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Authors
Oktawiec, Julia
Jiang, Henry ZH
Vitillo, Jenny G
et al.

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Negative cooperativity upon hydrogen bond-stabilized $\text{O}_2$ adsorption in a redox-active metal–organic framework

Julia Oktawiec$^1$, Henry Z. H. Jiang$^1$, Jenny G. Vitillo$^2$, Douglas A. Reed$^1$, Lucy E. Darago$^1$, Benjamin A. Trump$^3$, Varinia Bernales$^2$, Harriet Li$^4$, Kristen A. Colwell$^5$, Hiroyasu Furukawa$^1,6$, Craig M. Brown$^{3,7}$, Laura Gagliardi$^2$ & Jeffrey R. Long$^{1,5,6,*}$

The design of stable adsorbents capable of selectively capturing dioxygen with a high reversible capacity is a crucial goal in functional materials development. Drawing inspiration from biological $\text{O}_2$ carriers, we demonstrate that coupling metal-based electron transfer with secondary coordination sphere effects in the metal–organic framework $\text{Co}_2(\text{OH})_2(\text{bbta})$ ($\text{H}_2\text{bbta} = \text{1H,5H-benzo(1,2-d:4,5-d')bistriazole}$) leads to strong and reversible adsorption of $\text{O}_2$. In particular, moderate-strength hydrogen bonding stabilizes a cobalt(III)-superoxo species formed upon $\text{O}_2$ adsorption. Notably, $\text{O}_2$-binding in this material weakens as a function of loading, as a result of negative cooperativity arising from electronic effects within the extended framework lattice. This unprecedented behavior extends the tunable properties that can be used to design metal–organic frameworks for adsorption-based applications.
Allosteric binding of substrates to biomolecules is effortlessly accomplished in nature, but engineering synthetic materials to display similarly responsive behavior remains an ongoing challenge. In addition to non-cooperative substrate binding (e.g., O2 in myoglobin), biomolecules can exhibit cooperativity arising from structural changes that strengthen or weaken interactions with substrates. Positive cooperativity can be an enhanced response to ligands under certain conditions (e.g., O2 binding in hemoglobin), while negative cooperativity generates a weakened response to successive binding events and enables biomolecules to maintain molecule sensitivity over greater concentration ranges than observed for non-cooperative or positively cooperative proteins (e.g., insulin binding to the insulin receptor)1–4. The ability to reproduce similar performance in synthetic materials could be advantageous for a multitude of potential applications, including catalysis5,6, sensing7, and gas separations8,9.

Metal–organic frameworks provide an intriguing platform for the design and study of cooperative adsorption, owing to their crystallinity, chemical versatility, and extended network structure that can readily propagate minor structural changes10,11. Indeed, some of us have recently shown that cooperative CO2 uptake in alkylidiamine-appended $\text{M}_2(\text{dobpdc})$ ($\text{M} = \text{Mg, Mn, Fe, Co, Ni, Zn}$; $\text{H}_4(\text{dobpdc}) = 4.4'$-diodobiphenyl-3,3'-dicarboxylic acid) occurs as a result of the extended formation of ammonium carbamate chains down the framework pores8, while the propagation of an iron(II) spin transition upon CO binding gives rise to its cooperative adsorption in the frameworks $\text{Fe}_2\text{Cl}_2(\text{bbta})$ ($\text{H}_3\text{bbta} = 1\text{H}5\text{SH}-\text{benzo}(1,2-\text{d}:4,5-\text{d}')\text{bistriazole}$) and $\text{Fe}_2\text{Cl}_2(\text{btdl})$ ($\text{H}_3\text{btdl} = \text{bis}(1\text{H}-1,2,3\text{-triazolo}[4,5-b][4,5'-i]\text{dibenzo}[1,4]\text{dinoxin})$). The adsorption behavior of these materials stands in stark contrast to the non-cooperative, Langmuir-type uptake that is typical of frameworks featuring isolated binding sites (Fig. 1). As a result, these cooperative adsorbents exhibit exceptionally high selectivities and capacities and can be regenerated with far lower energy costs than traditional adsorbents, rendering them of interest for industrial separation applications.

The development of a metal–organic framework capable of cooperative O2 adsorption could be advantageous for a number of applications in industry, including energy-efficient O2 production12,13, O2 storage14–16, and catalysis17–19. Iron-20,21, chromium-20,21, manganese-22,23, copper-23, and cobalt-based24,25 frameworks have previously been shown to bind O2 via reversible reduction upon metal coordination, but the poor chemical stability of many of these materials to O2 limits their cyclable capacity under ambient conditions. In the search for improved, cooperative adsorbents for O2 capture, the active sites of proteins such as hemoglobin, hemerythrin, and hemocyanin can serve as sources of inspiration. These sites feature reducing transition metal centers that bind O2 via electron transfer to reversibly generate metal-superoxo or metal-peroxo species26,27, and crucially these species are often stabilized through directed hydrogen-bonding interactions28. For example, histidine residues in hemoglobin hydrogen bond to the iron-superoxo formed upon O2 uptake28,29, while in hemerythrin a bridging hydroxy group transfers a proton to iron-bound dioxygen to form a hydroperoxo species (Fig. 2a)30. These hydrogen bonding interactions are thought to play a key role in reversible O2 binding in these proteins, and may also be advantageous for the development of metal–organic frameworks for selective and reversible O2 capture.

Here, we report the detailed characterization of O2 adsorption in the frameworks $\text{Co}_2\text{X}_2(\text{bbta})$ ($X = \text{Cl}^-, \text{OH}^-$)31–34 and show that $\text{Co}_2(\text{OH})_2(\text{bbta})$ (Fig. 2c) is able to capture O2 with high affinity by leveraging both electron transfer and hydrogen bonding interactions (Fig. 2c). Remarkably, as a result of the close metal contacts within $\text{Co}_2(\text{OH})_2(\text{bbta})$, O2 interacts more weakly with the cobalt(II) centers upon increased loading, providing the first clear example of an adsorbent material that exhibits negative cooperativity upon gas binding.

### Results

#### Design, synthesis, and gas adsorption properties.

In our search for a cooperative, O2-selective metal–organic framework, we initially investigated the known framework $\text{Co}_2\text{Cl}_2(\text{bbta})$, which features a high density of coordinatively-unsaturated cobalt(II) ions31,32, as well as basic nitrogen-donor ligands that should enhance the reducing potential of the metal centers24. However, we found that $\text{Co}_2\text{Cl}_2(\text{bbta})$ exhibits only a weak interaction with oxygen (Fig. 3a), indicating that the ligand environment is not basic enough to facilitate metal-centered O2 reduction, and we thus turned our attention to the recently reported derivative $\text{Co}_2(\text{OH})_2(\text{bbta})$ (Fig. 2c)33. Synthesis of this material following a significantly modified procedure (see the Supporting Methods) led to a crystalline compound with a Brunauer–Emmett–Teller surface area of 1470 m² g⁻¹ (Supplementary Figs. 2–4).

At 195 K, the O2 adsorption isotherm for $\text{Co}_2(\text{OH})_2(\text{bbta})$ exhibits a sharp rise at low pressures (Fig. 3a), and the material achieves a capacity of ~3 mmol g⁻¹ (0.47 mmol O2 per mmol Co) at just 25 mbar. At 1 bar, the capacity is 7.57 mmol g⁻¹ (19.5 wt % or 1.17 mmol O2 per mmol Co), significantly higher than that of $\text{Co}_2\text{Cl}_2(\text{bbta})$ under the same conditions (3.24 mmol g⁻¹, or 0.63 mmol O2 per mmol Co) and higher than any other cobalt (II)-based framework studied for O2 adsorption24,25. To quantify the strength of the metal–O2 interactions in $\text{Co}_2(\text{OH})_2(\text{bbta})$, we determined the differential enthalpy of O2 adsorption ($\Delta h_{\text{ads}}$) from the Clausius–Clapeyron equation, using parameters extracted from the dual-site Langmuir fit of adsorption isotherms collected at 195, 213, and 223 K (Fig. 3b and Methods). At low loadings, O2 occupies a primary binding site with $\Delta h_{\text{ads}} = -49 ± 2$ kJ mol⁻¹, which is more than three times the differential enthalpy of O2 adsorption in $\text{Co}_2\text{Cl}_2(\text{bbta})$, and with a saturation capacity of $2.46 ± 0.02$ mmol g⁻¹ (approximately 0.38 mmol O2...
Consistent with these results, density functional theory (DFT) calculations performed on various model systems indicate that Co$_2$(OH)$_2$(bbta) has a much higher affinity for O$_2$ than Co$_2$Cl$_2$(bbta) (Supplementary Tables 43 and 47). In tandem with the comparatively high adsorption site density in Co$_2$(OH)$_2$(bbta) per formula weight$^{24,25}$, this large enthalpy of adsorption explains the high uptake capacity of the material. The primary binding site also exhibits a large differential entropy of adsorption ($\Delta s_{\text{ads}}$) of 186 ± 7 J mol$^{-1}$ K$^{-1}$, leading to a significant adsorption temperature dependence that accounts for the low uptake at 298 K (Fig. 3b; Supplementary Figs. 6 and 15). With increasing loading, O$_2$ occupies a secondary binding site with $\Delta h_{\text{ads}} = -18 \pm 2$ kJ mol$^{-1}$. Despite the high differential enthalpy observed at low loadings, O$_2$ adsorption was found to be fully reversible under all temperatures and pressures studied.

Ideal adsorbed solution theory$^{35}$ was used to calculate the O$_2$/N$_2$ selectivities for a mixture containing 21% O$_2$ and 79% N$_2$, representative of air (Supplementary Table 5). At 195 K, the calculated selectivity is 42, similar to that reported for the
framework Co-BTTri (Co3[(Co4Cl)3(BTTri)8]2; H3BTTri = 1,3,5-tri(1H-1,2,3-triazol-5-yl)benzene) under the same conditions (41)24, and this value decreases with increasing temperature to 14 at 223 K. These selectivities correspond, respectively, to 91% and 79% pure adsorbed O2 on Co2(OH)2(bbta) under equilibrium conditions. Notably, Co2(OH)2(bbta) also exhibits an O2 working capacity of 1.5 mmol g−1 (4.6 wt %) upon lowering the pressure from 0.21 to 0.05 bar at 195 K, which is higher than the values reported for Co-BTTri and Fe2(dobdc)24. Together, these results suggest that Co2(OH)2(bbta) could potentially be useful for air separation in a vacuum-swing adsorption process.

Fig. 4 Structures of activated and O2-dosed Co2(OH)2(bbta). a-c Structures of activated Co2(OH)2(bbta) as determined by Rietveld refinement against neutron powder diffraction data obtained at 8 K, showing a the hexagonal framework channels with the view down the c axis, b a truncated view of the coordinatively-un saturated metal centers lining the pores, and c a single coordinatively-un saturated cobalt(II) center. d Structure of Co2(OH)2(bbta) dosed with 1 bar of O2, as determined from Rietveld refinement against powder X-ray diffraction data obtained at 195 K. Hydrogen atom positions could not be determined from the measurement. The 0.46 equivalents of O2 found within the pores are not shown for clarity. e Structure of Co2(OH)2(bbta) (O2)1.74·(O2)0.17 determined from neutron powder diffraction data of Co2(OH)2(bbta) dosed with 1 equivalent of O2 per cobalt at 8 K. The 0.17 equivalents of O2 found within the pores are not shown for clarity. In b, c, and e, only one orientation is shown for the half-occupancy hydrogen atom of the hydroxo group. Slight deviations in the bond distances derived from the neutron and X-ray diffraction data are likely a result of differences in experimental conditions, as well as the improved scattering of the O atoms in neutron diffraction. Purple, red, blue, gray, and white spheres represent Co, O, N, C, and H atoms, respectively.

Structural, spectroscopic, and magnetic characterization. The solid-state structure of Co2(OH)2(bbta) was determined from Rietveld refinement against neutron powder diffraction data collected on the desolvated material (obtained under vacuum at 6 K; see Fig. 4a). The framework features hexagonal channels lined with rows of coordinatively-un saturated cobalt(II) centers that are bridged by a combination of hydroxo and triazolate groups (Fig. 4b,c). The Co–N bond lengths (2.066(17) and 2.102 (4) Å) are within the range expected for nitrogen-donor ligands bound to high-spin cobalt(II)35. Analysis of in situ X-ray powder diffraction data for a sample of Co2(OH)2(bbta) dosed with increasing pressures of O2 at 195 K revealed a gradual shift in the allowed reflections to higher angles, indicative of a unit cell contraction with increased O2 loading (Supplementary Fig. 23). For example, dosing with 1 bar of O2 resulted in an 8.6% decrease in the unit cell volume (Supplementary Tables 9 and 10) relative to the activated framework, concomitant with a decrease in the cobalt–ligand bond distances, from 2.072(6) to 1.956(5) Å (dCo–OH) and from 2.115(8)/2.007(13) Å to 1.932(10)/1.954(14) Å (dCo–N). Rietveld refinements against this variable-pressure data yielded structural models consistent with the presence of end-on cobalt(III)-superoxide species under all conditions (Fig. 4d; ∠Co–O–O = 119.9(4)°, 75(1)% occupancy)26. This metrical data is supported by values determined from periodic DFT calculations (dCo–O = 1.30 Å and dCo–O = 1.87 Å for Co2(OH)2(bbta)-2O2; see Supplementary Information Section 16). While there is evidence for physisorption of O2 along the pore walls at high pressures, the superoxide site occupancy also grows with increasing pressure at 195 K, a change associated with an increasing unit cell volume contraction (Supplementary Fig. 25).

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to further investigate the nature of the Co–O2 interaction upon O2 adsorption in Co2(OH)2(bbta). Dosing the framework with 1 mbar of 16O2 at 195 K afforded a new peak in the spectrum at 1151 cm−1 (Fig. 5a), which can be assigned to the ν(O–O) band of a superoxide (O2−) species bound end-on to cobalt(III) (1200–1100 cm−1)26. This peak shifts by 57 cm−1 to 1094 cm−1 when the material is dosed with...
1 mbar of $^{18}$O$_2$ (Fig. 5b), close to the isomer shift of 69.1 cm$^{-1}$ predicted from the single harmonic oscillator model for O$_2$ (Supplementary Figs. 49 and 50). Additionally, the superoxo overtone shifts from 2288 to 2182 cm$^{-1}$ (Supplementary Fig. 46). Consistent with our experimental results, Kohn-Sham DFT calculations predicted the formation of superoxo species exhibiting an O–O stretching frequency shift of $\sim$400 cm$^{-1}$ with respect to the gas phase value (Supplementary Information Section 17). As observed in the isotherm data (Supplementary Fig. 5), O$_2$ adsorption was found to be fully reversible upon evacuation of the sample at 195 K or heating at ambient pressure above 250 K.

Variable-temperature d.c. magnetic susceptibility data were collected on samples of Co$_2$(OH)$_2$(bbta) before and after exposure to O$_2$ ($H_{dc} = 0.1$ T). At 300 K, the molar magnetic susceptibility times temperature ($\chi M T$) for the desolvated material is 4.84 emu K mol$^{-1}$. This value is larger than that predicted for two high-spin S = 3/2 cobalt(II) centers (3.75 emu K mol$^{-1}$), likely due to contributions from orbital angular momentum (Supplementary Fig. 63). With decreasing temperature, $\chi M T$ decreases gradually, reaching 0.274 emu K mol$^{-1}$ at 2 K. Interestingly, the material also exhibits a negative Curie-Weiss constant ($\theta = -81.0$ K; Supplementary Fig. 65) and multireference methods and Kohn-Sham DFT calculations on di- and tetracobalt cluster models of Co$_2$(OH)$_2$(bbta), predict that an antiferromagnetic ground state for the high-spin cobalt ions is slightly more stable (4 kJ mol$^{-1}$, Supplementary Table 41) than a ferromagnetic ground state (Supplementary Information Section 15). The $\chi M T$ curves for Co$_2$(OH)$_2$(bbta)-O$_2$ and Co$_2$(OH)$_2$(bbta)-2O$_2$ exhibit a clear sigmoidal shape (Supplementary Fig. 64), which is reminiscent of that observed for spin crossover materials 38 and indicates temperature-dependent framework oxidation. At 100 K, the $\chi M T$ value for Co$_2$(OH)$_2$(bbta)-2O$_2$ (1 O$_2$ per Co) is 2.28 emu K mol$^{-1}$, very close to the spin-only value of 2.25 emu K mol$^{-1}$ expected for one cobalt(III) ion (S = 0), one cobalt(II) ion (S = 3/2), and one superoxide (S = 1/2), in the absence of magnetic exchange. DFT calculations at the PBE0-D3 level suggest that the spin density of cobalt changes from 2.67 to 0.07 upon O$_2$ adsorption, while the spin density of O$_2$ changes from 1.8 to 0.79 (Supplementary Table 43). Together with the diffraction and DRIFTS data, these results indicate that adsorbed O$_2$ is reduced by cobalt(II), yielding a superoxo-bound cobalt(III) species.
Hydrogen bond stabilization of the superoxo species. In the X-ray powder diffraction derived structure of Co₂(OH)₃(bbta) dosed with 1 bar of O₂ at 195 K, the terminal superoxo oxygen and the hydroxo oxygen are separated by only 2.886(8) Å, within the range for a moderate-strength O(H)···O hydrogen bonding interaction (Fig. 4c)³⁹. Refinement against neutron powder diffraction data collected on a sample dosed with 1 equiv. of O₂ per Co and cooled to 8 K notably revealed a hydrogen atom interacting with the terminal superoxo oxygen {∠O–H···O = 108°, Fig. 4d}³⁹,⁴⁰. Exclusion of this hydrogen atom from the refinement resulted in significantly worse goodness-of-fit parameters and a clear negative peak in the Fourier difference map (Supplementary Figs. 38 and 39). Notably, such a secondary coordination sphere effect upon O₂-binding has not previously been observed in a metal–organic framework⁴¹–⁴⁴.

The presence of hydrogen bonding is supported by a comparison of the infrared spectra for desolvated and O₂-dosed Co₂(OH)₃(bbta) (Fig. 5c,d). A single ν(OH) band is present at 3648 cm⁻¹ for the desolvated material (I, Fig. 4c, gray curve), while dosing with 1 bar of O₂ leads to additional sharp bands at 3614 and 3586 cm⁻¹ (II and III) and a broad band at ~3420 cm⁻¹ (IV). These three peaks redshift with increasing O₂ pressure up to 1 bar, and band III dominates at high pressures. The sharp features are assigned to —OH moieties that are not participating in hydrogen bonding but are affected by the redox changes of adjacent cobalt centers upon O₂ binding (Supplementary Fig. 54). Peak IV redshifts by >200 cm⁻¹ relative to other ν(OH) resonances observed upon oxidation, and its energy is consistent with those reported for ν(OH) bands associated with O(H)···O interactions between 2.8 and 2.9 Å⁴⁰. Thus, we assign this feature to an —OH adduct hydrogen bonding with a metal-bound superoxo. At higher O₂ occupancies (Fig. 4c) or lower temperatures (Fig. 4d), the broad band dominates and the sharp features at ~3610 and ~3580 cm⁻¹ diminish. This trend is expected as O₂ loading increases and free —OH groups increasingly become engaged in hydrogen bonding. Interestingly, we do not observe full O₂ occupancy under any of the conditions measured here.

Computed infrared spectra of the hydrogen-bonded cobalt (III)-superoxo in Co₂(OH)₃(bbta) successfully simulate the multiplicity of hydroxo peaks observed at low pressures (Supplementary Table 47 and Supplementary Fig. 87). Calculations examining three possible —OH group geometries indicate that the formation of a hydrogen bond to the cobalt(III)-superoxo lowers the O₂ adsorption energy by more than 20 kJ mol⁻¹ (Supplementary Table 43). Significantly, this value is similar in magnitude to the calculated decrease in O₂ binding energy upon changing the framework from Co₂Cl₂(bbta) to Co₂(OH)₃(bbta) (~30 kJ mol⁻¹). Stabilization afforded by hydrogen bonding thus appears to be a critical factor leading to the high differential enthalpy of O₂ adsorption in Co₂(OH)₃(bbta). This interaction likely also facilitates stable, reversible O₂ binding, despite the strong cobalt(II)–O₂ interaction.

Negative cooperativity of O₂ binding. Adsorbate binding at coordinatively unsaturated metal sites is typically much stronger than physisorptive interactions⁴⁵,⁴⁶. However, in the case of Co₂(OH)₂(bbta), the O₂ occupancy determined from X-ray powder diffraction data at 195 K (75(1)%) is much greater than the saturation capacity of the strong site determined through the dual-site Langmuir model (2.46 ± 0.02 mmol g⁻¹, 38% occupancy). Additionally, our analysis of the variable-pressure DRIFTS spectra (Fig. 5a,b) revealed an increase in integrated area that is greater than predicted for the strong binding site, based on analysis of adsorption data (Fig. 57)⁴⁷. These results indicate that the Langmuir model does not accurately describe the O₂ binding to cobalt at all pressures. Significant IR peak asymmetry at higher loadings could be modeled as two Lorentzian peaks from 1149–1152 cm⁻¹ and 1164–1167 cm⁻¹, with the higher energy band dominating at higher loadings (Supplementary Figs. 58–62). The same asymmetry is also clearly visible in spectra collected using ¹⁸O₂, confirming that it originates from changes in the bound superoxo species (Fig. 5b). The shift of the band to higher energies further suggests a greater amount of electron transfer from the cobalt to adsorbed O₂ at lower pressures, resulting in a weaker O–O bond. Based on these data, we hypothesize that isolated cobalt(III)-superoxo species dominate at lower pressures, while at higher pressures an increase in the number of adjacent cobalt(III)-superoxo neighbors reduces the driving force for subsequent O₂ binding and reduction.

Discussion

The foregoing results show that the framework Co₂(OH)₂(bbta) adsorbs O₂ at low temperatures via reversible reduction to form cobalt(III)-superoxo species. At low pressures, Co₂(OH)₂(bbta) exhibits higher capacities and stronger binding of O₂ than any other reported cobalt(II) metal–organic framework and may therefore be a promising candidate for O₂-selective air separations. Crucially, the highly basic hydroxo ligands in this material increase the reducing potential of the cobalt(II) sites and also

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engages in secondary-sphere hydrogen bonding interactions with bound superoxo groups, affording stabilization analogous to that observed in biological O2 carriers and biomimetic O2-binding molecules. Unexpectedly, this allosteric behavior also leads to a negative cooperativity for O2 binding, which is unprecedented in an extended framework material, though one previous example involving a molecular complex within a zeolite was found to display a Hill coefficient of 0.51. This behavior can be contrasted to the positive cooperativity observed of CO binding in the isostructural framework Fe2Cl2(bbta)9, demonstrating how precise atomic control in the synthesis and modification of these materials can yield complex and emergent biomimetic properties.

**Methods**

**General considerations.** The ligand H2(bbta) was synthesized according to a previously published procedure. All other reagents were obtained from commercial vendors and used as received. Ultra-high purity grade (99.999% purity, Praxair) He, N2, and O2 were used for all adsorption, spectroscopy, magnetometry, neutron, and X-ray diffraction measurements. After desolvation, all metal–organic framework samples were stored and handled under an N2 atmosphere using standard glove box techniques. Elemental analyses (C, H, and N) were obtained from the Microanalytical Laboratory at the University of California, Berkeley; Co and Cl analyses were obtained from Galbraith Laboratories, Inc. Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

**Synthesis of Co2(OH)2(bbta).** Co2Cl2(bbta) was synthesized and desolvated according to a previously reported procedure. Desolvated Co2Cl2(bbta) (100.0 mg, 0.3226 mmol) was soaked in a solution of 1 M (M = mol L\(^{-1}\)) aqueous ammonia (100 mL) at room temperature for 24 h. The suspension was filtered, rinsed with methanol, and the resulting yellow-orange powder was heated at 160 °C under vacuum for 12 h. Anal. Calcd for Co2O2C6N6H4 (%): C, 23.25; H, 1.30; N, 27.11; Co, 27.03; Cl, 0. Found (%): C, 24.08; H, 1.00; N, 27.38; Co, 26.6(4); Cl, <0.01; Cl/Co = <0.0037. *For Co3(OH)2(bbta)-7(H2O)

**Gas adsorption.** Gas adsorption isotherms for pressures in the range 0–1.2 bar were measured by a volumetric method using a Micromeritics ASAP 2020 instrument. A typical sample of ca. 50 mg of material was transferred to a preweighed analysis tube, which was capped with a trap and evacuated by heating under dynamic vacuum until an outgas rate of less than 2.6 μbar min\(^{-1}\) was achieved. The evacuated analysis tube containing the degassed sample was then carefully transferred to an electronic balance and weighed again to determine the mass of sample. The tube was then transferred back to the analysis port of the gas adsorption instrument. The outgas rate was again confirmed to be less than 2.6 μbar min\(^{-1}\). For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas; N2 isotherms at 77 K were measured in liquid nitrogen baths, using UHP-grade gas sources and all room temperature measurements were measured with an insulated water bath. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the evacuation process or of the feed gases during the isotherm measurements. Langmuir surface areas were determined from N2 adsorption data at 77 K using Micromeritics software. Gas adsorption isotherms at 195 K were measured using baths with dry ice and isopropanol, and temperatures between −70 and −40 °C were measured using a Julabo immersion cooler with silicone-based Julabo thermal bath fluid. In all measurements, equilibrium was determined by a change of less than 0.010% over a minute in the pressure over the sample, which typically involved each measurement point taking half an hour or longer.

**Adsorption isotherm fitting.** Adsorption isotherms for the uptake of O2 in Co2(OH)2(bbta) at 195, 213, and 223 K were adequately fitted with a dual-site Langmuir equation (Eq. 1), where \( n_{\text{sat}} \) is the saturation capacity in mmol g\(^{-1}\), \( b_1 \) is the Langmuir parameter in bar\(^{-1}\), and \( P \) is the pressure in bar.

\[
\frac{n}{n_{\text{sat}}} = \frac{b_1 P}{1 + b_1 P} + \frac{n_{\text{sat}} b_1 P}{1 + b_1 P}
\]

\[
b_1 = \frac{k}{RT} \left( \frac{v}{R} \right)^2
\]
\[ n_{\text{sat,i}} \]

The structural model for evacuated \( \text{Fe}_2\text{Cl}_2(\text{bbta}) \) was first used as a starting point for evacuated \( \text{Co}_2\text{Cl}_2(\text{bbta}) \). The positions and thermal displacement parameters of the carbon and nitrogen atoms of the \( \text{bbta}^{2-} \) ligand were fixed with soft constraints. A refined thermal displacement parameter was assigned to all atoms of the \( \text{bbta}^{2-} \) ligand. Consistent with previous work as well as the needle-like crystal habit observed in the SEM images of \( \text{Co}_2\text{Cl}_2(\text{bbta}) \) (Supplementary Fig. 45), a single Miller plane (0 0 1) direction along with the corresponding cell parameters in the goodness-of-fit parameters (\( R_{wp} \) improved by \( \sim 1.3\% \)). The Fourier difference map showed little evidence for electron density over the framework metal centers, indicating that the material was fully desolvated prior to the gas dosing experiments.

The Rietveld refinement using \( \text{O}_2 \)-dosed \( \text{Co}_2\text{Cl}_2(\text{bbta}) \) data obtained at 110 K was approached by examining the influence of \( \text{O}_2 \)-dosing on the diffraction pattern of the parent framework. Only a slight unit cell contraction was observed at this temperature (<0.9%), with some slight intensity changes being the chief difference between the two patterns. The Fourier difference map showed evidence for \( \text{O}_2 \) adsorbed within the pores, and a species was modeled along the locations indicated by the map and then allowed to freely refine. Upon this refinement, the closest distance of \( \text{O}_2 \) from the cobalt ions is \( \sim 2.7 \AA \), with few changes observed in the coordination environment of the cobalt ions otherwise. This distance suggests a weak interaction, consistent with the small differential enthalpy of adsorption of \( \text{O}_2 \) measured for this framework. As with the desolvated sample, a single March-Dollase correction applied along the (0 0 1) direction provided an improvement in the goodness-of-fit parameters (\( R_{wp} \) improved by 1.06%).

The obtained structural model of desolvated \( \text{Co}_2\text{Cl}_2(\text{bbta}) \) was used as the starting point for the Rietveld refinement using the diffraction pattern of evacuated \( \text{Co}_2\text{OH}_2(\text{bbta}) \). The hydroxo oxygen atom and cobalt atom were fixed in the exact positions of the parent material, and the ligand atom positions were refined within soft restraints. A single refined thermal displacement parameter was assigned to all atoms of the \( \text{bbta}^{2-} \) ligand. In the course of the refinement, it should be noted that the combination of the special positions of the \( \text{Co} \) and \( \text{O} \) atom and the shorter \( \text{Co} \text{--O} \) bond length (~2.1 Å) in comparison to the ~2.4 Å Co--Cl bond distances observed in \( \text{Co}_2\text{Cl}_2(\text{bbta}) \) did cause the O--O--Co angle to approach 170°, rather than 180° as observed in \( \text{Co}_2\text{OH}_2(\text{bbta}) \). As a result, the coordination environment of the cobalt centers deviates slightly from an ideal square pyramidal geometry. However, this geometry is also observed in the Rietveld refinements performed using the neutron powder diffraction data, and is not chemically unreasonable, particularly if some strain is imposed by the crystallographic lattice. The O--O--Co angle also appears to play a role in the unit cell volume of \( \text{Co}_2\text{OH}_2(\text{bbta}) \) being slightly bigger than that of \( \text{Co}_2\text{Cl}_2(\text{bbta}) \), despite \( \text{Cl}^- \) having a larger ionic radius than \( \text{OH}^- \). As with \( \text{Co}_2\text{Cl}_2(\text{bbta}) \), single March-Dollase correction was applied along the (0 0 1) direction and provided a slight improvement in the goodness-of-fit parameters (\( R_{wp} \) improved by 0.3%), consistent with the needle-like crystal habit observed in the SEM images of \( \text{Co}_2\text{OH}_2(\text{bbta}) \). Additionally, there was little to no observable electron density over the metal center, indicating complete desolvation prior to the gas dosing experiments on the same sample.

The structural model for the evacuated sample was used as the starting point for the determination of the structural models for \( \text{Co}_2\text{OH}_2(\text{bbta}) \) dosed with increasing pressures of \( \text{O}_2 \) (0.0067–1.01 bar). Upon gas dosing, significant unit cell contractions were observed (4427(3) Å\(^2\) to 4047(4) Å\(^2\)), necessitating care in the refinement of the structural models from the evacuated material, as the starting point was quite far off. Soft constraints on the \( \text{bbta}^{2-} \) ligand and angles were employed, and the cobalt and hydroxo oxygen atoms were refined within constraints. After the framework structure was approximately determined, a Fourier difference map was used to examine adsorbed species within the pores. From this map, a bent shape of unmodelled electron density could be distinguished above the metal centers of the framework, reminiscent of a disordered bent end on superxo species. When oxygen atoms were assigned to be within this unmodelled density and then freely refined, one atom appeared to be directly above the cobalt ion on the two-fold axis that runs through the metal center. The second atom, which refined to a position ~1.3 Å away from the first, was refined to a general position with an occupancy of ~0.3. The first position close to the hydroxo oxygen atom (~2.7–2.9 Å). At low pressures of \( \text{O}_2 \), the species over the metal centers appeared to be the only significant adsorbed species. At higher dosed pressures of \( \text{O}_2 \), additional electron density could be resolved in the pores. Specifically, a position in between the superxo species and over the ligand appeared to be a preferred location for a physisorbed oxygen. However, this position appears to be highly disordered under the measured conditions, in contrast to structural models obtained from the powder neutron diffraction data described below. As with desolvated \( \text{Co}_2\text{OH}_2(\text{bbta}) \), a single March-Dollase correction applied along the (0 0 1) direction provided an improvement in the goodness-of-fit parameters (\( R_{wp} \) improved by 0.4%).

In all structural models, hydrogen atoms were added to the benzene ring of \( \text{bbta}^{2-} \) ligand to yield a C--H distance of 1.09 Å. During the final refinement, all parameters were freely refined. The result of all Rietveld refinements using data collected on \( \text{Co}_2\text{Cl}_2(\text{bbta}) \) are reported in Supplementary Figs. 21 and 22, and the parameters are listed in Supplementary Tables 6–9. The Rietveld refinements using powder X-ray diffraction data collected on the \( \text{Co}_2\text{OH}_2(\text{bbta}) \) framework are reported in Supplementary Tables 10–12, and the refinements are shown in Supplementary Figs. 26–35.
We also collected powder X-ray diffraction data for desolvated Co₂(OH)₂(bbta) prepared according to a previously published procedure, via washing of Co₂Cl₂(bbta) with KOH. The sample was washed as previously described, before being fully desolvated (activation conditions: 100 °C for 24 h) and packed into a 1.0 mm borosilicate capillary inside a nitrogen glovebox that was flame-sealed. The sample was then measured at Beamline 12.2.2 at the Advanced Light Source of Lawrence Berkeley National Laboratory under an average wavelength of 0.4948 Å at room temperature (see Supplementary Fig. 19). The diffraction data confirms that in our hands, the known preparation resulted in synthesis of a significant amount of Co(OH)₂ alongside Co₂(OH)₂(bbta), in contrast to the preparation using aqueous ammonia washes.

**Neutron powder diffraction collection and analysis.** Powder neutron diffraction data were collected on 0.485 g of desolvated Co₂(OH)₂(bbta), loaded into a vanadium sample can in a helium glovebox. The sample can was sealed with an indium o-ring onto a copper heating block containing a valveated outlet for gas loading. Data were collected at the high-resolution powder diffractometer, BT1, at the National Institute of Standards and Technology Center for Neutron Research, utilizing a Ge (311) monochromator with an in-pile 60° collimator, corresponding to a neutron wavelength of 2.0772 Å. After mounting the sample to a bottom-loaded closed cycle refrigerator, the sample was cooled to 6 K for measurement, and subsequent measurements were collected at 150 and 300 K (Supplementary Fig. 33). For gas loading, the sample was dosed with ~1 equiv. of O₂ per cobalt at 100 K, with adsorption verified by thermodynamically prior to cooling to 8 K to avoid condensation. Measurements were then conducted at 8, 150, and 300 K, then at 150 and 8 K. Diffraction patterns for initial and final 8 and 150 K data sets were virtually identical (Supplementary Fig. 35).

Neutron powder diffraction data was analyzed using GSAS55. Initially, Le Bail refinements were performed to determine starting parameters, after which Rietveld refinements were conducted. Bond restraints were initially placed on all bonds, based on chemical information. Final refinements only included bond restraints on the phenyl ring, with minimal impact. Occupancies that refined within unity (the atoms of bbta⁻⁻ linkers, the Co atom, and the O atom of the OH groups), were fixed. The thermal parameter of the bbta⁻⁻ linkers were constrained to the same value. During the final refinements, the profile parameters, all atomic positions, and the occupancies were all refined, for both the gas-dosed and bare structures. The parameters are listed in Supplementary Tables 13–16, and the refinements are shown in Supplementary Figs. 34, 36, and 37. To confirm the position of the hydrogen atom of the hydroxo groups, a Rietveld refinement was performed with the hydroxo hydrogen atoms omitted from the structure, while keeping all other aspects of the refinement constant, and a Fourier difference map (\(F_{obs} - F_{calc}\)) was calculated from the refinement. The diminished goodness-of-fit parameters and the clear presence of well-localized atoms in the negative component of the map (Supplementary Figs. 38 and 39) confirm the assignment of the hydrogen atom and its ability to hydrogen bond to the superoxo oxygen (\(d(H, O) = 2.35(2) \text{ Å}\)).

**Infrared spectroscopy.** Infrared spectra were collected using a Bruker Vertex 70 spectrometer equipped with a glorybowl source, KBr beamsplitter, and a liquid nitrogen cooled mercury-cadmium-telluride detector. A custom-built diffuse reflectance platform. These samples include desolvated Co₂Cl₂(bbta) (9.8 mg), desolvated Co₂(OH)₂(bbta) (17.2 mg), methanol-solvated Co₂(OH)₂(bbta) (12.8 mg), Co₂(OH)₂(bbta) dosed with 0.5 equivalents of O₂ per cobalt (15.4 mg), and Co₂(OH)₂(bbta) dosed with 1 equivalent of O₂ per cobalt (11.4 mg). Sample powders were restrained with a plug of compacted glass wool that prevented crystalline torqueing, but enabled gas-dosing with O₂. The methanol-solvated sample was filtered on a polypropylene membrane filter (0.45 µm) and dried briefly at room temperature under vacuum, before being loaded into the quartz tube. Air-free elemental analysis of the sample was measured on the same day of sample preparation in order to accurately quantify the amount of solvent adsorbed in the pores of the material. The O₂-loaded samples were prepared by attaching the quartz tubes containing activated Co₂(OH)₂(bbta) to a Micromeritics ASAP 2020 gas adsorption analyzer. One equivalent of O₂ and 0.5 equivalents of O₂ for every Co atom within the structure was calculated and then exposed to the samples. All quartz tubes containing samples, including those loaded with O₂ gas, were flame-sealed while the sample was cooled with liquid nitrogen. Magnetic susceptibility measurements were performed using a Quantum Design MPMS2 SQUID magnetometer. Measurements of d.c. magnetic susceptibility were collected in the temperature range 2–300 K under applied magnetic fields of 1 T. Diamagnetic corrections were applied to the data using Pascal's constants to give \(\chi_0 = 0.00014552 \text{emu mol}^{-1}\) for desolvated Co₂Cl₂(bbta), \(\chi_0 = -0.0001752 \text{emu mol}^{-1}\) for desolvated Co₂(OH)₂(bbta), \(\chi_0 = -0.00019341 \text{emu mol}^{-1}\) for methanol-solvated Co₂(OH)₂(bbta), and \(\chi_0 = -0.0002672 \text{emu mol}^{-1}\) for Co₂(OH)₂(bbta) dosed with 0.5 equivalents of O₂ per cobalt, and \(\chi_0 = -0.0003592 \text{emu mol}^{-1}\) for Co₂(OH)₂(bbta) dosed with 1 equivalent of O₂ per cobalt. The collected data is shown in Supplementary Figs. 63–65.

**Theoretical calculations.** Periodic models for the desolvated and O₂-loaded Co₂Cl₂(bbta) and Co₂(OH)₂(bbta) were optimized using the PBE-D3 functional56,57, as implemented in the VASP 5.4.4 program58. Dioxoxygen adsorption energies were obtained by single point calculations using the PBE-D3 functional59 with the PBE-D3 optimized structures. The vibrational properties were modeled using tetraclobalt clusters, excised from the PBE-D3 optimized structures along a single coordination chain. Constraints were applied by optimizing the MO60 functional, where the dioxo molecules, cobalt atoms, and the first coordination sphere of the two central cobalt atoms were allowed to relax. The electronic structure of the frameworks was evaluated using complete active space self-consistent field (CASCF) single point calculations followed by second-order perturbation theory (CASPT2). The M06 functional was used. An additional set of tetraclobalt cluster models was employed, obtained from the experimental crystal structures of desolvated Co₂Cl₂(bbta) and Co₂(OH)₂(bbta). Dicobalt cluster models were obtained by replacing the external cobalt atoms by magnesium ions. Partial geometry optimizations were performed using the M06 functional by relaxing only C and H atoms. The computational details are further provided in the Supplementary Information.

**Markov chain simulations of negative cooperativity.** The framework material sites were simulated, in a simplified fashion, as a chain of twelve Co atoms whose occupations (bound or unbound to oxygen) at a given time were modeled as a
Markov chain. At each time step, a random Co atom was chosen. If bound, the states of the Co atoms remained unchanged, reflecting the negligible probability of a bound Co atom becoming unbound in the timescales observed. If unbound, the chosen Co atom was changed to a bound state with a probability that decreased with the number of bound neighboring Co atoms, reflecting negative cooperativity. Periodic boundary conditions, simulating the repetition of such short chains in the material, were used to determine the neighbors of the first and last Co atoms. The Markov chain was run for 200 timesteps; the probability of an unbound Co atom becoming bound at any timestep given zero, one, and two bound neighbors was 0.5, 0.0005, and 0.0001, respectively. This data is shown in Supplementary Fig. 68.

Data availability

The main data supporting the findings of this study are available in the paper and its Supplementary Information. The source data underlying Figs. 3 and 6 are provided as Source Data file. Other data are available from the corresponding author upon request. Metrical data for the solid-state structures of CoCl₂(btbA), O₂-dosed CoCl₂(btbA), Co₃(OH)₆(btbA) and O₂-dosed Co₃(OH)₆(btbA) are available free of charge from the Cambridge Crystallographic Data Centre under reference numbers 1965641–1965647.

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Author contributions

J.O. and J.R.L. formulated the project. J.O. synthesized the materials, as well as collected and analyzed the gas adsorption data, with support from H.F. D.A.R. contributed to initial experimental work. J.O., H.Z.H.J., and B.A.T. collected the powder X-ray diffraction data, and J.O. analyzed the data. H.Z.H.J. collected and analyzed the infrared spectroscopy data. J.G.V., V.B., and L.G. conducted the theoretical calculations and interpreted the results. L.E.D. collected and analyzed the magnetic susceptibility data. B.A.T. and C.M.B. collected and analyzed the powder neutron diffraction data. K.C. collected microscopy data. H.L. performed Markov chain simulations and analyzed the results. J.O. and J.R.L. wrote the paper, and all authors contributed to revising the paper.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to J.R.L.

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