

Supporting Information for

Selective, Tunable O₂ Binding in Cobalt(II)–Triazolate/Pyrazolate Metal–Organic Frameworks

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1. General considerations.

Unless otherwise noted, all procedures were performed under an N₂ atmosphere using standard glove box or Schlenk techniques. *N,N*-dimethylformamide (DMF) was dried using a commercial solvent purification system designed by JC Meyer Solvent Systems and then stored over 4 Å molecular sieves. Anhydrous methanol was purchased from commercial vendors, further dried over 3 Å sieves for 24 h, and deoxygenated prior to being transferred to an inert atmosphere glove box, where it was stored over 3 Å molecular sieves. Dimethylformamidium trifluoromethanesulfonate was purchased from Aldrich and dried under vacuum for at least 24 h before use. All other reagents were obtained from commercial vendors and used without further purification.

Powder X-ray diffraction patterns were collected on Beamline 17-BM-B at the Advanced Photon Source at Argonne National Laboratory. C, H, and N analyses were obtained from the Microanalytical Laboratory at the University of California, Berkeley. ¹H-NMR spectra were obtained using a Bruker AVB-400 instrument.

The percent relative humidity for Co-BTtri air and moisture stability tests was controlled using a saturated MgSO₄ salt bath.¹ To test stability against moisture, the saturated solution (15 mL in a 20-mL scintillation vial) and 40 mg of activated Co-BTtri were sealed together in a 100-mL jar for 24 h.

2. Single crystal X-ray diffraction.

X-ray diffraction analyses were performed on single crystals coated with Paratone-N oil and mounted on MiTeGen or Kapton loops. Crystals were frozen at a temperature of 100 K by an Oxford Cryosystems Cryostream. Data for CoBDTriP, CoBDTriP–MeOH, and CoBDTriP–O₂ were collected using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and a Bruker QUAZAR diffractometer equipped with a Bruker AXS APEX II detector. Data for CoBTTri, CoBTTri–MeOH, CoBTTri–O₂, and CoBDTriP–DMF were collected at Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory using synchrotron radiation ($\lambda = 0.7749 \text{ \AA}$ for CoBTTri, CoBTTri–O₂, and CoBDTriP–DMF; $\lambda = 0.8856 \text{ \AA}$ for CoBTTri–MeOH) with a Bruker AXS PHOTON100 CMOS diffractometer. Raw data were integrated and corrected for Lorentz and polarization effects using Bruker AXS SAINT software.² Absorption corrections were applied using SADABS.³ Space group assignments were determined by examination of systematic absences, E-statistics, and successive refinement of the structures. The structures were solved using direct methods with SHELXT⁴ and refined using SHELXL⁵ operated in the OLEX2⁶ interface. None of the crystals showed significant decay during data collection. Thermal parameters were refined anisotropically for all non-hydrogen atoms. Hydrogen atoms were placed in ideal positions and refined using a riding model for all structures. Extensive solvent disorder that could not be modeled was found in the pores for all structures and the unassigned electron density was accounted for using SQUEEZE⁷ as implemented in the PLATON⁸ interface. Disorder of the triazolate groups in CoBTTri and CoBTTri–MeOH, the triazolate and pyrazolate groups in all the CoBDTriP structures, and the solvent or O₂ molecules coordinated to the Co sites in CoBTTri–MeOH, CoBTTri–O₂, CoBDTriP–MeOH, CoBDTriP–DMF, and CoBDTriP required the use of displacement parameter and distance restraints during refinement. When disorder was found to be a product of crystal symmetry, site occupancy factors on disordered atoms were fixed to reflect a statistical average. In all other cases, the site occupancy factors were refined and then fixed in the final refinement.

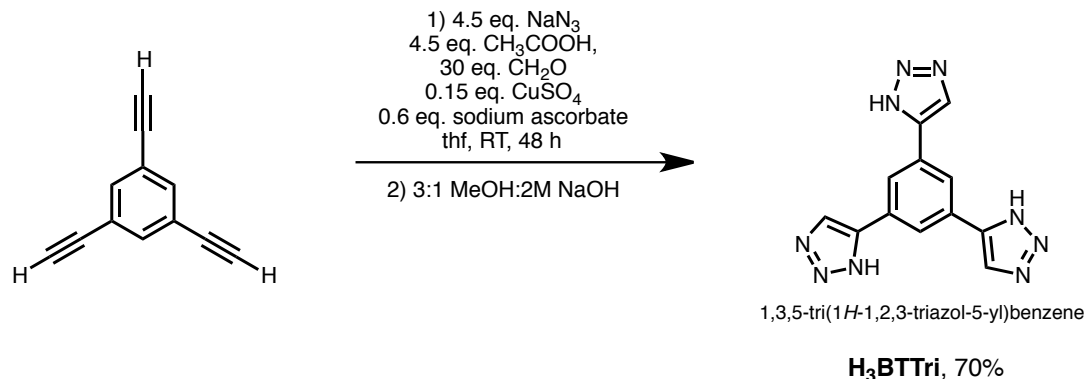
3. Magnetic measurements.

Samples were prepared by adding crystalline powder of Co-BTtri and DMF-solvated Co-BTtri (17.9 mg and 38.4 mg, respectively) to a 5 mm inner diameter quartz tube containing a raised quartz platform. Through elemental analysis, it was determined that the formula unit of Co-BTtri (following activation) contained 14 molar equivalents of DMF (M_r 7247.11 g/mol), while the DMF solvated Co-BTtri contained 58 molar equivalents of DMF (M_r 10463.29 g/mol). Solid eicosane was added to cover the sample to prevent crystallite torquing and to provide good thermal contact between the sample and the cryostat. The tubes were fitted with Teflon sealable adapters, evacuated on a Schlenk line, and flame-sealed under static vacuum. Following flame sealing, the solid eicosane was melted in a water bath held at 40 °C. Magnetic susceptibility measurements were performed using a Quantum Design MPMS2 SQUID magnetometer. Dc magnetic susceptibility measurements were collected in the temperature range 2-300 K under applied magnetic fields of 0.1 T, 0.5 T, and 1 T. Diamagnetic corrections were applied to the data using Pascal's constants to give $\chi_D = -0.00314282$ emu/mol (Co-BTtri), $\chi_D = -0.00511282$ emu/mol (DMF solvated Co-BTtri), and $\chi_D = -0.00024306$ emu/mol (eicosane).

Prior to fitting of the magnetic data ($H_{dc} = 1$ T), $\chi_M T$ data for the activated Co-BTtri sample (formula unit $[\text{Co}(\text{DMF})_{4.67}]_3[(\text{Co}_4\text{Cl})_3(\text{BTtri})_8]_2$) was simplified by subtracting the $\chi_M T$ product expected for the extra framework cations (3 $S = 3/2$ centers with $g = 2.00$) and dividing the resultant $\chi_M T$ data by six, the number of $\text{Co}_4(\mu_4\text{-Cl})$ clusters present in the formula unit. This data was fit across the temperature range 50–300 K using the program PHI⁹ using the simplex method. A more complicated Hamiltonian that permitted fitting of the g value of the extra framework cations was originally used. However, the g value obtained was within error of $g = 2.00$, so the much simpler Hamiltonian shown in Equation 5 in the main text was ultimately used.

4. Synthesis of H₃BTTri.

The synthesis of H₃BTTri was performed following the previously published procedure, with modifications in the last step.¹⁰⁻¹¹

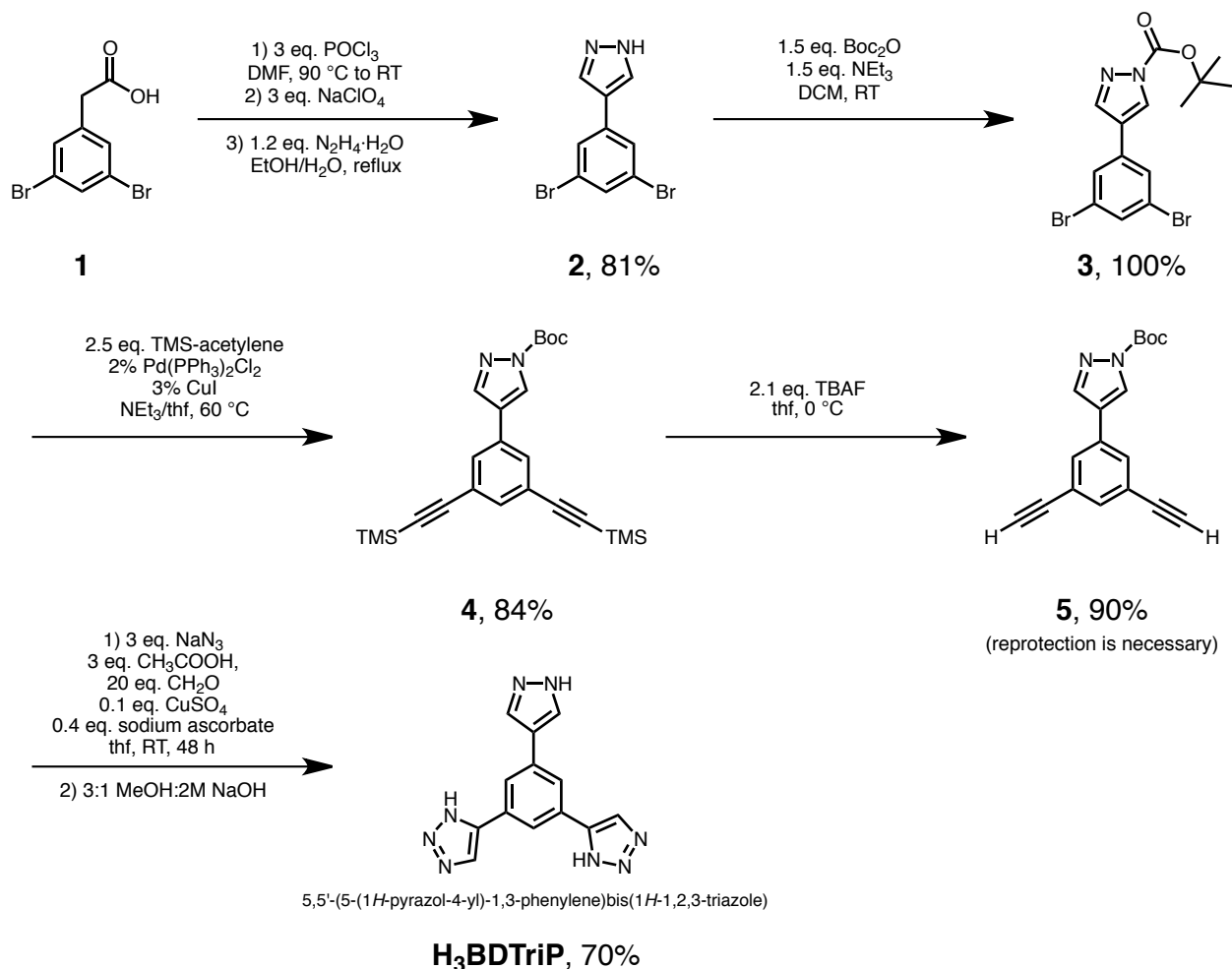


Scheme S1. Final step in the synthesis of H₃BTTri.

Synthesis of H₃BTTri from 1,3,5-triethynylbenzene:

To 100 mL of tetrahydrofuran was added 70 mL of formaldehyde (37 wt% in H₂O, 30 equiv) and 8.1 mL of acetic acid (4.5 equiv), and this mixture was stirred at room temperature for 15 min. Sodium azide (9.16 g, 4.5 equiv) was then added slowly, followed by 1,3,5-triethynylbenzene (4.7 g, 1 equiv). The mixture was stirred at room temperature for another 10 min, after which sodium ascorbate (3.7 g, 0.6 equiv) and a solution of 1.25 M aqueous copper sulfate (3.75 mL, 0.15 equiv) were added. After stirring at room temperature for 2 d, the reaction was diluted with water and the product was filtered and washed with more water. To deprotect the triazole groups, the product was redissolved in 3:1 MeOH:2M NaOH mixture (4 mL/mmol alkyne) and stirred at room temperature for 48 h. During this process, copper hydroxide crashed out as a blue/green solid. The blue precipitate was allowed to settle, and then filtered out and discarded. The filtrate was then neutralized with acetic acid. The white solid that precipitated out was then filtered, washed with water, and dried to give 6.1 g of H₃BTTri (yield: 70%). ¹H, EA, and IR spectra match those in the previously published procedure.²

5. Synthesis of H₃BDTriP.



Scheme S2. Overall synthesis of H₃BDTriP.

Synthesis of 2:

30 mL of anhydrous DMF were sparged with argon and cooled to 0 °C. While stirring, 2.85 mL of POCl₃ (3 equiv) were added dropwise, and the mixture was allowed to warm to room temperature and stirred for 1 h. Then 3 g of **1** (1 equiv.) was added, and the reaction was stirred at 90 °C for 4 h and at room temperature overnight. The flask was then cooled in an ice bath, and 26 g of ice was added and this mixture stirred for 15 min. Then, 3.75 g of NaClO₄ (3 equiv) dissolved in 4 mL of H₂O was added while stirring, resulting in precipitation of the iminium perchlorate salt, which was filtered, washed with cold water, and used directly in the next step without further purification.

To form the pyrazole ring, the isolated perchlorate salt was stirred in 67 mL of EtOH and 21 mL of H₂O. To this mixture was added 0.6 mL of hydrazine monohydrate (1.2 equiv). This mixture was refluxed for 2 h and then stirred at room temperature overnight. The product was precipitated with H₂O, filtered, and washed with H₂O to yield **2** in 81% yield (2.50 g). ¹H NMR (400 MHz, DMSO-d₆): 13.09 (s, 1H), 8.39 (s, 1H), 8.07 (s, 1H), 7.89 (d, *J* = 2 Hz, 2H), 7.60 (s, 1H).

Synthesis of **3**:

2.50 g of pyrazole **2** was stirred in 20 mL DCM and 1.73 mL NEt₃ (1.5 equiv). To this mixture was added 2.70 g di-*tert*-butyl dicarbonate (1.5 equiv), and this mixture was stirred overnight at room temperature. The reaction was quenched with water, extracted with EtOAc, and dried over MgSO₄. Removal of solvent led to isolation of **3** in quantitative yield (3.33 g). ¹H NMR (400 MHz, DMSO-d₆): 8.98 (s, 1H), 8.45 (s, 1H), 8.09 (d, *J* = 2 Hz, 2H), 7.73 (m, 1H), 1.60 (s, 8H).

Synthesis of **4**:

25 mL of THF and 25 mL of NEt₃ were sparged with argon for 1 h. Then, 3.30g of the Boc-protected pyrazole **3** were added, along with 130 mg of Pd(PPh₃)₂Cl₂ (2.2 mol%) and 53 mg of CuI (3.3 mol%), then the mixture was stirred for 5 min at room temperature. 2.60 mL ethynyltrimethylsilane (2.2 equiv) was subsequently added, and the mixture was heated to 60 °C and stirred for 18 h. When the reaction was complete, the solvent was removed *in vacuo* and the mixture was redissolved in Et₂O and filtered over celite. A silica plug was used to remove trace palladium, and evacuation of solvent led to 3.01 g of **4** (84% yield). ¹H NMR (400 MHz, DMSO-d₆): 8.97 (s, 1H), 8.45 (s, 1H), 7.92 (d, *J* = 1.6 Hz, 2H), 7.40 (s, 1H), 1.60 (s, 9H), 0.25 (s, 18H).

Synthesis of **5**:

2.03 g of **4** was stirred in 160 mL of THF cooled to 0 °C. To this mixture was added 10.0 mL of tetra-*n*-butylammonium fluoride (1.0 M in THF, 2.2 equiv), and the reaction was stirred for 30 minutes at 0 °C and allowed to warm to room temperature. The solvent was removed and the solid extracted with EtOAc, washed with NH₄Cl, and dried over MgSO₄. Because some of the pyrazole was deprotected during this procedure, the pyrazole was re-protected using di-*tert*-butyl dicarbonate in dichloromethane and NEt₃ (see synthesis of **3** for detailed procedures). Yield: 90%. ¹H NMR (400 MHz, DMSO-d₆): 8.94 (s, 1H), 8.43 (s, 1H), 7.97 (s, 2H), 7.45 (s, 1H), 4.41 (s, 2H), 1.60 (s, 9 H).

Synthesis of **H₃BDTriP**:

6.9 mL of formaldehyde solution (37 weight % in H₂O, 20 equiv), 0.79 mL of acetic acid (3 equiv), and 20 mL of THF were stirred at room temperature for 15 min. Then, 0.91 g of NaN₃ (3 equiv) and 1.36 g of alkyne **5** (1 equiv) were added and the reaction was stirred for 10 min. 0.37 g of sodium ascorbate (0.4 equiv) and 74 mg of CuSO₄ (0.1 equiv, dissolved in 0.3 mL of H₂O) were added and the reaction stirred at room temperature for 48 h. The solvent was removed *in vacuo*, the solid extracted with EtOAc, and the solution concentrated to give 1.69 g of protected H₃BDTriP. To deprotect both the pyrazole and triazole rings, the solid was stirred in 50 mL of 3:1 MeOH:2N NaOH for 24 h. The solution was filtered to remove precipitated Cu(OH)₂, then neutralized with acetic acid, filtered, washed with H₂O, and dried to give 0.75 g H₃BDTriP (58% over two steps). ¹H NMR (400 MHz, DMSO-d₆): 15.30 (s, 2H), 13.05 (s, 1H), 8.44 (s, 2H), 8.21 (s, 2H), 8.18 (s, 1H), 8.05 (s, 2H).

6. Supplementary tables.

Table S1. Langmuir parameters for Co-BTtri N₂ and O₂ isotherms. Variable-temperature N₂ and O₂ isotherms were each fit simultaneously, with a single set of parameters, using the dual-site Langmuir equation, $n = \frac{n_{sat,1}b_1P}{1+b_1P} + \frac{n_{sat,2}b_2P}{1+b_2P}$, where $b_i = e^{S_i/R}e^{-E_i \cdot 1000/RT}$.

Parameter	Co-BTtri, N ₂	Co-BTtri, O ₂
$n_{sat,1}$ (mmol/g)	0.26	2.78
E_1 (kJ/mol)	-19.87	-34.59
S_1 (J/mol·K)	-78.56	-132.49
$n_{sat,2}$ (mmol/g)	7.21	7.05
E_2 (kJ/mol)	-11.90	-5.18
S_2 (J/mol·K)	-70.17	-33.96

Table S2. Langmuir parameters for Co-BDtriP N₂ and O₂ isotherms. Variable-temperature N₂ and O₂ isotherms were each fit simultaneously, with a single set of parameters, using the multi-site Langmuir equation, $n = \frac{n_{sat,1}b_1P}{1+b_1P} + \frac{n_{sat,2}b_2P}{1+b_2P} + \frac{n_{sat,3}b_3P}{1+b_3P} + \frac{n_{sat,4}b_4P}{1+b_4P}$ where $b_i = e^{S_i/R}e^{-E_i \cdot 1000/RT}$.

Parameter	Co-BDtriP, N ₂	Co-BDtriP, O ₂
$n_{sat,1}$ (mmol/g)	0.57	0.25
E_1 (kJ/mol)	-19.73	-47.03
S_1 (J/mol·K)	-86.04	-124.62
$n_{sat,2}$ (mmol/g)	5.82	0.80
E_2 (kJ/mol)	-6.78	-36.23
S_2 (J/mol·K)	-45.81	-110.96
$n_{sat,3}$ (mmol/g)	-	1.08
E_3 (kJ/mol)	-	-32.36
S_3 (J/mol·K)	-	-120.60
$n_{sat,4}$ (mmol/g)	-	6.75
E_4 (kJ/mol)	-	-11.34
S_4 (J/mol·K)	-	-61.81

Table S3. Crystallographic Data.

	Co-BTTri-DMF (100 K)	Co-BTTri-DMF (298 K)	Co-BTTri- MeOH	Co-BTTri	Co-BTTri-O ₂
Formula	C264 H264 Cl6 Co24 N168 O24	C264 H264 Cl6 Co24 N168 O24	C108 H84 Cl3 Co13.5 N72 O12	C201 H123 Cl6 Co27.26 N144 O9	C192 H96 Cl6 Co27 N144 O48
Crystal System	Cubic	Cubic	Cubic	Cubic	Cubic
Space Group	<i>Fm</i> $\bar{3}$ <i>c</i>	<i>Fm</i> $\bar{3}$ <i>c</i>	<i>Pm</i> $\bar{3}$ <i>m</i>	<i>Fm</i> $\bar{3}$ <i>c</i>	<i>Fm</i> $\bar{3}$ <i>c</i>
a, b, c (Å)	37.4139(16)	37.7048(13)	18.7940(7)	37.0668(10)	37.0728(12)
α, β, γ (°)	90	90	90	90	90
<i>V</i> , (Å ³)	52372(7)	53603(6)	6638.3(7)	50928(4)	50953(5)
<i>Z</i>	4	4	1	4	4
Radiation, λ (Å)	Synchrotron, 0.7749 Å	Synchrotron, 0.7749 Å	Synchrotron, 0.8856	Synchrotron, 0.7749	Synchrotron, 0.7749
Data / Restraints / Parameters	2643 / 62 / 108	2322 / 21 / 96	2042 / 0 / 60	2059 / 0 / 87	2215 / 22 / 90
Goodness of Fit on <i>F</i> ²	1.071	1.104	1.074	1.082	1.088
<i>R</i> 1 ^{<i>a</i>} , <i>wR</i> 2 ^{<i>b</i>} (<i>I</i> > 2σ(<i>I</i>))	0.0671, 0.1996	0.0481, 0.1432	0.0638, 0.1891	0.0355, 0.0966	0.0557, 0.1570
<i>R</i> 1 ^{<i>a</i>} , <i>wR</i> 2 ^{<i>b</i>} (all data)	0.0768, 0.2164	0.0535, 0.1506	0.0706, 0.1996	0.0418, 0.1003	0.0627, 0.1649
Largest Diff. Peak and Hole (e Å ⁻³)	1.436 and – 0.623	1.338 and – 0.499	1.774 and – 2.075	0.406 and – 0.800	0.476 and – 0.682

$${}^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad {}^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}.$$

Table S4. Crystallographic Data.

	Co-BDTriP–DMF	Co-BDTriP–MeOH	Co-BDTriP	Co-BDTriP–O ₂
Formula	C140 H140 Cl3 Co14.40 N76 O14.40	C100 H76 Cl3 Co13.5 N80 O12	C109.02 H71.02 Cl3 Co13.44 N63.98 O5.04	C87.98 H39.98 Cl3 Co13.5 N80.02 O23.62
Crystal System	Cubic	Cubic	Cubic	Cubic
Space Group	<i>Pm</i> $\bar{3}$ <i>m</i>	<i>Pm</i> $\bar{3}$ <i>m</i>	<i>Pm</i> $\bar{3}$ <i>m</i>	<i>Pm</i> $\bar{3}$ <i>m</i>
a, b, c (Å)	18.8345(7)	18.7059(4)	18.6522(5)	18.6011(7)
α, β, γ (°)	90	90	90	90
<i>V</i> , (Å ³)	6681.3(7)	6545.4(4)	6489.2(5)	6436.0(7)
Z	1	1	1	1
Radiation, λ (Å)	Synchrotron, 0.7749	0.71073	0.71073	0.71073
Data / Restraints / Parameters	1577 / 0 / 57	1108 / 9 / 56	1208 / 0 / 53	1367 / 8 / 59
Goodness of Fit on F ²	1.114	1.078	1.118	1.159
R1 ^a , wR2 ^b (I > 2 σ (I))	0.0462, 0.1537	0.0593, 0.1690	0.0463, 0.1099	0.0619, 0.1830
R1 ^a , wR2 ^b (all data)	0.0503, 0.1590	0.0650, 0.1761	0.0610, 0.1233	0.0701, 0.1918
Largest Diff. Peak and Hole (e Å ⁻³)	0.773 and –0.441	1.405 and –0.682	0.484 and –0.897	1.399 and –0.508

$${}^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, {}^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}.$$

7. Supplementary figures.

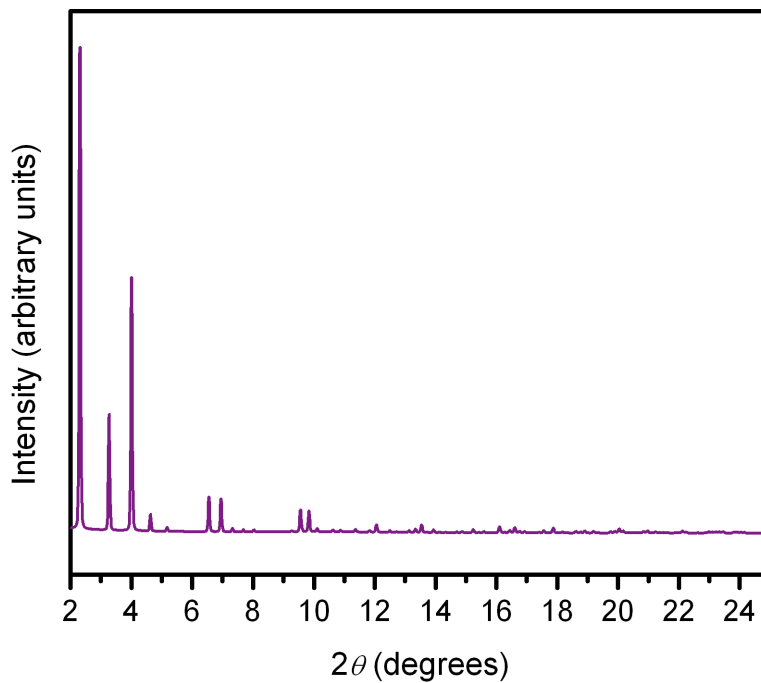


Figure S1. Powder diffraction pattern of as-synthesized Co-BTtri. $\lambda = 0.7500900 \text{ \AA}$.

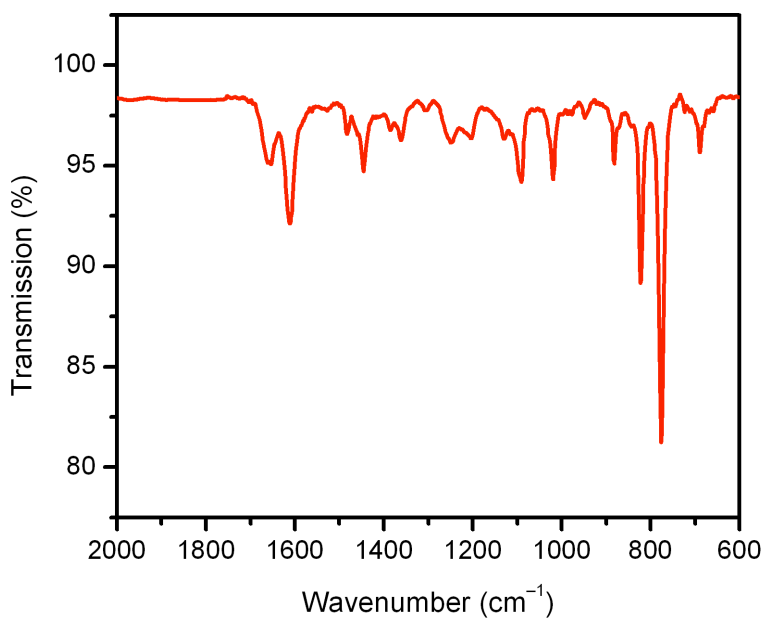


Figure S2. Infrared spectra of activated Co-BTtri. Peak at around 1620 cm^{-1} is assigned as residual DMF, bound to the extraframework cations.

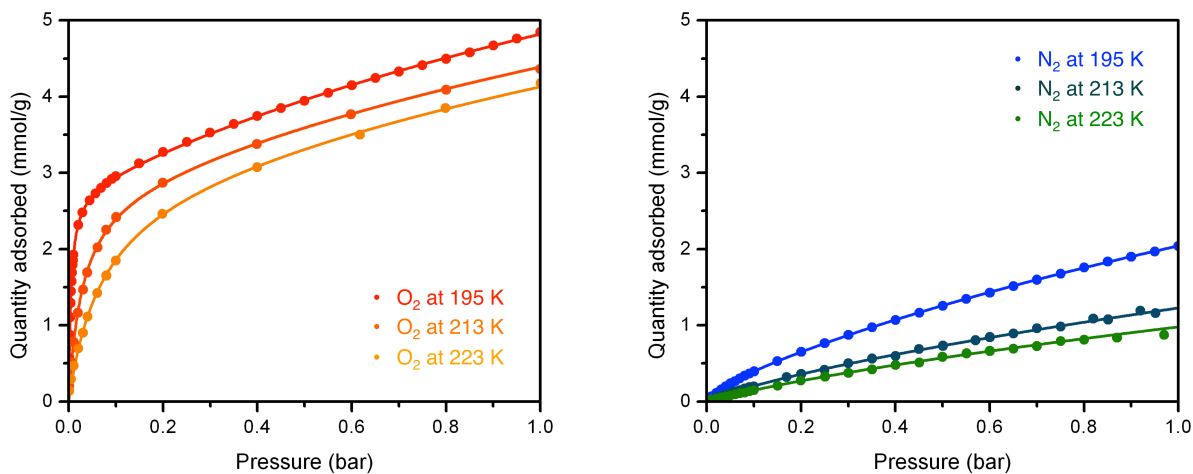


Figure S3. Variable temperature O₂ (left) and N₂ (right) isotherms for Co-BTTri. The three temperatures were fit simultaneously to a dual-site Langmuir equation.

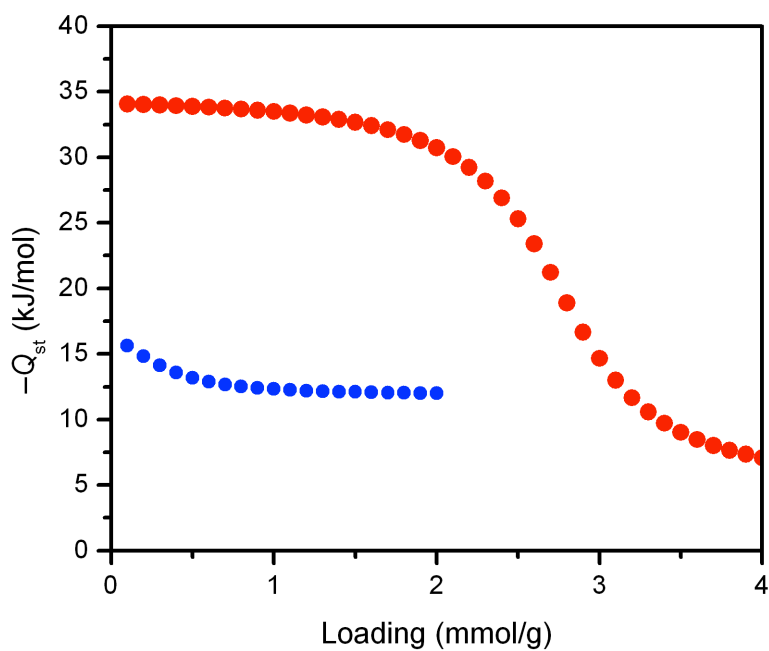


Figure S4. Isothermic heats of adsorption for O₂ (red circles) and N₂ (blue circles) in Co-BTTri.

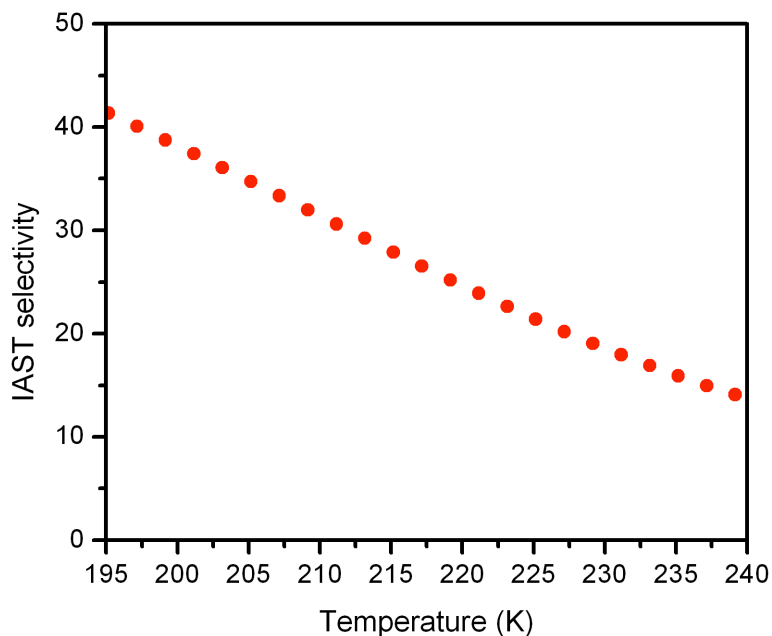


Figure S5. Ideal adsorbed solution theory (IAST) selectivities for Co-BTtri as a function of temperature, calculated using the Langmuir fits (see Supplementary Table S1), for a theoretical mixture of 0.21 bar O₂ and 0.79 bar N₂.

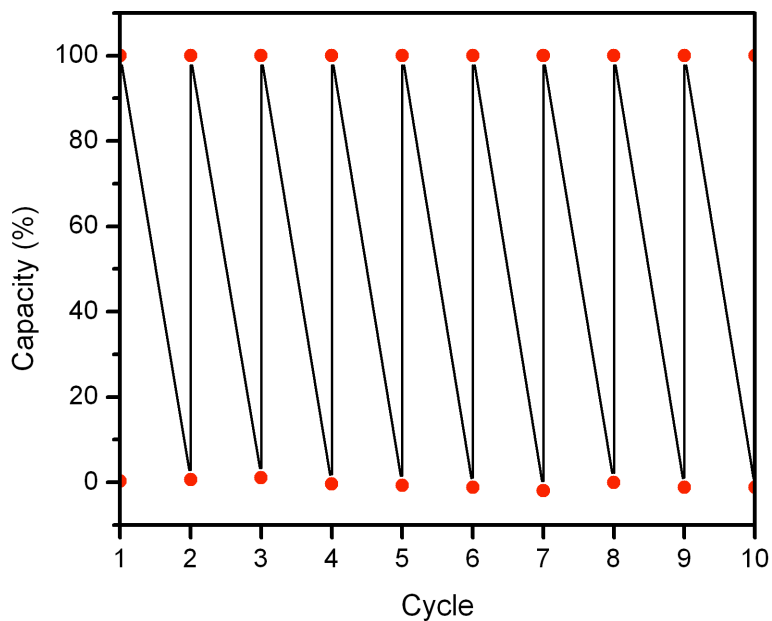


Figure S6. Cycling experiments for Co-BTtri, with O₂ adsorption occurring at 195 K and 0.21 bar. Desorption was performed by quickly heating the sample to 323 K for five minutes. Note that before the last cycle, the sample was exposed to humid air for 24 h and then reactivated at 423 K for 6 h, demonstrating the excellent air-stability of Co-BTtri.

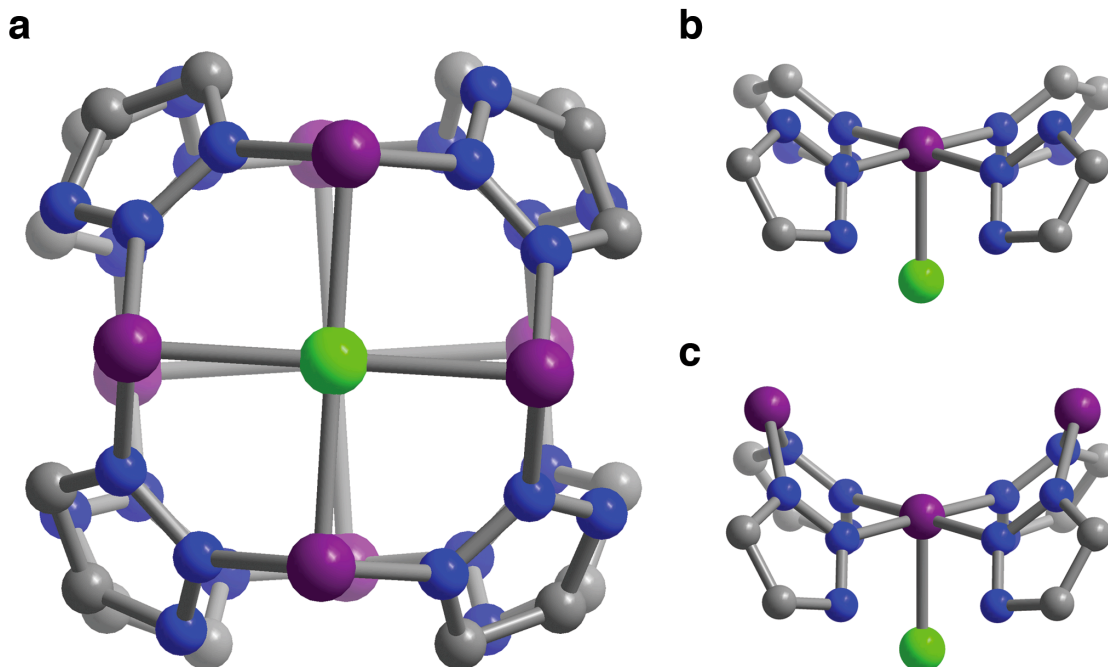


Figure S7. Distortion from $Pm\bar{3}m$ symmetry and structural changes observed after activating methanol-solvated Co-BTtri. a) Two opposing $[\text{Co}_4\text{Cl}]^{7+}$ squares overlaid on top of each other in the activated structure. The squares are not completely aligned, and are tilted with respect to each other. b) The orientations of the triazolate rings are largely ordered, such that the non-bonding nitrogen atoms of neighboring triazolates are pointed away from each other. c) A small amount of disorder is present in the material, as 7% of the non-bonding triazolate nitrogen atoms are pointed at each other with an extra-framework cation bridging between them. Purple, grey, blue, and green sphere represent Co, C, N, and Cl atoms, respectively; H atoms are omitted for clarity.

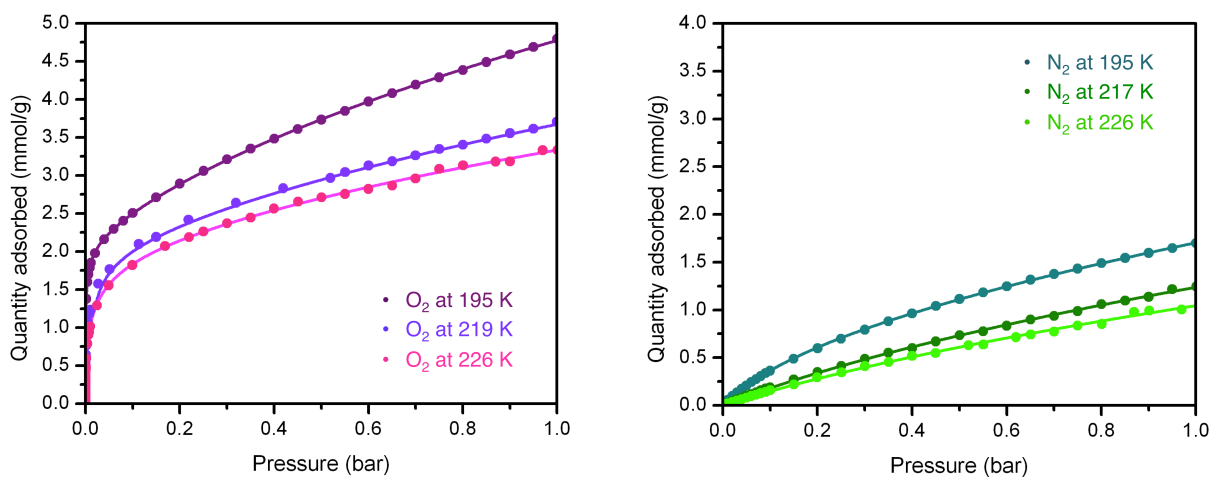


Figure S8. Variable temperature O_2 (left) and N_2 (right) isotherms for Co-BDtriP. The three temperatures were fit simultaneously to a dual-site Langmuir equation.

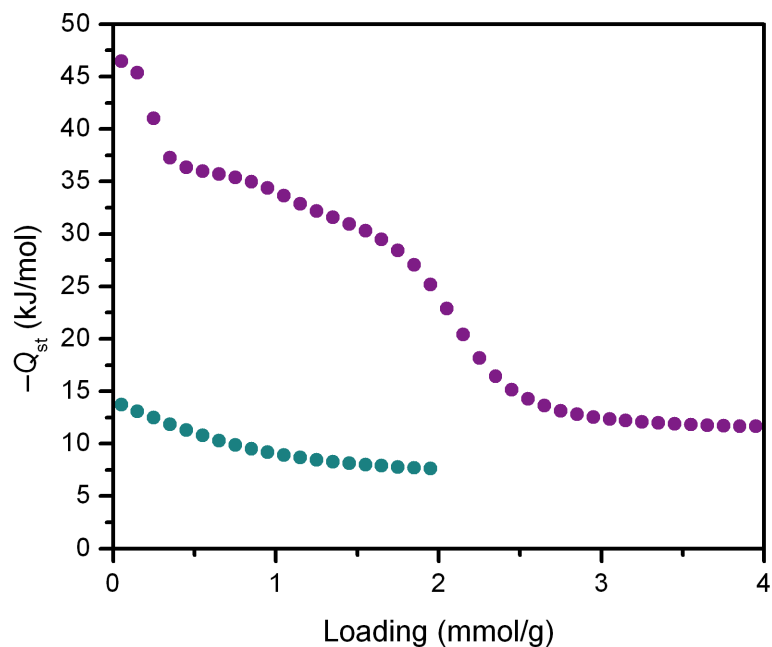


Figure S9. Isosteric heats for O_2 (purple circles) and N_2 (cyan circles) in Co-BDTriP.

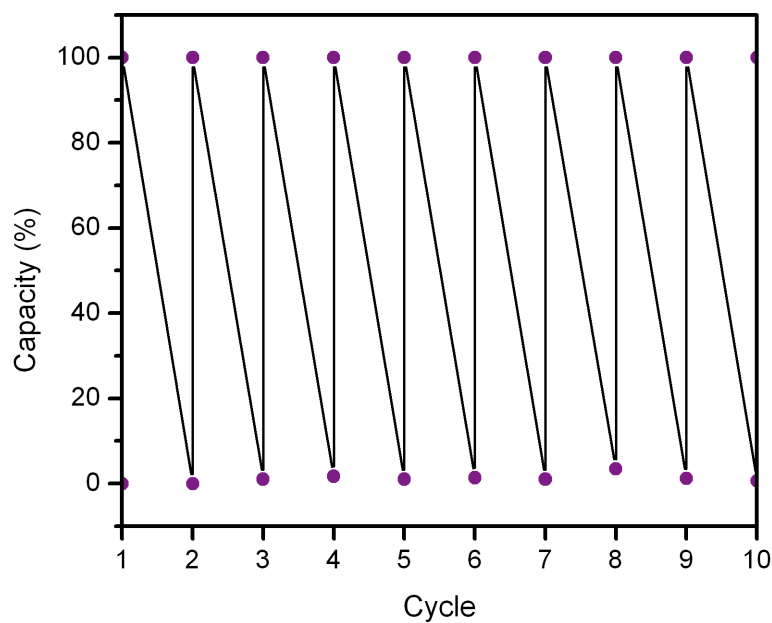


Figure S10. Cycling experiments for Co-BDTriP, with O_2 adsorption occurring at 195 K and 0.21 bar. Desorption was performed by quickly heating the sample to 323 K for five minutes.

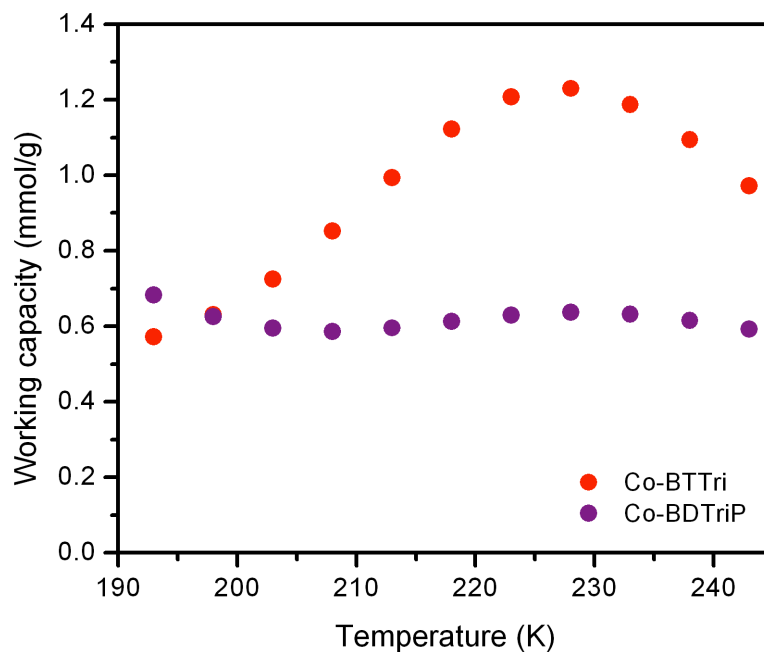


Figure S11. Vacuum swing adsorption (VSA) working capacity (cycling between ambient pressure and 0.05 bar) as a function of temperature for Co-BTtri (red circles) and Co-BDTriP (purple circles).

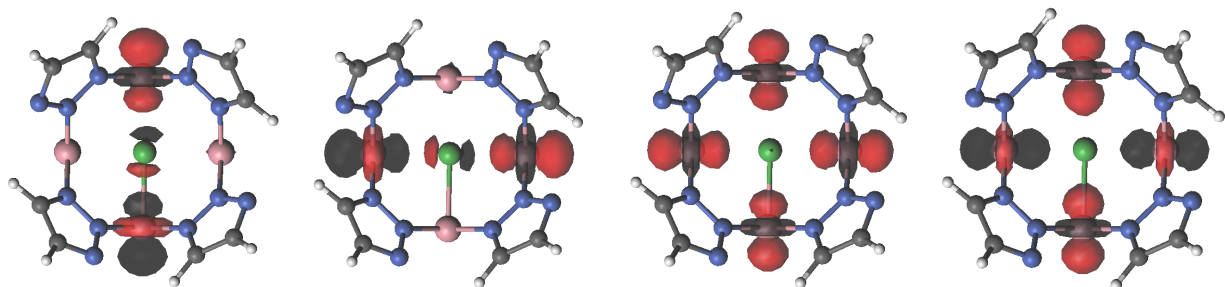


Figure S12. The four magnetic orbitals included in the CASSCF(4,4)/CASPT2(4,4) calculations.

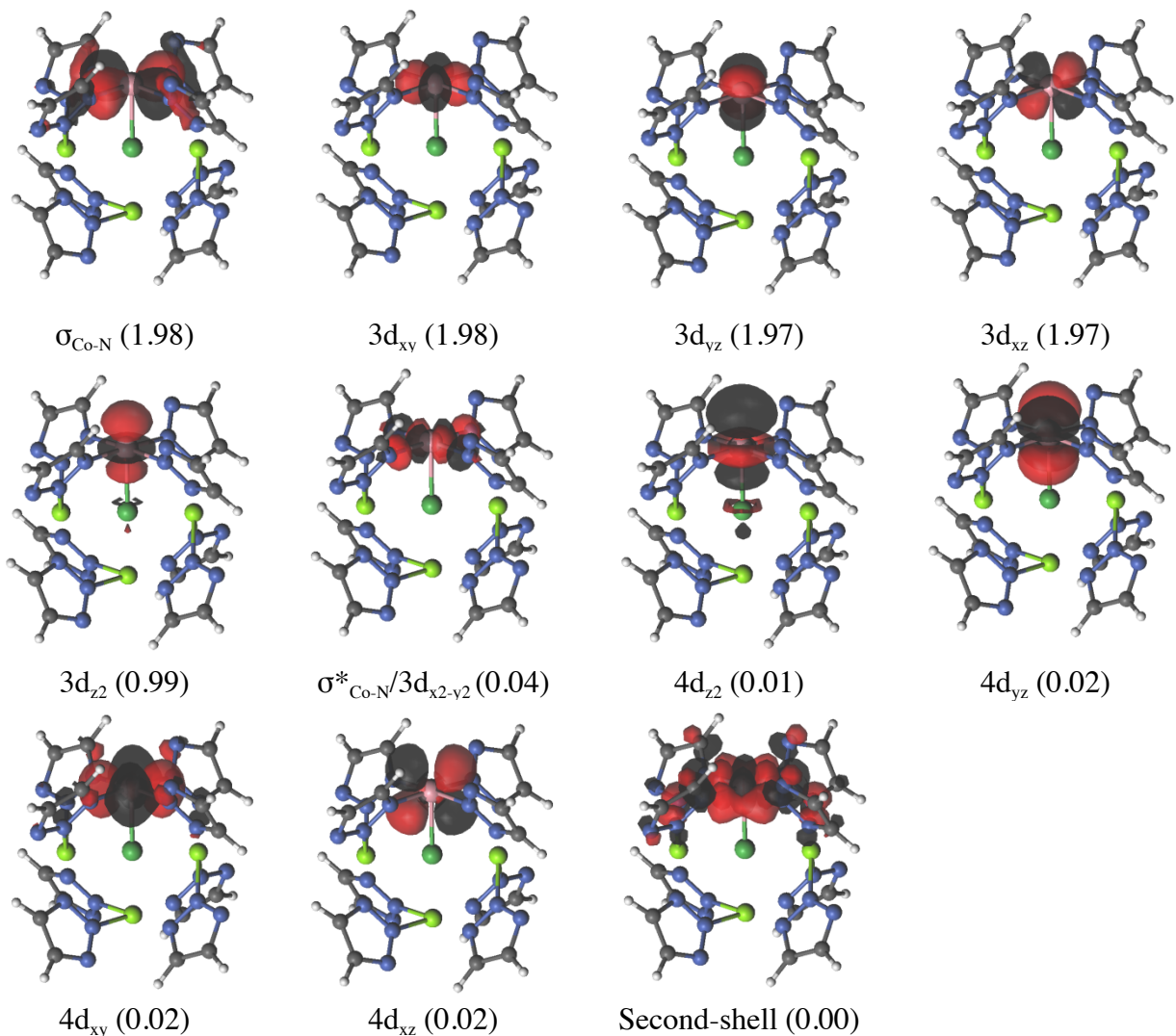


Figure S13. Natural orbitals included in the CASSCF(9,11)/CASPT2(9,11) calculations of the Co model complex of the Co-BTTri node. A short description of each orbital and their fractional occupation numbers are given under the corresponding natural orbital.

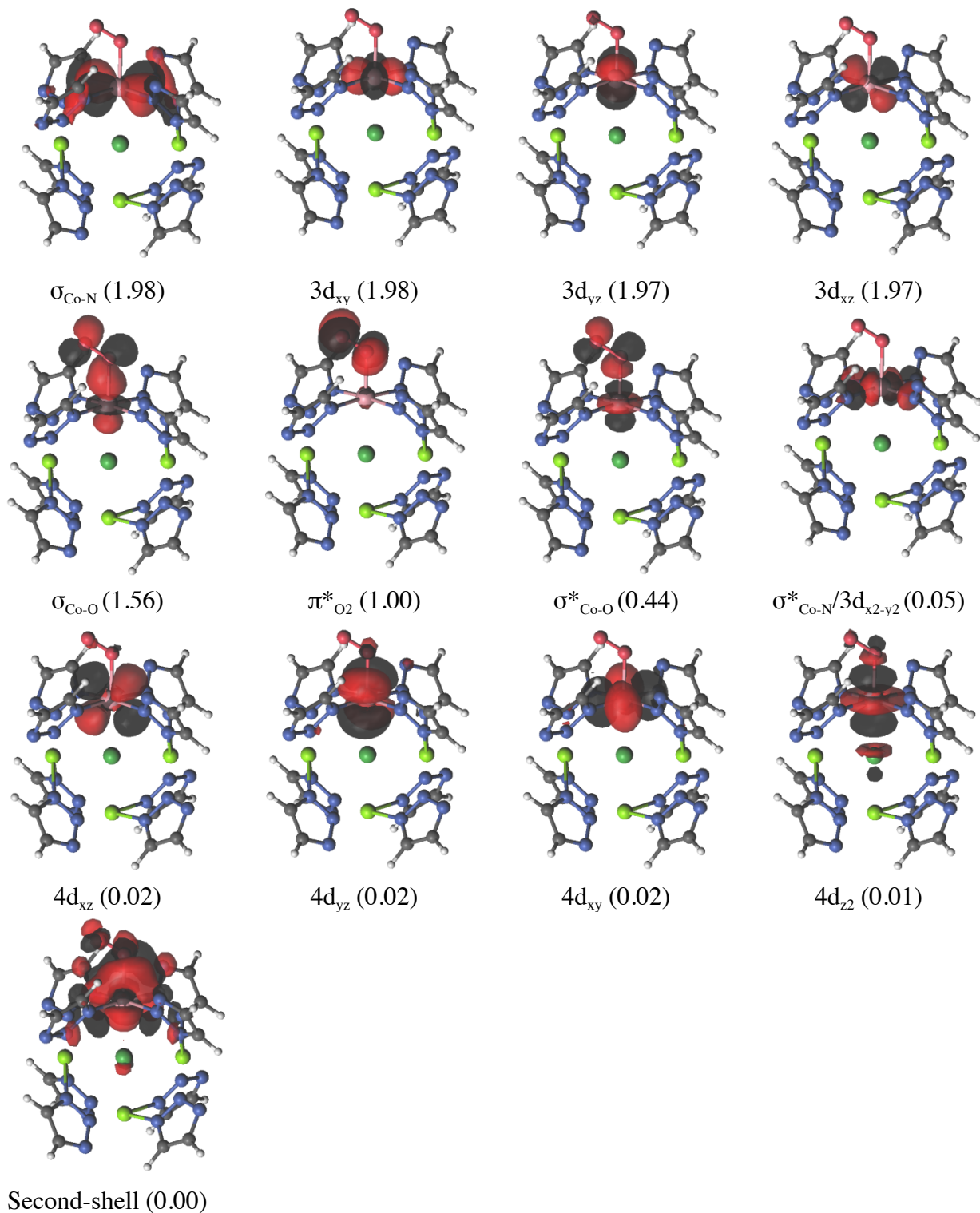


Figure S14. Natural orbitals included in the CASSCF(11,13)/CASPT2(11,13) calculations of the Co-O₂ model complex of the Co-BTTri node. A short description of each orbital and their fractional occupation numbers are given under the corresponding natural orbital.

8. Cluster model structures.

CoMg₃ model of the Co-BTtri node:

C	-2.83322200	-2.64694900	2.94373400
C	-2.77424400	2.67411600	2.98184400
C	-3.29893800	-1.50335800	2.29807500
C	-1.62036100	3.14677400	2.35962300
C	1.32254900	-3.18031900	2.35668800
C	-3.22567200	-1.45907000	-2.41450700
C	2.44865700	-2.76204000	3.04789000
C	2.55403500	2.61626100	3.05526900
C	-2.74879300	-2.60062000	-3.05652900
C	-2.68096400	2.72566100	-3.01041500
C	3.06188200	1.51041400	2.38254000
C	-1.54574300	3.18787500	-2.34839300
C	1.41108400	-3.13347700	-2.37192800
C	3.09084800	1.50377100	-2.31117900
C	2.56575800	-2.66171700	-2.99416800
C	2.63851900	2.65916400	-2.94347700
H	-3.20522600	-3.15117200	3.82179800
H	-3.28779200	3.03236200	3.86030900
H	-4.09340300	-0.81624200	2.54082100
H	-0.93250900	3.93298900	2.62517000
H	0.59855100	-3.95224200	2.56392400
H	-4.00814100	-0.76411600	-2.67317200
H	2.93822900	-3.11340500	3.93910700
H	2.89877100	3.10680900	3.95167800
H	-3.09940400	-3.09394000	-3.94951700
H	-3.16906900	3.09814000	-3.89743700
H	3.86965800	0.83317200	2.60793700
H	-0.84980800	3.97762700	-2.58093900
H	0.72338000	-3.91989400	-2.63668000
H	3.87738300	0.80506000	-2.54223000
H	3.07663700	-3.01836700	-3.87447000
H	3.01360700	3.16589500	-3.81867000
N	-3.22595500	1.59622500	2.28683900
N	-1.73719800	-3.09860100	2.27636700
N	-2.47842600	-1.28885300	1.25771100
N	-2.38649100	1.42343100	1.28814500
N	-1.55317300	-2.26880600	1.26681200
N	-1.39933300	2.34478700	1.30623800
N	-2.43489200	-1.26201700	-1.34816400
N	-2.34259400	1.44830400	-1.32559000
N	-3.15285200	1.63738500	-2.34641600
N	1.46217800	3.05623100	2.37935000

N	-1.51734900	-2.24969800	-1.34200200
N	1.15195000	-2.35575900	1.29735500
N	-1.35651700	2.36908800	-1.30170900
N	1.31010100	2.24882800	1.34715200
N	-1.67772400	-3.06810200	-2.36151800
N	2.89440300	-1.69336400	2.33848900
N	1.18473000	-2.32598700	-1.32383300
N	1.35066700	2.28739700	-1.27102100
N	1.55118400	3.12141000	-2.26969800
N	3.01295300	-1.57811600	-2.30570500
Cl	-0.05832600	0.00354800	0.02952800
Co	2.27084900	-0.07770600	0.02511400
Mg	-2.41404600	0.08101400	-0.03200000
Mg	-0.18609500	-2.30623900	-0.02572300
Mg	-0.02198800	2.31551700	0.02098100
N	2.14025600	-1.49185800	1.33529400
N	2.26578200	1.31560900	1.34599900
N	2.17762500	-1.43418000	-1.32063700
N	2.27509600	1.31988500	-1.28476800

O₂-CoMg₃ model of the Co-BTTri node:

C	2.71891900	2.93150500	2.95932000
C	3.22543200	-2.36568600	3.00345200
C	3.30809700	1.84357700	2.31834000
C	2.13276700	-2.95857300	2.37370900
C	-1.46573300	3.01996700	2.34242500
C	3.27349300	1.78960900	-2.39458700
C	-2.54591100	2.48470500	3.02619200
C	-2.07921800	-2.87436800	3.03935000
C	2.68259300	2.87372900	-3.04132200
C	3.18080800	-2.42958100	-2.98924700
C	-2.69693100	-1.82905600	2.36170900
C	2.09644800	-3.00951300	-2.33466200
C	-1.51512300	2.96180300	-2.38662400
C	-2.69300200	-1.82763700	-2.33206600
C	-2.60868100	2.36975000	-3.01637600
C	-2.11596700	-2.92873500	-2.95976700
H	3.02966900	3.47335800	3.83871000
H	3.76856000	-2.66752200	3.88523700
H	4.16935900	1.24497300	2.56753300
H	1.53052700	-3.81331200	2.63536000
H	-0.83137200	3.86666500	2.55133200
H	4.12731700	1.18189200	-2.64700900
H	-3.07705200	2.78230000	3.91307000
H	-2.37672600	-3.39822600	3.93371700

H	2.98564100	3.40146400	-3.93196800
H	3.71259000	-2.74892200	-3.87179900
H	-3.57952400	-1.24894300	2.57491600
H	1.49000300	-3.86885000	-2.57096800
H	-0.91452900	3.81843400	-2.64520300
H	-3.55453600	-1.22437500	-2.56265200
H	-3.14822900	2.66864700	-3.90093500
H	-2.42918300	-3.47243500	-3.83699600
N	3.56498700	-1.24621700	2.31033100
N	1.58588100	3.26381700	2.28372200
N	2.52244400	1.54261500	1.27250000
N	2.71903300	-1.16405700	1.30556300
N	1.49825900	2.41870600	1.27390900
N	1.83526800	-2.18508800	1.31783100
N	2.50055600	1.51012300	-1.33359000
N	2.69663200	-1.19464400	-1.30839100
N	3.52964600	-1.29702000	-2.32326100
N	-0.94198500	-3.19608100	2.37168100
N	1.48323700	2.39470200	-1.33507300
N	-1.20085600	2.21772600	1.28530700
N	1.81383900	-2.21498900	-1.29032700
N	-0.86924700	-2.37756900	1.33956900
N	1.56299500	3.22506100	-2.35441900
N	-2.87049900	1.37427900	2.31504800
N	-1.21167600	2.18338900	-1.33598500
N	-0.88683400	-2.42141100	-1.27876000
N	-0.99049200	-3.27249400	-2.27781600
N	-2.94307500	1.24505200	-2.32977500
Cl	0.22269300	-0.00343900	0.01864700
Co	-2.09279400	-0.16718800	0.00931500
Mg	2.61317500	0.17308800	-0.01597600
Mg	0.14417000	2.31001100	-0.02825500
Mg	0.47178800	-2.30290800	0.02288700
N	-2.09325500	1.25523400	1.31927200
N	-1.91752100	-1.55312600	1.33166800
N	-2.10645400	1.19318100	-1.33992300
N	-1.90879300	-1.56007200	-1.30051800
O	-4.13045800	-0.41910600	0.02565900
O	-4.86016900	0.55889400	0.03762400

CoMg₃ model of the Co-BTT node:

C	2.71403600	2.42224200	3.05690700
C	2.79425800	2.47260600	-2.94182200
C	-1.41722900	3.22752900	2.36776400
C	-1.34548700	3.27391700	-2.34025200

C	2.25537700	-2.93752000	3.03833200
C	2.37185700	-2.83189400	-3.00359400
C	-2.59897400	2.83038400	2.99047400
C	-2.50939700	2.88876400	-3.00177900
C	-3.39792700	-1.30206200	2.29860300
C	-3.32731900	-1.25239600	-2.41397200
C	-3.00765200	-2.47519900	2.94125200
C	-2.92725600	-2.42142100	-3.05900500
H	3.13034600	2.84318800	3.95613400
H	3.23961000	2.90794400	-3.82004800
H	-0.68411200	3.97132700	2.63382900
H	-0.60472100	4.02185300	-2.57171400
H	2.65072100	-3.39120100	3.92754100
H	2.79135900	-3.28249800	-3.88547300
H	-3.08740500	3.22064800	3.86943300
H	-2.97337700	3.29516100	-3.88668700
H	-4.14929300	-0.56785000	2.54071300
H	-4.06706600	-0.51037200	-2.66737000
H	-3.41288600	-2.95936900	3.81580900
H	-3.31214800	-2.89189700	-3.95011900
N	1.65269500	2.93457200	2.38330600
N	1.74046100	3.00390900	-2.26567300
N	1.44673500	2.14102400	1.34967900
N	1.48676800	2.18254100	-1.26856300
N	2.76976100	-1.89862300	2.33066700
N	2.89015200	-1.78144000	-2.31351600
N	-1.25060500	2.41506400	1.31241600
N	-1.20928700	2.44218800	-1.29554200
N	0.98586400	-2.44304300	1.29025500
N	1.01774700	-2.40969800	-1.33081100
N	-2.29622000	1.56062100	1.29364700
N	-2.25379000	1.58825400	-1.32008200
N	-3.12137000	1.78604600	2.29378000
N	-3.05103900	1.83241700	-2.33945900
N	-1.70743600	-2.17838700	1.26348700
N	-1.67344700	-2.15598300	-1.34532800
N	-2.56629600	-1.13968000	1.25763600
N	-2.52408100	-1.11009100	-1.34822200
N	-1.94445500	-2.99646200	2.27152400
N	-1.88844000	-2.95981700	-2.36635700
Cl	-0.02877600	-0.00242700	0.01287900
Co	2.31013800	-0.22093900	0.02516700
Mg	0.12026300	2.29805300	0.02529200
Mg	-0.34729000	-2.30272500	-0.03086400
Mg	-2.41350200	0.22577600	-0.02925900
N	3.16167700	1.33164300	2.43366400

N	3.20511500	1.36042700	-2.33658900
N	2.37890500	1.18271200	1.39915200
N	2.40002900	1.20609900	-1.32000500
N	2.03157000	-1.63900100	1.33270400
N	2.07516200	-1.57442200	-1.32965900
N	1.11620900	-3.27905900	2.35615700
N	1.22120100	-3.21227700	-2.39397800

O₂-CoMg₃ model of the Co-BTT node:

C	-2.09345800	2.83692000	-3.04292800
C	-2.11978700	2.90899600	2.95611900
C	2.11900800	2.95333700	-2.38517700
C	2.09079100	3.01812300	2.32308600
C	-2.52162300	-2.52528800	-3.01287500
C	-2.57436500	-2.39266000	3.02941700
C	3.21476800	2.36641800	-3.01513300
C	3.18046000	2.44794600	2.97742300
C	3.32886900	-1.84007500	-2.31761500
C	3.30234800	-1.77223200	2.39518500
C	2.74635900	-2.93410600	-2.95428000
C	2.72041000	-2.85861500	3.04622700
H	-2.44172600	3.31887900	-3.94040600
H	-2.48110600	3.41272700	3.83633900
H	1.51577800	3.80687100	-2.64799900
H	1.48407400	3.87759200	2.55761400
H	-2.99248700	-2.90917600	-3.89814600
H	-3.05546800	-2.76672300	3.91559700
H	3.75437000	2.66999600	-3.89836700
H	3.71168600	2.77412600	3.85769400
H	4.18862500	-1.23930100	-2.56692000
H	4.15550500	-1.16095700	2.64126000
H	3.06026800	-3.47979400	-3.83015900
H	3.02955300	-3.38473500	3.93570900
N	-0.95735000	3.16881300	-2.37824900
N	-0.99804000	3.25879000	2.27106600
N	-0.87684800	2.35399900	-1.34386200
N	-0.89011800	2.40557300	1.27435600
N	-2.85323500	-1.41482900	-2.30459900
N	-2.91815200	-1.27244400	2.34014700
N	1.82897100	2.18092100	-1.32645100
N	1.81201900	2.21848600	1.28163600
N	-1.17510800	-2.24372600	-1.27512700
N	-1.18177200	-2.20143300	1.34588400
N	2.72006200	1.16628600	-1.31274400
N	2.70214000	1.20453700	1.30114300

N	3.56359700	1.25149700	-2.31929100
N	3.53621800	1.31592600	2.31418500
N	1.52508400	-2.42504400	-1.26818400
N	1.51458600	-2.39334300	1.34073300
N	2.54297300	-1.54162000	-1.27124900
N	2.52552800	-1.50148300	1.33475600
N	1.61695200	-3.27251300	-2.27563300
N	1.60213000	-3.22002700	2.36241100
Cl	0.22193800	-0.00000900	-0.01067500
Co	-2.12684400	0.16926300	-0.00695700
Mg	0.46703500	2.29293000	-0.02940600
Mg	0.17263900	-2.32229200	0.03606900
Mg	2.62620200	-0.16763200	0.01295800
N	-2.70998000	1.83662200	-2.41207100
N	-2.71273200	1.87949600	2.35539300
N	-1.95332700	1.56347300	-1.38408300
N	-1.95025700	1.59416700	1.33504300
N	-2.07568900	-1.27950500	-1.31306200
N	-2.08808400	-1.20455500	1.35061500
N	-1.44901900	-3.04861500	-2.33763600
N	-1.50646600	-2.95823000	2.41250000
O	-4.30147900	0.35240200	0.00023700
O	-4.97214800	-0.64323000	-0.06379300

CoMg₃ model of the Co-BTP node:

C	-2.77163400	-2.69426500	2.96523300
C	-2.77925800	2.62707600	3.00990500
C	-3.25826300	-1.55585200	2.32588400
C	-1.63783200	3.11497400	2.37659800
C	1.38428900	-3.17453300	2.33518900
C	-3.23359300	-1.50490600	-2.38713800
C	2.51204200	-2.74293400	3.01544000
C	2.54981100	2.63626800	3.02904700
C	-2.74895600	-2.63957300	-3.03551300
C	-2.74771700	2.68708000	-2.98293200
C	3.06473800	1.53778200	2.34976300
C	-1.61172400	3.16274600	-2.33187000
C	1.42408900	-3.12081000	-2.39398000
C	3.04593800	1.53718900	-2.34420200
C	2.56629500	-2.63378600	-3.02734200
C	2.57256700	2.68753300	-2.97024000
H	-3.12811700	-3.20409300	3.84665300
H	-3.28902600	2.97880500	3.89328800
H	-4.06119400	-0.88203500	2.57761500
H	-1.02855800	3.96517900	2.62043900

H	0.67249200	-3.95165300	2.56376100
H	0.83696200	3.91615100	2.54677500
H	-4.02938600	-0.82220100	-2.63740900
H	2.93974000	-3.18339200	3.90389800
H	2.97782400	3.07926000	3.91834100
H	-3.10213000	-3.13596800	-3.92594500
H	-3.24993900	3.05510300	-3.86400500
H	3.86533200	-1.06506700	2.49492900
H	3.92300800	0.92440000	2.56153900
H	-0.99162600	4.01020500	-2.55866300
H	0.72271400	-3.89115200	-2.67090200
H	0.90819600	4.01448400	-2.43780900
H	3.88168900	0.90716500	-2.58586100
H	3.91708300	-1.00122500	-2.40196600
H	3.03130600	-3.04705100	-3.91142800
H	3.01082000	3.14462500	-3.84769800
N	-3.22443100	1.54442200	2.31807200
N	-1.67686700	-3.13125600	2.28614100
N	-2.45117100	-1.32975100	1.27751500
N	-2.39308000	1.38343200	1.31066000
N	-1.51359900	-2.29799300	1.27588600
N	-1.41745600	2.31714900	1.31993900
N	-2.43453700	-1.29920500	-1.32862400
N	-2.37613900	1.41203500	-1.30335300
N	-3.19907600	1.59213300	-2.31562600
N	-1.50461600	-2.27527300	-1.33313400
N	1.19215700	-2.35114100	1.27860100
N	-1.40153900	2.34516000	-1.28826300
N	1.29320700	2.25533900	1.33316300
N	-1.66506200	-3.09437200	-2.35206200
N	1.19816600	-2.31756800	-1.34254500
N	1.30665800	2.29760000	-1.28522300
C	1.47022500	3.06921900	2.35302600
C	2.99420600	-1.67233000	2.31321500
C	1.51178900	3.13828900	-2.27640300
C	3.03096000	-1.59913600	-2.27837200
Cl	-0.07808100	0.00002800	0.03063200
Co	2.24940700	-0.04979400	0.01026000
Mg	-2.41720300	0.04236700	-0.01093000
Mg	-0.15943300	-2.31670700	-0.03049800
Mg	-0.05303300	2.30686000	0.02072000
N	2.18977600	-1.44915300	1.28874700
N	2.26291200	1.33279300	1.32227400
N	2.18731800	-1.41584300	-1.28029300
N	2.24371900	1.33606400	-1.31139700

O₂-CoMg₃ model of the Co-BTP node:

C	-2.69999000	-2.93614200	2.97485800
C	-3.18319500	2.36305600	3.03533600
C	-3.29091500	-1.84432300	2.34216600
C	-2.09439500	2.95261100	2.39584700
C	1.47775100	-3.04124000	2.31552400
C	-3.30364800	-1.78030000	-2.37074500
C	2.56709300	-2.51209000	2.98945400
C	2.12369700	2.84888500	3.01875100
C	-2.72398800	-2.86553900	-3.02571500
C	-3.19878600	2.43972800	-2.95736100
C	2.73008100	1.80245100	2.33277200
C	-2.10538400	3.01358500	-2.31253800
C	1.47970400	-2.97304800	-2.41363500
C	2.67878200	1.81121100	-2.36093300
C	2.56937600	-2.38430700	-3.05317300
C	2.10010100	2.91607500	-2.98036600
H	-3.00471100	-3.47903900	3.85574000
H	-3.71783600	2.66688500	3.92157400
H	-4.14913200	-1.24577700	2.60155300
H	-1.56079500	3.85238200	2.63877900
H	0.84319700	-3.88337800	2.54076400
H	0.30325400	3.97702100	2.54449700
H	-4.15919300	-1.17128300	-2.61384200
H	3.04129100	-2.91543600	3.87160500
H	2.51988600	3.32714500	3.90408700
H	-3.03879500	-3.39047000	-3.91397000
H	-3.73944200	2.76443400	-3.83249900
H	3.78018200	-0.73871900	2.45459700
H	3.65105500	1.27995500	2.52003300
H	-1.56391800	3.91268600	-2.54150800
H	0.84946600	-3.80441600	-2.68448400
H	0.33076100	4.09239200	-2.42512500
H	3.57626300	1.27014500	-2.59356300
H	3.79152600	-0.65797000	-2.42219600
H	3.06477600	-2.75306200	-3.94014100
H	2.49285200	3.41289700	-3.85733600
N	-3.53455500	1.24656000	2.34330500
N	-1.57527300	-3.27185300	2.28714500
N	-2.51458300	-1.54446700	1.28908200
N	-2.69914800	1.16294800	1.32986900
N	-1.49420700	-2.42495600	1.27828900
N	-1.81091100	2.18016000	1.33537400
N	-2.51885300	-1.50643600	-1.31700900
N	-2.70299900	1.19909000	-1.28410700

N	-3.54576300	1.30723600	-2.29028900
N	-1.50542100	-2.39538200	-1.33065000
N	1.20541500	-2.23584700	1.26270300
N	-1.81568100	2.21561700	-1.27279300
N	0.89444900	2.36105400	1.33021600
N	-1.59903900	-3.22315900	-2.35090400
N	1.19023600	-2.19570300	-1.35830700
N	0.88587200	2.41050200	-1.28806200
C	1.00543800	3.18641900	2.34984100
C	2.95004200	-1.40193500	2.28928800
C	1.00851200	3.26972500	-2.27647700
C	2.95175800	-1.31764000	-2.30417700
Cl	-0.18801000	-0.00003900	0.02212500
Co	2.07983300	0.15104800	-0.00566600
Mg	-2.61242300	-0.17178900	0.00450600
Mg	-0.15291900	-2.31938400	-0.03721300
Mg	-0.46009900	2.29502400	0.02699500
N	2.12132600	-1.25170300	1.27119500
N	1.93900800	1.53082300	1.31267500
N	2.10182100	-1.21543000	-1.29994500
N	1.90157600	1.53890500	-1.32566600
O	3.96461300	0.43843200	-0.05918500
O	4.75041100	-0.53081100	0.11289500

9. References.

- (1) Winston, P. W.; Bates, D. H. *Ecology*. **1960**, *41*, 232-237.
- (2) Bruker Analytical X-ray Systems, Inc. Bruker Analytical X-ray Systems, Inc.: Madison, WI, USA 2000.
- (3) Sheldrick, G. M. Bruker Analytical X-ray Systems, Inc.: Madison, WI, USA 2014.
- (4) Sheldrick, G. M. *Acta Crystallogr A Found Adv* **2015**, *71* (Pt 1), 3.
- (5) Sheldrick, G. M. *Acta Crystallogr C Struct Chem* **2015**, *71* (Pt 1), 3.
- (6) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
- (7) Spek, A. L. *Acta Crystallogr C Struct Chem* **2015**, *71* (Pt 1), 9.
- (8) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.
- (9) Chilton, N. F.; Anderson, R. P.; Turner, L. D.; Soncini, A.; Murray, K. S. *J. Chem. Comput.* **2013**, *34*, 1164.
- (10) Demessence, A.; D'Alessandro, D. M.; Foo, M. L.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 8784.
- (11) Kalisiak, J.; Sharpless, B.; Fokin, V. V. *Org. Lett.* **2008**, *10*, 3171.