5}$].

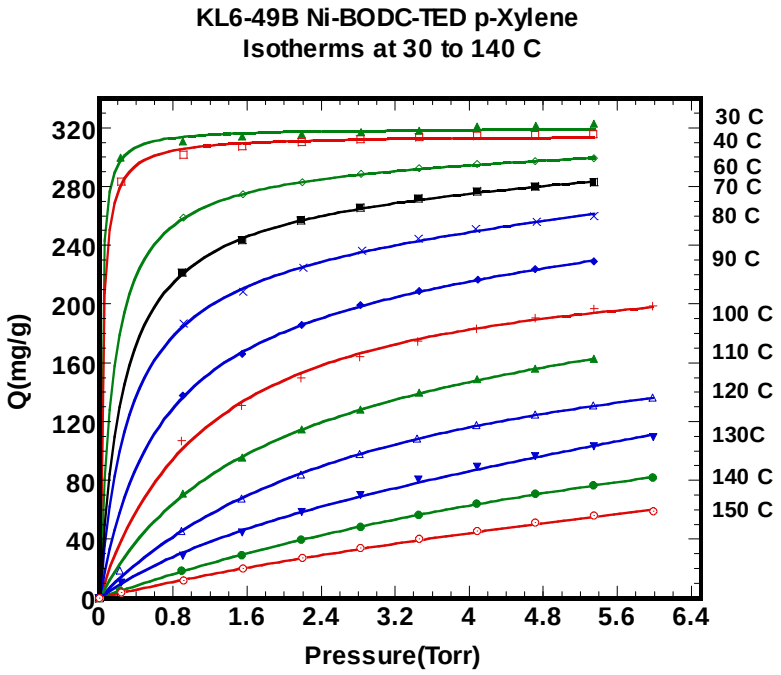



Figure S19. p-Xylene adsorption isotherms for [Ni(bodc)(ted)$_{0.5}$].

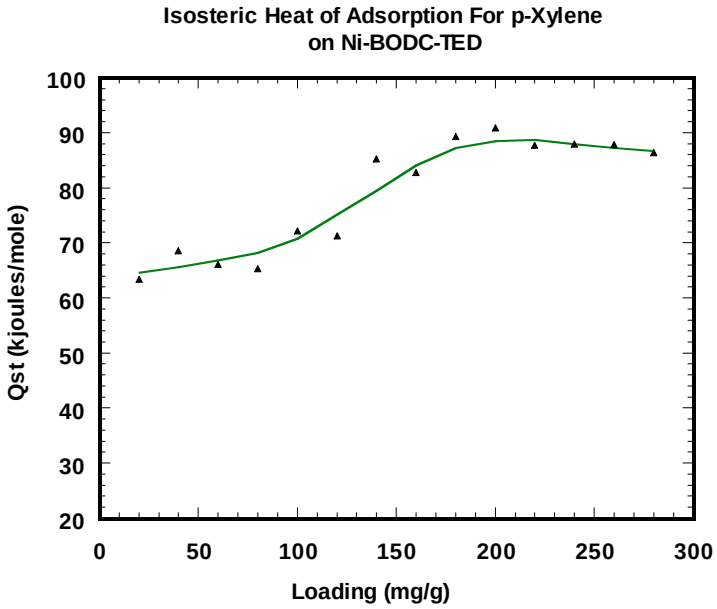



Figure S20. Isosteric heats of adsorption of p-xylene for [Ni(bodc)(ted)$_{0.5}$].

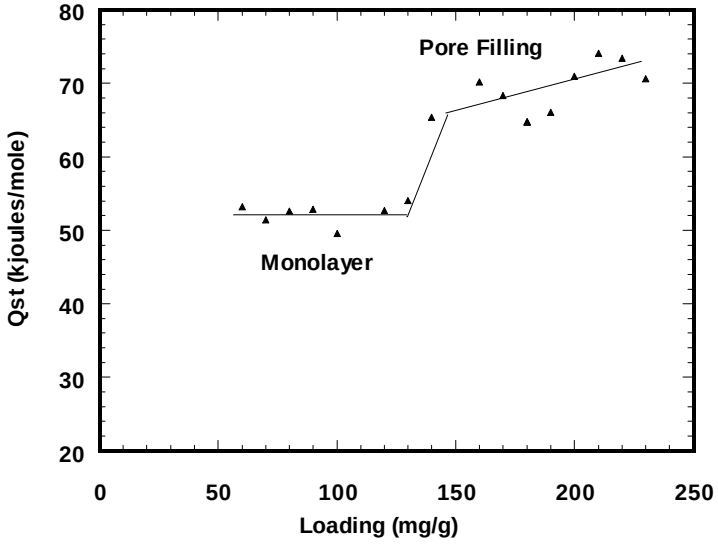



Figure S21. Isosteric heats of adsorption of cyclohexane for [Ni(bodc)(ted)$_{0.5}$].

Table S1. Outgassing and $H_2$ uptake for [Ni(bodc)(ted)$_{0.5}$].

| ***No.*** | **Weight (mg)** | | | | **$H_2$ uptakes** | | | |
|---|---|---|---|---|---|---|---|---|
| | Loading | After OG[#] | loss(%)[@] | Loss % (calc'd) | 77K | $D_{H2}$ at 77K (g/cc) | 87K | **Qst (kJ/mol)** |
| 1 | 155 | **87** | **43.9** | | **1.29** | | **0.78** | **5.69~6.46** |
| 2 | [@]TGA : 31.2 % loss | | | | | | | |

[#]Outgassing condition: 100°C for 16h.

[@] The weight loss observed was later found to be due to solvent on the surface of crystals, which can be removed by diethyl ether rinse during work-up.

Table S2. Measured micropore volume for [Ni(bodc)(ted)$_{0.5}$].

| *No.* | **$N_2$ sorption at 77K** | | | **Ar sorption at 87K** | | |
|---|---|---|---|---|---|---|
| | DA MicroPore Volume(cc/g) | DR MicroPore Volume(cc/g) | Total Pore Volume (cc/g) (at P/P0 = 1.0) | DA MicroPore Volume(cc/g) | DR MicroPore Volume(cc/g) | Total Pore Volume (cc/g) (at P/P0 = 1.0) |
| 1 | | | | **0.45** | **0.42** | **0.47*** |
| 2 | | | | | | |

*Toal Pore Volume at P/P0 = 0.99

Table S3. Measured surface areas for $[Ni(bodc)(ted)_{0.5}]$.

| *No.* | **$N_2$ sorption at 77K** | | | **Ar sorption at 87K** | | |
|---|---|---|---|---|---|---|
| | Single point BET($m^2/g$) | Multi Point BET($m^2/g$) | Langmuir ($m^2/g$) | Single point BET($m^2/g$) | Multi Point BET($m^2/g$) | Langmuir ($m^2/g$) |
| 1 | | | | **942*** | **958** | **1244** |
| 2 | | | | | | |

*Single Point at P/P0 = 0.05

## References:

[1] B. F. Cain, G. J. Atwell, *J. Med. Chem.* **1976**, *19*, 1417.
[2] J. Y. Lee, D. H. Olson, L. Pan, T. J. Emge, J. Li, *Adv. Funct. Mater.* **2007**, *17*, 1255.

**Appendix.** Selected crystallographic information

Attempts to refine in space groups containing m or i symmetry elements yielded A) grossly unrealistic thermal parameters, B) disorder at nearly all non-metal sites, and C) chemically unrealistic bond geometries.

In addition to the above, the asymmetry of the partially occupied and disordered solvent molecules breaks the near m symmetry, resulting in over 130 systematic absence violations for reflections of moderate or

strong intensity. Also, reflections that violate a near I-centering are of moderate to strong intensity, and quite numerous (over 1200 significant unique reflections would violate the I-centering systematic absence rule).

Table 1. Crystal data and structure refinement for kl6-59bb.

| | | |
|---|---|---|
| Identification code | kl6-59bb | |
| Empirical formula | C36.5 H60.5 Co2 N5.5 O11.5 | |
| Formula weight | 878.26 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Tetragonal | |
| Space group | P4(2)2(1)2 | |
| Unit cell dimensions | a = 15.2597(6) Å | α= 90°. |
| | b = 15.2597(6) Å | β= 90°. |
| | c = 19.0917(14) Å | γ = 90°. |
| Volume | 4445.7(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.312 $Mg/m^3$ | |
| Absorption coefficient | 0.806 $mm^{-1}$ | |
| F(000) | 1856 | |
| Crystal size | 0.12 x 0.06 x 0.04 $mm^3$ | |
| Theta range for data collection | 1.71 to 28.28°. | |
| Index ranges | -20<=h<=20, -20<=k<=20, -25<=l<=25 | |
| Reflections collected | 47149 | |
| Independent reflections | 5522 [R(int) = 0.0368] | |
| Completeness to theta = 28.28° | 99.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9685 and 0.9095 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5522 / 877 / 335 | |
| Goodness-of-fit on $F^2$ | 1.002 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0529, wR2 = 0.1559 | |
| R indices (all data) | R1 = 0.1102, wR2 = 0.1852 | |
| Absolute structure parameter | 0.41(13) | |
| Largest diff. peak and hole | 1.050 and -1.202 $e.Å^{-3}$ | |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for kl6-59bb. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Co(1) | 5000 | 5000 | 1788(1) | 25(1) |
| Co(2) | 5000 | 5000 | 3213(1) | 25(1) |
| N(1) | 5000 | 5000 | 673(2) | 28(2) |
| N(2) | 5000 | 5000 | 4315(3) | 32(2) |
| O(1) | 3921(3) | 4243(3) | 1924(2) | 50(1) |
| O(2) | 3936(3) | 4220(3) | 3097(2) | 52(1) |
| O(3) | 761(3) | 1086(3) | 3086(2) | 47(1) |
| O(4) | 772(3) | 1062(3) | 1929(2) | 52(1) |
| C(1) | 3640(3) | 3991(3) | 2508(3) | 39(1) |
| C(3) | 1020(3) | 1363(3) | 2492(3) | 33(1) |
| C(11) | 5822(6) | 5323(9) | 384(6) | 57(3) |
| C(12) | 4291(8) | 5608(8) | 406(5) | 58(3) |
| C(13) | 4777(8) | 4149(5) | 407(5) | 43(3) |
| C(21) | 4771(9) | 5860(6) | 4588(6) | 51(3) |
| C(22) | 4282(9) | 4403(9) | 4589(5) | 66(3) |
| C(23) | 5803(7) | 4669(10) | 4598(7) | 65(4) |
| C(2A) | 2884(4) | 3323(4) | 2488(4) | 35(1) |
| C(31A) | 2194(4) | 3503(5) | 3047(4) | 42(2) |
| C(32A) | 3307(5) | 2419(4) | 2654(4) | 53(2) |
| C(33A) | 2475(5) | 3269(6) | 1769(4) | 67(2) |
| C(2B) | 2916(8) | 3290(8) | 2513(8) | 35(1) |
| C(34B) | 2705(12) | 3005(13) | 3258(7) | 55(4) |
| C(35B) | 3189(13) | 2456(11) | 2110(10) | 52(4) |
| C(36B) | 2086(12) | 3642(11) | 2193(10) | 53(4) |
| C(4A) | 1702(6) | 2076(6) | 2494(4) | 36(1) |
| C(41A) | 1442(6) | 2816(6) | 2999(5) | 66(2) |
| C(42A) | 2568(6) | 1743(6) | 2737(5) | 64(2) |
| C(43A) | 1812(6) | 2506(5) | 1776(3) | 65(2) |
| C(4B) | 1685(17) | 2128(16) | 2514(9) | 36(1) |
| C(44B) | 1778(12) | 2556(13) | 3232(8) | 42(4) |
| C(45B) | 2550(14) | 1713(13) | 2319(9) | 46(4) |
| C(46B) | 1497(14) | 2854(12) | 1983(9) | 45(4) |
| O(51A) | 2542(8) | 1191(9) | 5(7) | 157(2) |
| C(51A) | 3276(9) | 1505(10) | 123(8) | 157(2) |
| N(51A) | 3828(10) | 1206(10) | 603(10) | 157(2) |

| | | | | |
|---|---|---|---|---|
| C(52A) | 3620(12) | 417(10) | 1003(10) | 157(2) |
| C(53A) | 4563(10) | 1736(12) | 841(10) | 157(2) |
| O(51B) | 3264(11) | 2384(8) | 70(9) | 157(2) |
| C(51B) | 3899(9) | 1970(9) | 307(10) | 157(2) |
| N(51B) | 3842(12) | 1188(10) | 608(12) | 157(2) |
| C(52B) | 3066(12) | 648(10) | 509(13) | 157(2) |
| C(53B) | 4474(13) | 911(13) | 1142(11) | 157(2) |
| O(61C) | 2579(16) | 7421(16) | 0 | 235(4) |
| C(61C) | 2289(16) | 6703(16) | 190(20) | 235(4) |
| N(61C) | 1505(17) | 6588(19) | 480(20) | 235(4) |
| C(62C) | 833(19) | 7260(30) | 410(30) | 235(4) |
| C(63C) | 1290(30) | 5770(20) | 830(30) | 235(4) |
| O(61B) | 1927(16) | 6176(10) | 90(20) | 235(4) |
| C(61B) | 1809(12) | 6974(10) | 90(30) | 235(4) |
| N(61B) | 2436(11) | 7564(11) | 0 | 235(4) |
| C(62B) | 3330(12) | 7300(18) | -170(30) | 235(4) |
| C(63B) | 2242(19) | 8498(10) | 0(30) | 235(4) |
| O(61A) | 0 | 5000 | 2579(8) | 235(4) |
| C(61A) | 229(18) | 5317(16) | 2018(8) | 235(4) |
| N(61A) | 0 | 5000 | 1391(8) | 235(4) |
| C(62A) | -757(14) | 4426(17) | 1328(8) | 235(4) |
| C(63A) | 236(16) | 5522(13) | 768(8) | 235(4) |

Table 3. Bond lengths [Å] and angles [°] for kl6-59bb.

| | | | |
|---|---|---|---|
| Co(1)-O(1)#1 | 2.029(4) | N(1)-C(11) | 1.456(8) |
| Co(1)-O(1) | 2.029(4) | N(1)-C(12) | 1.513(7) |
| Co(1)-O(3)#2 | 2.038(4) | N(2)-C(23) | 1.431(9) |
| Co(1)-O(3)#3 | 2.038(4) | N(2)-C(21) | 1.455(8) |
| Co(1)-N(1) | 2.130(5) | N(2)-C(22) | 1.518(8) |
| Co(1)-Co(2) | 2.7196(7) | O(1)-C(1) | 1.253(6) |
| Co(2)-O(4)#2 | 2.022(4) | O(2)-C(1) | 1.263(6) |
| Co(2)-O(4)#3 | 2.022(4) | O(3)-C(3) | 1.273(5) |
| Co(2)-O(2)#1 | 2.024(4) | O(3)-Co(1)#4 | 2.038(4) |
| Co(2)-O(2) | 2.024(4) | O(4)-C(3) | 1.229(5) |
| Co(2)-N(2) | 2.105(5) | O(4)-Co(2)#4 | 2.022(4) |
| N(1)-C(13) | 1.435(7) | C(1)-C(2B) | 1.537(9) |

| | | | |
|---|---|---|---|
| C(1)-C(2A) | 1.540(6) | C(35B)-H(35A) | 0.9700 |
| C(3)-C(4A) | 1.506(11) | C(35B)-H(35B) | 0.9700 |
| C(3)-C(4B) | 1.55(3) | C(36B)-C(46B) | 1.554(13) |
| C(11)-C(13)#5 | 1.520(12) | C(36B)-H(36A) | 0.9700 |
| C(11)-H(11A) | 0.9700 | C(36B)-H(36B) | 0.9700 |
| C(11)-H(11B) | 0.9700 | C(4A)-C(42A) | 1.492(9) |
| C(12)-C(12)#5 | 1.567(18) | C(4A)-C(43A) | 1.529(9) |
| C(12)-H(12A) | 0.9700 | C(4A)-C(41A) | 1.537(9) |
| C(12)-H(12B) | 0.9700 | C(41A)-H(41A) | 0.9700 |
| C(13)-C(11)#5 | 1.520(12) | C(41A)-H(41B) | 0.9700 |
| C(13)-H(13A) | 0.9700 | C(42A)-H(42A) | 0.9700 |
| C(13)-H(13B) | 0.9700 | C(42A)-H(42B) | 0.9700 |
| C(21)-C(23)#6 | 1.564(13) | C(43A)-H(43A) | 0.9700 |
| C(21)-H(21A) | 0.9700 | C(43A)-H(43B) | 0.9700 |
| C(21)-H(21B) | 0.9700 | C(4B)-C(45B) | 1.510(14) |
| C(22)-C(22)#6 | 1.591(19) | C(4B)-C(44B) | 1.525(15) |
| C(22)-H(22A) | 0.9700 | C(4B)-C(46B) | 1.530(14) |
| C(22)-H(22B) | 0.9700 | C(44B)-H(44A) | 0.9700 |
| C(23)-C(21)#6 | 1.564(13) | C(44B)-H(44B) | 0.9700 |
| C(23)-H(23A) | 0.9700 | C(45B)-H(45A) | 0.9700 |
| C(23)-H(23B) | 0.9700 | C(45B)-H(45B) | 0.9700 |
| C(2A)-C(33A) | 1.510(7) | C(46B)-H(46A) | 0.9700 |
| C(2A)-C(31A) | 1.524(7) | C(46B)-H(46B) | 0.9700 |
| C(2A)-C(32A) | 1.557(7) | O(51A)-C(51A) | 1.240(4) |
| C(31A)-C(41A) | 1.556(8) | C(51A)-N(51A) | 1.325(4) |
| C(31A)-H(31A) | 0.9700 | C(51A)-H(51A) | 0.9300 |
| C(31A)-H(31B) | 0.9700 | N(51A)-C(53A) | 1.456(4) |
| C(32A)-C(42A) | 1.536(9) | N(51A)-C(52A) | 1.462(5) |
| C(32A)-H(32A) | 0.9700 | C(52A)-H(52A) | 0.9600 |
| C(32A)-H(32B) | 0.9700 | C(52A)-H(52B) | 0.9600 |
| C(33A)-C(43A) | 1.543(8) | C(52A)-H(52C) | 0.9600 |
| C(33A)-H(33A) | 0.9700 | C(53A)-H(53A) | 0.9600 |
| C(33A)-H(33B) | 0.9700 | C(53A)-H(53B) | 0.9600 |
| C(2B)-C(36B) | 1.505(9) | C(53A)-H(53C) | 0.9600 |
| C(2B)-C(34B) | 1.522(9) | O(51B)-C(51B) | 1.242(5) |
| C(2B)-C(35B) | 1.544(8) | C(51B)-N(51B) | 1.327(4) |
| C(34B)-C(44B) | 1.572(13) | C(51B)-H(51B) | 0.9300 |
| C(34B)-H(34A) | 0.9700 | N(51B)-C(52B) | 1.455(5) |
| C(34B)-H(34B) | 0.9700 | N(51B)-C(53B) | 1.465(5) |
| C(35B)-C(45B) | 1.549(13) | C(52B)-H(52D) | 0.9600 |

| | | | |
|---|---|---|---|
| C(52B)-H(52E) | 0.9600 | N(61B)-C(63B) | 1.456(4) |
| C(52B)-H(52F) | 0.9600 | N(61B)-C(62B) | 1.458(5) |
| C(53B)-H(53D) | 0.9600 | C(62B)-H(62D) | 0.9600 |
| C(53B)-H(53E) | 0.9600 | C(62B)-H(62E) | 0.9600 |
| C(53B)-H(53F) | 0.9600 | C(62B)-H(62F) | 0.9600 |
| O(61C)-C(61C) | 1.236(5) | C(63B)-H(63D) | 0.9600 |
| C(61C)-N(61C) | 1.332(5) | C(63B)-H(63E) | 0.9600 |
| C(61C)-H(61C) | 0.9300 | C(63B)-H(63F) | 0.9600 |
| N(61C)-C(62C) | 1.452(5) | O(61A)-C(61A) | 1.226(4) |
| N(61C)-C(63C) | 1.454(4) | C(61A)-N(61A) | 1.339(5) |
| C(62C)-H(62G) | 0.9600 | C(61A)-H(61A) | 0.9300 |
| C(62C)-H(62H) | 0.9600 | N(61A)-C(62A) | 1.454(5) |
| C(62C)-H(62I) | 0.9600 | N(61A)-C(63A) | 1.476(4) |
| C(63C)-H(63G) | 0.9600 | C(62A)-H(62A) | 0.9600 |
| C(63C)-H(63H) | 0.9600 | C(62A)-H(62B) | 0.9600 |
| C(63C)-H(63I) | 0.9600 | C(62A)-H(62C) | 0.9600 |
| O(61B)-C(61B) | 1.231(5) | C(63A)-H(63A) | 0.9600 |
| C(61B)-N(61B) | 1.325(4) | C(63A)-H(63B) | 0.9600 |
| C(61B)-H(61B) | 0.9300 | C(63A)-H(63C) | 0.9600 |

| | | | |
|---|---|---|---|
| O(1)#1-Co(1)-O(1) | 165.3(2) | O(2)#1-Co(2)-O(2) | 167.49(19) |
| O(1)#1-Co(1)-O(3)#2 | 89.19(14) | O(4)#2-Co(2)-N(2) | 97.68(10) |
| O(1)-Co(1)-O(3)#2 | 89.08(14) | O(4)#3-Co(2)-N(2) | 97.68(10) |
| O(1)#1-Co(1)-O(3)#3 | 89.09(14) | O(2)#1-Co(2)-N(2) | 96.25(10) |
| O(1)-Co(1)-O(3)#3 | 89.19(14) | O(2)-Co(2)-N(2) | 96.25(10) |
| O(3)#2-Co(1)-O(3)#3 | 166.49(19) | O(4)#2-Co(2)-Co(1) | 82.32(10) |
| O(1)#1-Co(1)-N(1) | 97.36(10) | O(4)#3-Co(2)-Co(1) | 82.32(10) |
| O(1)-Co(1)-N(1) | 97.36(10) | O(2)#1-Co(2)-Co(1) | 83.75(10) |
| O(3)#2-Co(1)-N(1) | 96.76(10) | O(2)-Co(2)-Co(1) | 83.75(10) |
| O(3)#3-Co(1)-N(1) | 96.76(10) | N(2)-Co(2)-Co(1) | 180.0 |
| O(1)#1-Co(1)-Co(2) | 82.64(10) | C(13)-N(1)-C(11) | 112.1(5) |
| O(1)-Co(1)-Co(2) | 82.64(10) | C(13)-N(1)-C(12) | 105.5(6) |
| O(3)#2-Co(1)-Co(2) | 83.24(10) | C(11)-N(1)-C(12) | 106.4(6) |
| O(3)#3-Co(1)-Co(2) | 83.24(10) | C(13)-N(1)-Co(1) | 110.7(4) |
| N(1)-Co(1)-Co(2) | 180.0 | C(11)-N(1)-Co(1) | 112.2(5) |
| O(4)#2-Co(2)-O(4)#3 | 164.6(2) | C(12)-N(1)-Co(1) | 109.6(4) |
| O(4)#2-Co(2)-O(2)#1 | 89.38(15) | C(23)-N(2)-C(21) | 112.9(6) |
| O(4)#3-Co(2)-O(2)#1 | 88.96(15) | C(23)-N(2)-C(22) | 106.0(6) |
| O(4)#2-Co(2)-O(2) | 88.95(15) | C(21)-N(2)-C(22) | 104.2(6) |
| O(4)#3-Co(2)-O(2) | 89.38(15) | C(23)-N(2)-Co(2) | 112.1(6) |

| | | | |
|---|---|---|---|
| C(21)-N(2)-Co(2) | 111.0(5) | C(23)#6-C(21)-H(21B) | 109.8 |
| C(22)-N(2)-Co(2) | 110.1(4) | H(21A)-C(21)-H(21B) | 108.3 |
| C(1)-O(1)-Co(1) | 124.4(3) | N(2)-C(22)-C(22)#6 | 109.0(5) |
| C(1)-O(2)-Co(2) | 123.2(3) | N(2)-C(22)-H(22A) | 109.9 |
| C(3)-O(3)-Co(1)#4 | 123.5(3) | C(22)#6-C(22)-H(22A) | 109.9 |
| C(3)-O(4)-Co(2)#4 | 126.6(3) | N(2)-C(22)-H(22B) | 109.9 |
| O(2)-C(1)-O(1) | 125.8(4) | C(22)#6-C(22)-H(22B) | 109.9 |
| O(2)-C(1)-C(2B) | 116.4(7) | H(22A)-C(22)-H(22B) | 108.3 |
| O(1)-C(1)-C(2B) | 117.7(7) | N(2)-C(23)-C(21)#6 | 112.8(9) |
| O(2)-C(1)-C(2A) | 118.2(5) | N(2)-C(23)-H(23A) | 109.0 |
| O(1)-C(1)-C(2A) | 115.9(5) | C(21)#6-C(23)-H(23A) | 109.0 |
| C(2B)-C(1)-C(2A) | 3.2(7) | N(2)-C(23)-H(23B) | 109.0 |
| O(4)-C(3)-O(3) | 124.1(4) | C(21)#6-C(23)-H(23B) | 109.0 |
| O(4)-C(3)-C(4A) | 119.0(5) | H(23A)-C(23)-H(23B) | 107.8 |
| O(3)-C(3)-C(4A) | 116.9(5) | C(33A)-C(2A)-C(31A) | 111.2(6) |
| O(4)-C(3)-C(4B) | 120.5(8) | C(33A)-C(2A)-C(1) | 111.6(6) |
| O(3)-C(3)-C(4B) | 115.4(8) | C(31A)-C(2A)-C(1) | 112.5(5) |
| C(4A)-C(3)-C(4B) | 3.1(10) | C(33A)-C(2A)-C(32A) | 107.9(6) |
| N(1)-C(11)-C(13)#5 | 111.6(8) | C(31A)-C(2A)-C(32A) | 107.7(5) |
| N(1)-C(11)-H(11A) | 109.3 | C(1)-C(2A)-C(32A) | 105.7(5) |
| C(13)#5-C(11)-H(11A) | 109.3 | C(2A)-C(31A)-C(41A) | 110.3(6) |
| N(1)-C(11)-H(11B) | 109.3 | C(2A)-C(31A)-H(31A) | 109.6 |
| C(13)#5-C(11)-H(11B) | 109.3 | C(41A)-C(31A)-H(31A) | 109.6 |
| H(11A)-C(11)-H(11B) | 108.0 | C(2A)-C(31A)-H(31B) | 109.6 |
| N(1)-C(12)-C(12)#5 | 108.8(4) | C(41A)-C(31A)-H(31B) | 109.6 |
| N(1)-C(12)-H(12A) | 109.9 | H(31A)-C(31A)-H(31B) | 108.1 |
| C(12)#5-C(12)-H(12A) | 109.9 | C(42A)-C(32A)-C(2A) | 108.2(6) |
| N(1)-C(12)-H(12B) | 109.9 | C(42A)-C(32A)-H(32A) | 110.1 |
| C(12)#5-C(12)-H(12B) | 109.9 | C(2A)-C(32A)-H(32A) | 110.1 |
| H(12A)-C(12)-H(12B) | 108.3 | C(42A)-C(32A)-H(32B) | 110.1 |
| N(1)-C(13)-C(11)#5 | 110.4(8) | C(2A)-C(32A)-H(32B) | 110.1 |
| N(1)-C(13)-H(13A) | 109.6 | H(32A)-C(32A)-H(32B) | 108.4 |
| C(11)#5-C(13)-H(13A) | 109.6 | C(2A)-C(33A)-C(43A) | 107.7(6) |
| N(1)-C(13)-H(13B) | 109.6 | C(2A)-C(33A)-H(33A) | 110.2 |
| C(11)#5-C(13)-H(13B) | 109.6 | C(43A)-C(33A)-H(33A) | 110.2 |
| H(13A)-C(13)-H(13B) | 108.1 | C(2A)-C(33A)-H(33B) | 110.2 |
| N(2)-C(21)-C(23)#6 | 109.2(8) | C(43A)-C(33A)-H(33B) | 110.2 |
| N(2)-C(21)-H(21A) | 109.8 | H(33A)-C(33A)-H(33B) | 108.5 |
| C(23)#6-C(21)-H(21A) | 109.8 | C(36B)-C(2B)-C(34B) | 107.6(9) |
| N(2)-C(21)-H(21B) | 109.8 | C(36B)-C(2B)-C(1) | 110.7(12) |

| | | | |
|---|---|---|---|
| C(34B)-C(2B)-C(1) | 111.0(11) | C(4A)-C(43A)-C(33A) | 113.8(7) |
| C(36B)-C(2B)-C(35B) | 108.6(9) | C(4A)-C(43A)-H(43A) | 108.8 |
| C(34B)-C(2B)-C(35B) | 106.7(9) | C(33A)-C(43A)-H(43A) | 108.8 |
| C(1)-C(2B)-C(35B) | 112.0(12) | C(4A)-C(43A)-H(43B) | 108.8 |
| C(2B)-C(34B)-C(44B) | 106.6(11) | C(33A)-C(43A)-H(43B) | 108.8 |
| C(2B)-C(34B)-H(34A) | 110.4 | H(43A)-C(43A)-H(43B) | 107.7 |
| C(44B)-C(34B)-H(34A) | 110.4 | C(45B)-C(4B)-C(44B) | 108.7(13) |
| C(2B)-C(34B)-H(34B) | 110.4 | C(45B)-C(4B)-C(46B) | 107.7(13) |
| C(44B)-C(34B)-H(34B) | 110.4 | C(44B)-C(4B)-C(46B) | 107.6(13) |
| H(34A)-C(34B)-H(34B) | 108.6 | C(45B)-C(4B)-C(3) | 104.5(16) |
| C(2B)-C(35B)-C(45B) | 107.8(12) | C(44B)-C(4B)-C(3) | 114.1(15) |
| C(2B)-C(35B)-H(35A) | 110.2 | C(46B)-C(4B)-C(3) | 113.9(15) |
| C(45B)-C(35B)-H(35A) | 110.2 | C(4B)-C(44B)-C(34B) | 107.4(14) |
| C(2B)-C(35B)-H(35B) | 110.2 | C(4B)-C(44B)-H(44A) | 110.2 |
| C(45B)-C(35B)-H(35B) | 110.2 | C(34B)-C(44B)-H(44A) | 110.2 |
| H(35A)-C(35B)-H(35B) | 108.5 | C(4B)-C(44B)-H(44B) | 110.2 |
| C(2B)-C(36B)-C(46B) | 108.4(12) | C(34B)-C(44B)-H(44B) | 110.2 |
| C(2B)-C(36B)-H(36A) | 110.0 | H(44A)-C(44B)-H(44B) | 108.5 |
| C(46B)-C(36B)-H(36A) | 110.0 | C(4B)-C(45B)-C(35B) | 107.9(16) |
| C(2B)-C(36B)-H(36B) | 110.0 | C(4B)-C(45B)-H(45A) | 110.1 |
| C(46B)-C(36B)-H(36B) | 110.0 | C(35B)-C(45B)-H(45A) | 110.1 |
| H(36A)-C(36B)-H(36B) | 108.4 | C(4B)-C(45B)-H(45B) | 110.1 |
| C(42A)-C(4A)-C(3) | 111.5(7) | C(35B)-C(45B)-H(45B) | 110.1 |
| C(42A)-C(4A)-C(43A) | 109.2(7) | H(45A)-C(45B)-H(45B) | 108.4 |
| C(3)-C(4A)-C(43A) | 112.6(7) | C(4B)-C(46B)-C(36B) | 106.3(14) |
| C(42A)-C(4A)-C(41A) | 106.4(7) | C(4B)-C(46B)-H(46A) | 110.5 |
| C(3)-C(4A)-C(41A) | 110.7(7) | C(36B)-C(46B)-H(46A) | 110.5 |
| C(43A)-C(4A)-C(41A) | 106.0(7) | C(4B)-C(46B)-H(46B) | 110.5 |
| C(4A)-C(41A)-C(31A) | 110.0(7) | C(36B)-C(46B)-H(46B) | 110.5 |
| C(4A)-C(41A)-H(41A) | 109.7 | H(46A)-C(46B)-H(46B) | 108.6 |
| C(31A)-C(41A)-H(41A) | 109.7 | O(51A)-C(51A)-N(51A) | 124.6(5) |
| C(4A)-C(41A)-H(41B) | 109.7 | O(51A)-C(51A)-H(51A) | 117.7 |
| C(31A)-C(41A)-H(41B) | 109.7 | N(51A)-C(51A)-H(51A) | 117.7 |
| H(41A)-C(41A)-H(41B) | 108.2 | C(51A)-N(51A)-C(53A) | 121.0(5) |
| C(4A)-C(42A)-C(32A) | 112.9(7) | C(51A)-N(51A)-C(52A) | 120.5(4) |
| C(4A)-C(42A)-H(42A) | 109.0 | C(53A)-N(51A)-C(52A) | 117.5(5) |
| C(32A)-C(42A)-H(42A) | 109.0 | N(51A)-C(52A)-H(52A) | 109.5 |
| C(4A)-C(42A)-H(42B) | 109.0 | N(51A)-C(52A)-H(52B) | 109.5 |
| C(32A)-C(42A)-H(42B) | 109.0 | H(52A)-C(52A)-H(52B) | 109.5 |
| H(42A)-C(42A)-H(42B) | 107.8 | N(51A)-C(52A)-H(52C) | 109.5 |

| | | | |
|---|---|---|---|
| H(52A)-C(52A)-H(52C) | 109.5 | H(63G)-C(63C)-H(63H) | 109.5 |
| H(52B)-C(52A)-H(52C) | 109.5 | N(61C)-C(63C)-H(63I) | 109.5 |
| N(51A)-C(53A)-H(53A) | 109.5 | H(63G)-C(63C)-H(63I) | 109.5 |
| N(51A)-C(53A)-H(53B) | 109.5 | H(63H)-C(63C)-H(63I) | 109.5 |
| H(53A)-C(53A)-H(53B) | 109.5 | O(61B)-C(61B)-N(61B) | 124.6(5) |
| N(51A)-C(53A)-H(53C) | 109.5 | O(61B)-C(61B)-H(61B) | 117.7 |
| H(53A)-C(53A)-H(53C) | 109.5 | N(61B)-C(61B)-H(61B) | 117.7 |
| H(53B)-C(53A)-H(53C) | 109.5 | C(61B)-N(61B)-C(63B) | 121.2(4) |
| O(51B)-C(51B)-N(51B) | 124.4(6) | C(61B)-N(61B)-C(62B) | 121.1(4) |
| O(51B)-C(51B)-H(51B) | 117.8 | C(63B)-N(61B)-C(62B) | 117.5(4) |
| N(51B)-C(51B)-H(51B) | 117.8 | N(61B)-C(62B)-H(62D) | 109.5 |
| C(51B)-N(51B)-C(52B) | 120.4(4) | N(61B)-C(62B)-H(62E) | 109.5 |
| C(51B)-N(51B)-C(53B) | 121.2(5) | H(62D)-C(62B)-H(62E) | 109.5 |
| C(52B)-N(51B)-C(53B) | 117.5(5) | N(61B)-C(62B)-H(62F) | 109.5 |
| N(51B)-C(52B)-H(52D) | 109.5 | H(62D)-C(62B)-H(62F) | 109.5 |
| N(51B)-C(52B)-H(52E) | 109.5 | H(62E)-C(62B)-H(62F) | 109.5 |
| H(52D)-C(52B)-H(52E) | 109.5 | N(61B)-C(63B)-H(63D) | 109.5 |
| N(51B)-C(52B)-H(52F) | 109.5 | N(61B)-C(63B)-H(63E) | 109.5 |
| H(52D)-C(52B)-H(52F) | 109.5 | H(63D)-C(63B)-H(63E) | 109.5 |
| H(52E)-C(52B)-H(52F) | 109.5 | N(61B)-C(63B)-H(63F) | 109.5 |
| N(51B)-C(53B)-H(53D) | 109.5 | H(63D)-C(63B)-H(63F) | 109.5 |
| N(51B)-C(53B)-H(53E) | 109.5 | H(63E)-C(63B)-H(63F) | 109.5 |
| H(53D)-C(53B)-H(53E) | 109.5 | O(61A)-C(61A)-N(61A) | 124.4(6) |
| N(51B)-C(53B)-H(53F) | 109.5 | O(61A)-C(61A)-H(61A) | 117.8 |
| H(53D)-C(53B)-H(53F) | 109.5 | N(61A)-C(61A)-H(61A) | 117.8 |
| H(53E)-C(53B)-H(53F) | 109.5 | C(61A)-N(61A)-C(62A) | 119.9(5) |
| O(61C)-C(61C)-N(61C) | 124.2(7) | C(61A)-N(61A)-C(63A) | 117.6(5) |
| O(61C)-C(61C)-H(61C) | 117.9 | C(62A)-N(61A)-C(63A) | 116.9(5) |
| N(61C)-C(61C)-H(61C) | 117.9 | N(61A)-C(62A)-H(62A) | 109.5 |
| C(61C)-N(61C)-C(62C) | 120.2(5) | N(61A)-C(62A)-H(62B) | 109.5 |
| C(61C)-N(61C)-C(63C) | 120.9(5) | H(62A)-C(62A)-H(62B) | 109.5 |
| C(62C)-N(61C)-C(63C) | 118.7(4) | N(61A)-C(62A)-H(62C) | 109.5 |
| N(61C)-C(62C)-H(62G) | 109.5 | H(62A)-C(62A)-H(62C) | 109.5 |
| N(61C)-C(62C)-H(62H) | 109.5 | H(62B)-C(62A)-H(62C) | 109.5 |
| H(62G)-C(62C)-H(62H) | 109.5 | N(61A)-C(63A)-H(63A) | 109.5 |
| N(61C)-C(62C)-H(62I) | 109.5 | N(61A)-C(63A)-H(63B) | 109.5 |
| H(62G)-C(62C)-H(62I) | 109.5 | H(63A)-C(63A)-H(63B) | 109.5 |
| H(62H)-C(62C)-H(62I) | 109.5 | N(61A)-C(63A)-H(63C) | 109.5 |
| N(61C)-C(63C)-H(63G) | 109.5 | H(63A)-C(63A)-H(63C) | 109.5 |
| N(61C)-C(63C)-H(63H) | 109.5 | H(63B)-C(63A)-H(63C) | 109.5 |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,z  #2 x+1/2,-y+1/2,-z+1/2  #3 -x+1/2,y+1/2,-z+1/2
#4 -x+1/2,y-1/2,-z+1/2  #5 -y+1,-x+1,-z  #6 y,x,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for kl6-59bb. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Co(1) | 30(1) | 27(1) | 18(1) | 0 | 0 | 1(1) |
| Co(2) | 31(1) | 28(1) | 17(1) | 0 | 0 | 0(1) |
| N(1) | 37(3) | 32(3) | 14(2) | 0 | 0 | -2(2) |
| N(2) | 37(4) | 38(4) | 22(3) | 0 | 0 | -8(3) |
| O(1) | 54(3) | 62(3) | 34(2) | 10(2) | 1(2) | -27(2) |
| O(2) | 54(3) | 68(3) | 36(2) | -5(2) | 1(2) | -29(3) |
| O(3) | 62(3) | 46(3) | 33(2) | 2(2) | 7(2) | -23(2) |
| O(4) | 70(3) | 48(3) | 38(2) | -3(2) | -1(2) | -30(2) |
| C(1) | 40(3) | 41(3) | 36(3) | 0(3) | 4(3) | -15(2) |
| C(3) | 37(2) | 32(2) | 29(2) | -1(3) | 4(3) | -4(2) |
| C(11) | 39(5) | 102(9) | 29(5) | -5(6) | -12(5) | -30(6) |
| C(12) | 71(7) | 84(8) | 18(4) | -8(6) | -12(5) | 36(6) |
| C(13) | 87(8) | 32(5) | 10(4) | -7(4) | -5(5) | -11(5) |
| C(21) | 94(8) | 43(6) | 16(4) | -2(4) | 4(6) | 19(6) |
| C(22) | 87(8) | 95(8) | 15(4) | -3(6) | 4(6) | -50(7) |
| C(23) | 49(6) | 105(9) | 41(6) | -3(7) | 6(5) | 39(7) |
| C(2A) | 37(2) | 35(2) | 31(2) | -1(3) | -1(3) | -17(2) |
| C(31A) | 39(3) | 42(4) | 44(3) | -14(3) | 10(3) | -22(3) |
| C(32A) | 42(4) | 40(3) | 77(5) | -9(3) | 1(4) | -6(3) |
| C(33A) | 71(5) | 79(5) | 50(4) | 21(4) | -26(4) | -38(4) |
| C(2B) | 37(2) | 35(2) | 31(2) | -1(3) | -1(3) | -17(2) |
| C(34B) | 62(7) | 55(7) | 47(6) | -17(6) | -1(6) | -29(6) |
| C(35B) | 54(7) | 39(7) | 64(8) | -20(7) | 11(7) | -6(6) |
| C(36B) | 58(7) | 43(7) | 59(7) | 7(6) | -9(6) | -15(6) |
| C(4A) | 45(2) | 35(2) | 27(2) | 0(3) | 1(3) | -9(2) |
| C(41A) | 52(5) | 62(5) | 85(5) | -24(5) | 17(4) | -11(4) |
| C(42A) | 55(4) | 36(4) | 100(6) | -2(4) | -12(5) | -5(3) |
| C(43A) | 85(6) | 78(5) | 32(3) | 3(3) | -12(4) | -60(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(4B) | 45(2) | 35(2) | 27(2) | 0(3) | 1(3) | -9(2) |
| C(44B) | 39(7) | 46(7) | 41(6) | -9(6) | 6(6) | -10(6) |
| C(45B) | 49(7) | 32(6) | 58(8) | -6(7) | 1(7) | -9(5) |
| C(46B) | 43(7) | 43(7) | 49(7) | 13(6) | -20(6) | -17(6) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for kl6-59bb.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(11A) | 6306 | 5001 | 590 | 68 |
| H(11B) | 5892 | 5936 | 506 | 68 |
| H(12A) | 4343 | 6176 | 631 | 69 |
| H(12B) | 3718 | 5369 | 516 | 69 |
| H(13A) | 4233 | 3954 | 618 | 52 |
| H(13B) | 5232 | 3734 | 532 | 52 |
| H(21A) | 4226 | 6057 | 4380 | 61 |
| H(21B) | 5225 | 6279 | 4470 | 61 |
| H(22A) | 4315 | 3838 | 4358 | 79 |
| H(22B) | 3713 | 4657 | 4491 | 79 |
| H(23A) | 6290 | 4978 | 4384 | 78 |
| H(23B) | 5857 | 4054 | 4478 | 78 |
| H(31A) | 1956 | 4087 | 2983 | 50 |
| H(31B) | 2462 | 3476 | 3507 | 50 |
| H(32A) | 3695 | 2246 | 2275 | 64 |
| H(32B) | 3648 | 2455 | 3082 | 64 |
| H(33A) | 2924 | 3165 | 1419 | 80 |
| H(33B) | 2180 | 3815 | 1657 | 80 |
| H(34A) | 2694 | 3508 | 3569 | 66 |
| H(34B) | 3142 | 2595 | 3427 | 66 |
| H(35A) | 3786 | 2295 | 2230 | 63 |
| H(35B) | 3160 | 2560 | 1610 | 63 |
| H(36A) | 2224 | 3992 | 1783 | 64 |
| H(36B) | 1782 | 4011 | 2528 | 64 |
| H(41A) | 1328 | 2574 | 3460 | 79 |
| H(41B) | 911 | 3097 | 2835 | 79 |

| | | | | |
|---|---|---|---|---|
| H(42A) | 2717 | 1221 | 2473 | 77 |
| H(42B) | 2523 | 1579 | 3227 | 77 |
| H(43A) | 1247 | 2724 | 1621 | 78 |
| H(43B) | 2002 | 2065 | 1443 | 78 |
| H(44A) | 1729 | 2119 | 3599 | 50 |
| H(44B) | 1321 | 2990 | 3300 | 50 |
| H(45A) | 2471 | 1311 | 1931 | 56 |
| H(45B) | 2783 | 1387 | 2714 | 56 |
| H(46A) | 884 | 3020 | 1998 | 54 |
| H(46B) | 1638 | 2659 | 1513 | 54 |
| H(51A) | 3452 | 1984 | -143 | 189 |
| H(52A) | 4096 | 283 | 1314 | 236 |
| H(52B) | 3531 | -65 | 687 | 236 |
| H(52C) | 3097 | 513 | 1271 | 236 |
| H(53A) | 4900 | 1410 | 1176 | 236 |
| H(53B) | 4346 | 2262 | 1056 | 236 |
| H(53C) | 4927 | 1886 | 449 | 236 |
| H(51B) | 4450 | 2225 | 271 | 189 |
| H(52D) | 3129 | 113 | 768 | 236 |
| H(52E) | 2999 | 516 | 20 | 236 |
| H(52F) | 2559 | 959 | 672 | 236 |
| H(53D) | 4329 | 332 | 1300 | 236 |
| H(53E) | 4455 | 1310 | 1530 | 236 |
| H(53F) | 5053 | 910 | 944 | 236 |
| H(61C) | 2640 | 6212 | 123 | 282 |
| H(62G) | 280 | 7022 | 564 | 353 |
| H(62H) | 792 | 7437 | -66 | 353 |
| H(62I) | 983 | 7751 | 701 | 353 |
| H(63G) | 676 | 5773 | 957 | 353 |
| H(63H) | 1633 | 5715 | 1252 | 353 |
| H(63I) | 1405 | 5288 | 528 | 353 |
| H(61B) | 1240 | 7177 | 152 | 282 |
| H(62D) | 3639 | 7788 | -367 | 353 |
| H(62E) | 3317 | 6826 | -498 | 353 |
| H(62F) | 3622 | 7113 | 252 | 353 |
| H(63D) | 2761 | 8821 | -117 | 353 |
| H(63E) | 2047 | 8669 | 461 | 353 |
| H(63F) | 1790 | 8620 | -333 | 353 |
| H(61A) | 587 | 5810 | 2030 | 282 |
| H(62A) | -1036 | 4522 | 884 | 353 |

| | | | | |
|---|---|---|---|---|
| H(62B) | -1163 | 4552 | 1699 | 353 |
| H(62C) | -570 | 3827 | 1361 | 353 |
| H(63A) | -50 | 5283 | 362 | 353 |
| H(63B) | 860 | 5505 | 701 | 353 |
| H(63C) | 52 | 6118 | 834 | 353 |

Table 6. Torsion angles [°] for kl6-59bb.

| | |
|---|---|
| O(1)#1-Co(1)-Co(2)-O(4)#2 | -89.0(3) |
| O(1)-Co(1)-Co(2)-O(4)#2 | 91.0(3) |
| O(3)#2-Co(1)-Co(2)-O(4)#2 | 1.0(2) |
| O(3)#3-Co(1)-Co(2)-O(4)#2 | -179.0(2) |
| O(1)#1-Co(1)-Co(2)-O(4)#3 | 91.0(3) |
| O(1)-Co(1)-Co(2)-O(4)#3 | -89.0(3) |
| O(3)#2-Co(1)-Co(2)-O(4)#3 | -179.0(2) |
| O(3)#3-Co(1)-Co(2)-O(4)#3 | 1.0(2) |
| O(1)#1-Co(1)-Co(2)-O(2)#1 | 1.2(2) |
| O(1)-Co(1)-Co(2)-O(2)#1 | -178.8(2) |
| O(3)#2-Co(1)-Co(2)-O(2)#1 | 91.2(2) |
| O(3)#3-Co(1)-Co(2)-O(2)#1 | -88.8(2) |
| O(1)#1-Co(1)-Co(2)-O(2) | -178.8(2) |
| O(1)-Co(1)-Co(2)-O(2) | 1.2(2) |
| O(3)#2-Co(1)-Co(2)-O(2) | -88.8(2) |
| O(3)#3-Co(1)-Co(2)-O(2) | 91.2(2) |
| O(1)#1-Co(1)-N(1)-C(13) | 139.7(5) |
| O(1)-Co(1)-N(1)-C(13) | -40.3(5) |
| O(3)#2-Co(1)-N(1)-C(13) | 49.7(5) |
| O(3)#3-Co(1)-N(1)-C(13) | -130.3(5) |
| O(1)#1-Co(1)-N(1)-C(11) | 13.6(6) |
| O(1)-Co(1)-N(1)-C(11) | -166.4(6) |
| O(3)#2-Co(1)-N(1)-C(11) | -76.4(6) |
| O(3)#3-Co(1)-N(1)-C(11) | 103.6(6) |
| O(1)#1-Co(1)-N(1)-C(12) | -104.3(6) |
| O(1)-Co(1)-N(1)-C(12) | 75.7(6) |
| O(3)#2-Co(1)-N(1)-C(12) | 165.6(6) |
| O(3)#3-Co(1)-N(1)-C(12) | -14.4(6) |
| O(4)#2-Co(2)-N(2)-C(23) | 31.6(7) |
| O(4)#3-Co(2)-N(2)-C(23) | -148.4(7) |
| O(2)#1-Co(2)-N(2)-C(23) | -58.7(7) |
| O(2)-Co(2)-N(2)-C(23) | 121.3(7) |
| O(4)#2-Co(2)-N(2)-C(21) | 158.9(6) |
| O(4)#3-Co(2)-N(2)-C(21) | -21.1(6) |
| O(2)#1-Co(2)-N(2)-C(21) | 68.7(6) |
| O(2)-Co(2)-N(2)-C(21) | -111.3(6) |
| O(4)#2-Co(2)-N(2)-C(22) | -86.3(7) |
| O(4)#3-Co(2)-N(2)-C(22) | 93.7(7) |
| O(2)#1-Co(2)-N(2)-C(22) | -176.5(7) |
| O(2)-Co(2)-N(2)-C(22) | 3.5(7) |

| | |
|---|---|
| O(1)#1-Co(1)-O(1)-C(1) | -3.8(5) |
| O(3)#2-Co(1)-O(1)-C(1) | 79.5(5) |
| O(3)#3-Co(1)-O(1)-C(1) | -87.1(5) |
| N(1)-Co(1)-O(1)-C(1) | 176.2(5) |
| Co(2)-Co(1)-O(1)-C(1) | -3.8(5) |
| O(4)#2-Co(2)-O(2)-C(1) | -81.6(5) |
| O(4)#3-Co(2)-O(2)-C(1) | 83.2(5) |
| O(2)#1-Co(2)-O(2)-C(1) | 0.8(5) |
| N(2)-Co(2)-O(2)-C(1) | -179.2(5) |
| Co(1)-Co(2)-O(2)-C(1) | 0.8(5) |
| Co(2)-O(2)-C(1)-O(1) | -4.2(8) |
| Co(2)-O(2)-C(1)-C(2B) | 171.2(7) |
| Co(2)-O(2)-C(1)-C(2A) | 174.0(4) |
| Co(1)-O(1)-C(1)-O(2) | 6.0(8) |
| Co(1)-O(1)-C(1)-C(2B) | -169.3(7) |
| Co(1)-O(1)-C(1)-C(2A) | -172.3(4) |
| Co(2)#4-O(4)-C(3)-O(3) | -6.1(8) |
| Co(2)#4-O(4)-C(3)-C(4A) | 170.9(5) |
| Co(2)#4-O(4)-C(3)-C(4B) | 173.9(9) |
| Co(1)#4-O(3)-C(3)-O(4) | 7.4(7) |
| Co(1)#4-O(3)-C(3)-C(4A) | -169.6(4) |
| Co(1)#4-O(3)-C(3)-C(4B) | -172.6(9) |
| C(13)-N(1)-C(11)-C(13)#5 | 48.3(11) |
| C(12)-N(1)-C(11)-C(13)#5 | -66.5(11) |
| Co(1)-N(1)-C(11)-C(13)#5 | 173.6(9) |
| C(13)-N(1)-C(12)-C(12)#5 | -69.3(15) |
| C(11)-N(1)-C(12)-C(12)#5 | 50.0(15) |
| Co(1)-N(1)-C(12)-C(12)#5 | 171.5(12) |
| C(11)-N(1)-C(13)-C(11)#5 | -60.2(10) |
| C(12)-N(1)-C(13)-C(11)#5 | 55.1(11) |
| Co(1)-N(1)-C(13)-C(11)#5 | 173.6(9) |
| C(23)-N(2)-C(21)-C(23)#6 | -59.8(11) |
| C(22)-N(2)-C(21)-C(23)#6 | 54.8(12) |
| Co(2)-N(2)-C(21)-C(23)#6 | 173.3(10) |
| C(23)-N(2)-C(22)-C(22)#6 | 48.6(17) |
| C(21)-N(2)-C(22)-C(22)#6 | -70.8(17) |
| Co(2)-N(2)-C(22)-C(22)#6 | 170.1(13) |
| C(21)-N(2)-C(23)-C(21)#6 | 46.6(13) |
| C(22)-N(2)-C(23)-C(21)#6 | -66.8(13) |
| Co(2)-N(2)-C(23)-C(21)#6 | 172.9(10) |

| | |
|---|---|
| O(2)-C(1)-C(2A)-C(33A) | 167.4(6) |
| O(1)-C(1)-C(2A)-C(33A) | -14.2(8) |
| C(2B)-C(1)-C(2A)-C(33A) | -139(13) |
| O(2)-C(1)-C(2A)-C(31A) | 41.7(8) |
| O(1)-C(1)-C(2A)-C(31A) | -139.9(6) |
| C(2B)-C(1)-C(2A)-C(31A) | 96(12) |
| O(2)-C(1)-C(2A)-C(32A) | -75.6(7) |
| O(1)-C(1)-C(2A)-C(32A) | 102.8(6) |
| C(2B)-C(1)-C(2A)-C(32A) | -22(12) |
| C(33A)-C(2A)-C(31A)-C(41A) | 53.6(9) |
| C(1)-C(2A)-C(31A)-C(41A) | 179.5(7) |
| C(32A)-C(2A)-C(31A)-C(41A) | -64.4(8) |
| C(33A)-C(2A)-C(32A)-C(42A) | -67.9(9) |
| C(31A)-C(2A)-C(32A)-C(42A) | 52.2(9) |
| C(1)-C(2A)-C(32A)-C(42A) | 172.7(7) |
| C(31A)-C(2A)-C(33A)-C(43A) | -60.8(8) |
| C(1)-C(2A)-C(33A)-C(43A) | 172.8(6) |
| C(32A)-C(2A)-C(33A)-C(43A) | 57.1(8) |
| O(2)-C(1)-C(2B)-C(36B) | 119.1(11) |
| O(1)-C(1)-C(2B)-C(36B) | -65.2(12) |
| C(2A)-C(1)-C(2B)-C(36B) | -8(12) |
| O(2)-C(1)-C(2B)-C(34B) | -0.4(13) |
| O(1)-C(1)-C(2B)-C(34B) | 175.3(9) |
| C(2A)-C(1)-C(2B)-C(34B) | -128(13) |
| O(2)-C(1)-C(2B)-C(35B) | -119.6(10) |
| O(1)-C(1)-C(2B)-C(35B) | 56.2(12) |
| C(2A)-C(1)-C(2B)-C(35B) | 113(13) |
| C(36B)-C(2B)-C(34B)-C(44B) | 39.9(15) |
| C(1)-C(2B)-C(34B)-C(44B) | 161.2(12) |
| C(35B)-C(2B)-C(34B)-C(44B) | -76.5(14) |
| C(36B)-C(2B)-C(35B)-C(45B) | -73.2(16) |
| C(34B)-C(2B)-C(35B)-C(45B) | 42.6(16) |
| C(1)-C(2B)-C(35B)-C(45B) | 164.2(15) |
| C(34B)-C(2B)-C(36B)-C(46B) | -77.3(15) |
| C(1)-C(2B)-C(36B)-C(46B) | 161.2(14) |
| C(35B)-C(2B)-C(36B)-C(46B) | 37.8(17) |
| O(4)-C(3)-C(4A)-C(42A) | -107.1(8) |
| O(3)-C(3)-C(4A)-C(42A) | 70.1(8) |
| C(4B)-C(3)-C(4A)-C(42A) | 132(18) |
| O(4)-C(3)-C(4A)-C(43A) | 16.0(9) |

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|---|---|
| O(3)-C(3)-C(4A)-C(43A) | -166.8(6) |
| C(4B)-C(3)-C(4A)-C(43A) | -104(18) |
| O(4)-C(3)-C(4A)-C(41A) | 134.5(7) |
| O(3)-C(3)-C(4A)-C(41A) | -48.2(8) |
| C(4B)-C(3)-C(4A)-C(41A) | 14(17) |
| C(42A)-C(4A)-C(41A)-C(31A) | 53.3(10) |
| C(3)-C(4A)-C(41A)-C(31A) | 174.7(7) |
| C(43A)-C(4A)-C(41A)-C(31A) | -62.8(10) |
| C(2A)-C(31A)-C(41A)-C(4A) | 9.9(11) |
| C(3)-C(4A)-C(42A)-C(32A) | 172.4(8) |
| C(43A)-C(4A)-C(42A)-C(32A) | 47.3(11) |
| C(41A)-C(4A)-C(42A)-C(32A) | -66.7(11) |
| C(2A)-C(32A)-C(42A)-C(4A) | 12.2(12) |
| C(42A)-C(4A)-C(43A)-C(33A) | -58.3(10) |
| C(3)-C(4A)-C(43A)-C(33A) | 177.3(6) |
| C(41A)-C(4A)-C(43A)-C(33A) | 56.0(10) |
| C(2A)-C(33A)-C(43A)-C(4A) | 4.3(11) |
| O(4)-C(3)-C(4B)-C(45B) | -73.9(12) |
| O(3)-C(3)-C(4B)-C(45B) | 106.2(11) |
| C(4A)-C(3)-C(4B)-C(45B) | -13(17) |
| O(4)-C(3)-C(4B)-C(44B) | 167.5(10) |
| O(3)-C(3)-C(4B)-C(44B) | -12.4(15) |
| C(4A)-C(3)-C(4B)-C(44B) | -131(18) |
| O(4)-C(3)-C(4B)-C(46B) | 43.4(15) |
| O(3)-C(3)-C(4B)-C(46B) | -136.5(11) |
| C(4A)-C(3)-C(4B)-C(46B) | 104(18) |
| C(45B)-C(4B)-C(44B)-C(34B) | 40.1(19) |
| C(46B)-C(4B)-C(44B)-C(34B) | -76.2(18) |
| C(3)-C(4B)-C(44B)-C(34B) | 156.3(15) |
| C(2B)-C(34B)-C(44B)-C(4B) | 31.1(16) |
| C(44B)-C(4B)-C(45B)-C(35B) | -74.6(18) |
| C(46B)-C(4B)-C(45B)-C(35B) | 41.7(19) |
| C(3)-C(4B)-C(45B)-C(35B) | 163.2(15) |
| C(2B)-C(35B)-C(45B)-C(4B) | 28.3(18) |
| C(45B)-C(4B)-C(46B)-C(36B) | -77.2(19) |
| C(44B)-C(4B)-C(46B)-C(36B) | 40(2) |
| C(3)-C(4B)-C(46B)-C(36B) | 167.4(16) |
| C(2B)-C(36B)-C(46B)-C(4B) | 31.8(18) |
| O(51A)-C(51A)-N(51A)-C(53A) | -163(2) |
| O(51A)-C(51A)-N(51A)-C(52A) | 5(3) |

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|---|---|
| O(51B)-C(51B)-N(51B)-C(52B) | 17(3) |
| O(51B)-C(51B)-N(51B)-C(53B) | -151.6(19) |
| O(61C)-C(61C)-N(61C)-C(62C) | 18(6) |
| O(61C)-C(61C)-N(61C)-C(63C) | -166(4) |
| O(61B)-C(61B)-N(61B)-C(63B) | -180(5) |
| O(61B)-C(61B)-N(61B)-C(62B) | 6(7) |
| O(61A)-C(61A)-N(61A)-C(62A) | 20(4) |
| O(61A)-C(61A)-N(61A)-C(63A) | 172(3) |

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z  #2 x+1/2,-y+1/2,-z+1/2  #3 -x+1/2,y+1/2,-z+1/2

#4 -x+1/2,y-1/2,-z+1/2  #5 -y+1,-x+1,-z  #6 y,x,-z+1