Structural characterization of framework–gas interactions in the metal–organic framework Co$_2$(dobdc) by in situ single-crystal X-ray diffraction†


The crystallographic characterization of framework–guest interactions in metal–organic frameworks allows the location of guest binding sites and provides meaningful information on the nature of these interactions, enabling the correlation of structure with adsorption behavior. Here, techniques developed for in situ single-crystal X-ray diffraction experiments on porous crystals have enabled the direct observation of CO, CH$_4$, N$_2$, O$_2$, Ar, and P$_2$ adsorption in Co$_2$(dobdc) (dobdc$^{4-}$ = 2,5-dioxido-1,4-benzenedicarboxylate), a metal–organic framework bearing coordinatively unsaturated cobalt(II) sites. All these molecules exhibit such weak interactions with the high-spin cobalt(II) sites in the framework that no analogous molecular structures exist, demonstrating the utility of metal–organic frameworks as crystalline matrices for the isolation and structural determination of unstable species. Notably, the Co–CH$_4$ and Co–Ar interactions observed in Co$_2$(dobdc) represent, to the best of our knowledge, the first single-crystal structure determination of a metal–CH$_4$ interaction and the first crystallographically characterized metal–Ar interaction. Analysis of low-pressure gas adsorption isotherms confirms that these gases exhibit mainly physisorptive interactions with the cobalt(II) sites in Co$_2$(dobdc), with differential enthalpies of adsorption as weak as $-17(1)$ kJ mol$^{-1}$ (for Ar). Moreover, the structures of Co$_2$(dobdc)–3.8N$_2$, Co$_2$(dobdc)–5.9O$_2$, and Co$_2$(dobdc)–2.0Ar reveal the location of secondary (N$_2$, O$_2$, and Ar) and tertiary (O$_2$) binding sites in Co$_2$(dobdc), while high-pressure CO$_2$, CO, CH$_4$, N$_2$, and Ar adsorption isotherms show that these binding sites become more relevant at elevated pressures.

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growing utility of molecular single-crystal matrices, their general applicability remains limited by the scarcity of structures that retain crystallinity upon binding and reaction of the molecular guests. In addition, the tendency of molecules to pack closely in the crystalline state engenders only small or transient apertures in the crystal. This inability to support larger pore structures severely restricts the size of guests that can be incorporated. The need to develop new crystalline matrices to address these challenges outlines an opportunity for alternative materials to contribute to the advancement of the field.

Metal–organic frameworks are a class of materials composed of inorganic clusters or metal ions connected in three dimensions by organic linkers. These materials exhibit the ability to adopt highly porous crystalline structures with well-defined pore architectures, leading to their extensive evaluation for applications in gas storage, gas separations, and catalysis. In contrast to the non-covalent interactions in molecular crystals, the coordinate-covalent bonds linking the inorganic and organic units in metal–organic frameworks give rise to their inherently greater thermal and chemical stability. Consequently, these materials are capable of maintaining porous structures that accommodate the removal, inclusion, exchange, or reaction of a more diverse selection of molecular guests over a wider range of conditions compared to molecular assemblies. In particular, frameworks that exhibit permanent and open porosity are uniquely suited to the study of gaseous species. Furthermore, these materials can be designed to facilitate explicit framework–guest interactions through synthetic control over pore size, shape, and functionality.

Indeed, research on metal–organic frameworks has increasingly relied on in situ diffraction experiments to provide critical insight into the contribution of the pore structure to adsorption behavior and reactivity. Such studies also complement and validate computational efforts focused on understanding and predicting the properties of these materials. Despite the greater accessibility, simplicity, and precision associated with single-crystal X-ray diffraction, the majority of work involving gases has been accomplished using powder X-ray and neutron diffraction methods. This primarily stems from the following challenges: (i) the difficulty in preparing single crystals of sufficient size and quality to be suitable for diffraction experiments, (ii) the tendency of some crystals to fracture under the evacuation or gas-dosing conditions, and (iii) the exceptionally high sensitivity to contaminants inherent to the small sample sizes used in single-crystal measurements (~500 ng for a typical 200 µm wide single crystal). The third challenge is especially problematic in studying frameworks bearing metals with open coordination sites, due to the propensity of these sites to bind water over more weakly coordinating species. Nevertheless, several studies have proven to be successful in employing single-crystal X-ray diffraction experiments to observe framework–gas interactions.

The M2(dobdc) series of metal–organic frameworks [M = MgII, MnII, FeII, CoII, NiII, CuII, ZnII, and CdII; dobdc4− = 2,5-dioxido-1,4-benzenedicarboxylate; also referred to as M-MOF-74 or CPO-27(M)] have been intensely studied due to their high density of exposed metal(n) sites, which can interact favorably with guest molecules. Much of the work evaluating the adsorption properties and reactivity of these materials has depended on powder X-ray or neutron diffraction for in situ characterization of gas binding. Comparatively few studies have been performed using single-crystal X-ray diffraction due to the intrinsic

![Fig. 1 Structures determined by single-crystal X-ray diffraction. (Left) A portion of the crystal structure of Co2(dobdc) (dobdc4− = 2,5-dioxido-1,4-benzenedicarboxylate) at 296 K viewed along the c axis. (Right) First coordination spheres for CoII in the structures of Co2, CO2, N2, O2, CH4, Ar, and P4 in Co2(dobdc) (at 150 K for CO2; at 100 K for N2, O2, CH4, and P4; at 90 K for CO and Ar); purple, red, gray, blue, light blue, light orange, and white spheres represent Co, O, C, N, Ar, P, and H atoms, respectively. Note that the O2 molecules bound to the CoII sites in Co2(dobdc)-5.9O2 were found to be disordered over two orientations with relative occupancies of 73(3)% and 27(3)% (Fig. S8†), but only one of these orientations (73(3)% occupancy) is shown for clarity. The structure of Co2(dobdc)-2.9CO2 has been reported previously and is shown here to facilitate comparisons.](image-url)
difficulty that accompanies \textit{in situ} gas-dosing experiments on materials with open coordination sites and because only Co$_2$(dobdc) and Zn$_2$(dobdc) readily form single crystals. This work seeks to expand on these studies through techniques developed to dose gases into single crystals under rigorously air-free conditions. Herein, we report the direct structural characterization of CO, CH$_4$, N$_2$, O$_2$, Ar, and P$_4$ adsorption in single crystals of Co$_2$(dobdc) (Fig. 1). The resulting structures confirm that each gas binds first to the exposed cobalt(ii) site and allow the identification of secondary (for N$_2$, O$_2$, and Ar) and tertiary (for O$_2$) binding sites within the framework. Remarkably, further inspection of Co$^{11}$-gas distances reveals that binding occurs primarily through weak covalent (for CO) or non-covalent (for CH$_4$, N$_2$, O$_2$, and Ar) interactions, which have never been observed by single-crystal X-ray diffraction. Finally, a combination of low- and high-pressure gas adsorption isotherms are used to evaluate the relationship between structure and adsorption behavior.

**Experimental**

**Materials and methods**

$N,N$-Dimethylformamide (DMF), ethanol, and methanol were obtained from commercial sources and used without further purification. Hexanes was deoxygenated by purging with Ar for 1 h and dried using a commercial solvent purification system designed by JC Meyer Solvent Systems. The compounds Co(NO$_3$)$_3$$\cdot$6H$_2$O and 2,5-dihydroxy-1,4-benzenedicarboxylic acid (H$_2$dobdc) were purchased from Sigma-Aldrich and used as received. White phosphorus (P$_4$) was prepared by heating red phosphorus under vacuum (~80 µbar) in a flame-sealed borosilicate glass tube over a Bunsen burner flame. The crude white phosphorus was then purified by recrystallization from hexanes. **Caution**: white phosphorus is highly toxic and reacts violently with O$_2$ in air. Single crystals of Co$_2$(dobdc) were synthesized using a slight modification to a previously published procedure.$^{7}$

Briefly, a 100 mL Pyrex jar was charged with H$_2$dobdc (198 mg, 1.00 mmol), Co(NO$_3$)$_3$$\cdot$6H$_2$O (970 mg, 3.34 mmol), and a 1 : 1 : 1 (v/v/v) mixture of DMF/ethanol/water (80 mL), and was then sealed with a Teflon cap. The resulting mixture was sonicated until all reactants were fully dissolved to form a violet solution. The reaction mixture was then placed in an oven that was preheated to 100 °C and kept at this temperature for 24 h, yielding violet needle-shaped single crystals. The crystals were then evacuated three times in 80 mL of DMF for 24 h at 120 °C, followed by soaking three times in 80 mL of methanol at 60 °C. The crystals were then stored in methanol in a 20 mL PTFE-capped vial prior to use for single-crystal X-ray diffraction experiments or gas-adsorption measurements. The Langmuir surface area of the sample used for gas adsorption measurements was determined to be 1400 ± 2 m$^2$ g$^{-1}$.

**Single-crystal X-ray diffraction**

**Gas dosing in the gas cell.** For Co$_2$(dobdc), Co$_2$(dobdc)-0.58CO, Co$_2$(dobdc)-2.0CH$_4$, and Co$_2$(dobdc)-2.0Ar, a methanol-solvated crystal of Co$_2$(dobdc) was mounted on a MiTeGen loop using a minimal amount of epoxy to ensure that the crystal pores remained accessible. The sample was then placed in a custom-made gas cell equipped with a quartz capillary, an O-ring seal, and Beswick ball valves for gas-dosing (Fig. 2a). The cell was connected to a gas-dosing manifold using PTFE tubing, and was then evacuated under reduced pressure using a turbomolecular pump at an external temperature of 180 °C for 4–5 h to remove solvent molecules that fill the pores and coordinate to the exposed Co sites within the crystal. After obtaining the structure to confirm that the crystal was fully desolvated, the crystal was cooled to 25 °C and then dosed with the desired gas at a specified pressure (1.00 bar for CO and CH$_4$; 1.14 bar for Ar).

**Gas dosing in capillaries.** For Co$_2$(dobdc)-5.9O$_2$ and Co$_2$(dobdc)-3.8N$_2$, methanol-solvated crystals of Co$_2$(dobdc) were mounted on a borosilicate glass fiber using a minimal amount of epoxy, ensuring that the crystal pores remained accessible. The glass fiber was then inserted into a 1.0 mm borosilicate glass capillary, which was connected to a HiP Taper Seal valve using a Swagelok® Ultra-Torr vacuum fitting with a Viton® O-ring (Fig. 2b). The capillary-dosing assembly was then attached to a port on a Micromeritics ASAP 2020 instrument using a Cajon® VCO fitting. The capillary was evacuated under reduced pressure at 180 °C for 24 h to remove solvent molecules that fill the pores and coordinate to the exposed Co sites within the crystal. The capillary was dosed with a specific gas at a specified pressure (0.8 bar for N$_2$; 0.5 bar for O$_3$), and then was flame-sealed with a methane/oxygen torch.

**Vapor dosing of P$_4$.** For Co$_2$(dobdc)-1.3P$_4$, methanol-solvated Co$_2$(dobdc) crystals (~20 mg) were desolvated in a glass tube under reduced pressure at 180 °C on a Micromeritics ASAP 2020 instrument. In an N$_2$-filled VAC Atmospheres glovebox, the desolvated crystals were transferred into...
a 4 mL vial, which was then placed in a 20 mL vial containing excess white phosphorus. **Caution:** white phosphorus is highly toxic and reacts violently with O₂ in air. The 20 mL vial was sealed with a PTFE-lined cap then heated for 24 h at 80 °C. The P₂O₅-dosed crystals were then coated with Paratone-N oil prior to use for single-crystal X-ray diffraction experiments.

**Data collection and refinement.** X-ray diffraction data for all samples were collected at Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory using synchrotron radiation (λ = 0.7749 Å for Co₂(doCd)·Co₂(doCd)·0.58CO₂, Co₂(doCd)·1.19CO₂, Co₂(doCd)·2.0CH₄, and Co₂(doCd)·5.9O₂, and Co₂(doCd)·1.3P₄; λ = 0.6525 Å for Co₂(doCd)·2.0Ar; λ = 0.6199 Å for Co₂(doCd)·3.8N₂) with either a Bruker AXS APEX II CCD detector (Co₂(doCd), Co₂(doCd)·0.58CO₂, Co₂(doCd)·1.2CO₂, Co₂(doCd)·2.0CH₄, Co₂(doCd)·3.8N₂, and Co₂(doCd)·2.0Ar) or a Bruker PHOTON100 CMOS detector (Co₂(doCd)·5.9O₂ and Co₂(doCd)·1.3P₄) on a D8 diffractometer. The samples were cooled to a specified temperature (296 K for Co₂(doCd); 100 K for Co₂(doCd)·1.2CO₂, Co₂(doCd)·2.0CH₄, Co₂(doCd)·3.8N₂, Co₂(doCd)·5.9O₂, and Co₂(doCd)·1.3P₄; 90 K for Co₂(doCd)·0.58CO₂ and Co₂(doCd)·2.0Ar) using an Oxford Cryosystems cryostream for data collection.

All crystals were found to be obverse/reverse twins based on analysis of their diffraction patterns. For each structure, CELL_NOW⁷² was used to determine the orientation matrices. Raw data for both twin matrices were integrated and corrected for Lorentz and polarization effects using Bruker AXS SAINT⁺⁺ software and corrected for absorption using TWINABS.⁷⁴ TWI-NABS was used to produce a merged HKLF file for structure solution and initial refinement and an HKLF5 file for final structure refinement. The structures were solved using direct methods with SHELXLS⁷⁵,⁷⁶ and refined using SHELXL⁷⁵,⁷⁶ operated in the OLEX2 interface.⁷⁸ Thermal parameters were refined anisotropically for all non-hydrogen atoms. Disorder and thermal motion of the bound gas molecules required the use of displacement parameter (for Co₂(doCd)·1.2CO₂, Co₂(doCd)·5.9O₂, Co₂(doCd)·3.8N₂, Co₂(doCd)·2.0Ar, and Co₂(doCd)·1.3P₄) and distance (for Co₂(doCd)·5.9O₂, Co₂(doCd)·3.8N₂, and Co₂(doCd)·1.3P₄) restraints. All hydrogen atoms were refined using the riding model.

**Gas adsorption**

**Low-pressure gas adsorption measurements.** Pure-component gas adsorption isotherms for pressures in the range 0–1.2 bar were measured by a volumetric method using Micromeritics ASAP 2020 and ASAP 2420 instruments. UHP-grade gases (99.999% purity He, Ar, N₂, CO, CO₂, and CH₄; 99.998% purity CO₂; 99.993% purity O₂) were used for all measurements. A typical sample of 30–100 mg of Co₂(doCd) was transferred to a pre-weighted analysis tube, which was capped with a Micromeritics TranSeal and evacuated by heating at either 180 °C, reached by ramping at a rate of 1 °C min⁻¹, under dynamic vacuum until an outgas rate of less than 3 bar 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 3 bar min⁻¹. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas. Nitrogen gas adsorption isotherms at 77 K were measured in liquid nitrogen using UHP-grade gas sources. 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, assuming a value of 16.2 Å² for the molecular cross-sectional area of N₂. Adsorption isotherms between 293 and 332 K were measured using a recirculating dewar connected to a Julabo F32-MC isothermal bath.

**High-pressure gas adsorption measurements.** High-pressure gas adsorption isotherms in the range of 0–100 bar were measured on an HPVA-II-100 from Particulate Systems, a Micromeritics company. In a typical measurement, 0.5–1.0 g of activated sample was loaded into a tared stainless steel sample holder inside a glovebox under a N₂ atmosphere. Prior to connecting the sample holder to the VCR fitting of the complete high-pressure assembly inside the glovebox, the sample holder was weighed to determine the sample mass. The sample holder was then transferred to the HPVA-II-100 instrument, connected to the instrument’s analysis port via an OCR fitting, and evacuated at room temperature for at least 2 h. The sample holder was placed inside an aluminum recirculating Dewar connected to a Julabo FP89-HL isothermal bath filled with Julabo Thermal C2 fluid. The temperature stability of the isothermal bath is ±0.02 °C. Methods for accurately measuring the relevant sample free space, which involve the expansion of He from a calibrated volume at 0.7 bar and 25 °C to the evacuated sample holder, have been described in detail previously.²² Non-ideality corrections were performed using the compressibility factors tabulated in the NIST REFPROP database²⁹,⁸⁰ at each measured temperature and pressure.

**Adsorption isotherm fitting.** Low-pressure Ar, N₂, and O₂ isotherms at 298, 308, and 318 K were fit with a single-site Langmuir equation, while low-pressure CH₄ isotherms at 293, 298, 303, 313, and 323 K were fit using a dual-site Langmuir equation (eqn (1)), where n is the total amount adsorbed in mmol g⁻¹, P is the pressure in bar, n_sat is the saturation capacity in mmol g⁻¹, and b is the Langmuir parameter in bar⁻¹.

\[
n = n_{\text{sat,1}} b_1 P + n_{\text{sat,2}} b_2 P \\
1 + b_1 P \
1 + b_2 P
\]  \hspace{1cm} (1)

\[
b_i = e^{-S_i/R} e^{-E_i/RT} \hspace{1cm} (2)
\]

The Langmuir parameter can be expressed using eqn (2), where Sᵢ is the site-specific integral entropy of adsorption in J mol⁻¹ K⁻¹; Eᵢ is the site-specific differential enthalpy of adsorption in kJ mol⁻¹, R is the gas constant in J mol⁻¹ K⁻¹, and T is the temperature in K. For all gases, isotherms were fit both independently for each temperature (Fig. S11, S13, S15, and S17†) and simultaneously for all temperatures (Fig. S12, S14, S16, and S18†).
**Differential enthalpy of adsorption calculations.** Using the Langmuir fits, the differential enthalpy of adsorption, $\Delta h_{\text{ad}}$, can be calculated as a function of the total amount of gas adsorbed, $n$, by using the Clausius-Clapeyron equation (eqn (3)), where $R$ is the gas constant in J mol$^{-1}$ K$^{-1}$, $T$ is the temperature in K, $n$ is the total amount adsorbed in mmol g$^{-1}$, and $P$ is the pressure in bar.

$$
\Delta h_{\text{ad}} = -RT\left(\frac{\partial \ln P}{\partial T}\right)_{n}
$$

(3)

The Langmuir fits for each gas (fit independently for each temperature) were used to obtain the exact pressures that correspond to specific loadings at different temperatures (298, 308, and 318 K for N$_2$, O$_2$, and Ar; 293, 298, 303, 313, and 323 K for CH$_4$). This was done at loading intervals of 0.05 mmol g$^{-1}$. At each loading, the slope of the best-fit line to $\ln(P)$ versus $1/T$ was calculated to obtain the differential enthalpy.

**Results and discussion**

**Structural characterization**

Two methods were developed for dosing gases into single crystals. The first involves using an environmental gas cell (Fig. 2a), which was designed and built at ALS beamline 11.3.1. Similar to other gas cells that have recently been developed, the cell allows the collection of single-crystal X-ray diffraction data on samples under vacuum or dosed with a desired gas. With this method, the structure of the framework can be monitored throughout the evacuation and gas dosing of the crystal. This capability affords appreciable flexibility, as the temperature, gas pressure, and time can be changed at each stage of the experiment in response to structural data. As a result, the gas cell is especially useful for studying unfamiliar samples that still require experimental conditions to be optimized. Alternatively, a single crystal can be inserted into a borosilicate capillary, which is then heated under vacuum and subsequently dosed using a manifold or gas adsorption analyzer. The capillary is then flame-sealed with the crystal kept under a specified pressure of gas that is lower than 1 bar. Unlike the gas cell, using capillaries requires the evacuation time and temperature and the gas-dosing pressure to be determined prior to data collection. Although less versatile, the capillary method benefits from higher sample throughput compared to the gas cell because diffraction experiments are only conducted on gas-dosed samples. Consequently, this method can be preferable for samples that have established activation parameters and gas adsorption properties.

The metal–organic framework Co$_2$(dobdc) crystallizes in the space group R3, in which the special positions are exclusively situated along the one-dimensional helical chains of Co atoms, at the center of the organic linkers, and through the center of the hexagonal pores. This makes the framework particularly amenable to the crystallographic characterization of guest species as no crystallographic symmetry is enforced on sites...
above and within the vicinity of the coordinatively unsaturated cobalt(II) centers. This is evident in the exceptionally ordered structures of gases within Co2(dobdc) even in cases where the interactions are weak, as described previously and discussed below.

Inspection of the structures of Co2(dobdc)-1.2CO, Co2(dobdc)-0.58CO, and Co2(dobdc)-2.0CH4 (Fig. 3), where only a single adsorption site is populated, shows that CO and CH4 first bind to the open coordination site of cobalt(n), confirming that this site has the greatest contribution to the adsorption of these gases in the material. Multiple adsorption sites could be located in the structures of Co2(dobdc)-3.8N2, Co2(dobdc)-5.9O2, Co2(dobdc)-2.0Ar, and Co2(dobdc)-1.3P4 (Fig. 3), which complicates the determination of the primary adsorption sites. Comparison of relative site occupancies, displacement parameters, and framework–guest distances, however, indicates that N2, O2, Ar, and P4 also bind primarily to the cobalt(n) sites. Remarkably, the secondary binding sites for N2, O2, and Ar were found to have nearly identical locations (Fig. S1 and S2†), close to the non-bridging carboxylate and phenoxy oxygen atoms of dobdc⁻. Previous reports also identify the same secondary binding site in structures of CO2 (ref. 29) (Fig. 3) and H2O in Co2(dobdc) (Fig. S1 and S2†). The similarity of these binding pockets likely arises from a slightly polarizing environment generated by the partial negative charges on surrounding linker oxygen atoms. In other metal–organic frameworks, the linker carboxylate oxygen atoms have been shown to facilitate similar weak interactions with gases.32,34

The structures of Co2(dobdc)-1.2CO at 100 K and Co2(dobdc)-0.58CO at 90 K (Fig. 3) were obtained under 1.00 bar of CO in the gas cell. In these structures, CO loading was found to be lower than one per cobalt(n) site, which likely results from slow diffusion of CO as the crystals were rapidly cooled after CO dosing. Nevertheless, both structures display Co–C(–O) distances of 2.215(6) Å (Fig. 1) and similar Co–C–O angles (175.7(12)° for Co2(dobdc)-1.2CO and 178.0(11)° for Co2(dobdc)-0.58CO). These distances and angles are comparable to those previously obtained from powder neutron diffraction at 10 K, Co–C(–O) distance = 2.18(2) Å and Co–C–O angle = 171(2)°.48 The long Co–C(–O) distance and deviation of the Co–C–O angle from 180° are both consistent with a weak interaction between cobalt(n) and CO with limited CoIII–CO π backbonding. This is further supported by larger CO oxygen displacement parameters compared to carbon, which suggests that the bound CO is free to bend out of the axis along the CoIII–CO bond. Surveying the Cambridge Crystal Structure Database (CCSD),46 single-crystal structures of cobalt carboxyl complexes with Co–C(–O) distances longer than 2.0 Å are unprecedented. Examples of cobalt(n)–carboxyl complexes are exceedingly rare and all exhibit a low-spin configuration with Co–C(–O) bond distances around 1.8 Å, which are typical to strong Co–CO bonds.48 The weak-field dobdc⁻ ligands in Co2(dobdc) impose a high-spin configuration for cobalt(n), which is maintained after binding CO.46 Population of the anti-bonding cobalt(n) orbitals makes the Co–CO σ interaction less favorable, lengthening the Co–C(–O) distance. This diminishes CoIII–CO π back-donation by preventing overlap between the Co 3d and CO π* orbitals. Together, these interdependent effects manifest in the exceptionally weak and fully reversible M–CO interaction in Co2(dobdc), which has been shown to be a major advantage of Co2(dobdc) and its MgII, MnII, FeIII, NiII, and ZnII analogs as prospective materials for industrial CO separations.40

X-ray analysis of a single crystal of Co2(dobdc) under 0.8 bar N2 at 100 K resulted in the structure of Co2(dobdc)-3.8N2 (Fig. 3). The structure shows that N2 binds to cobalt(n) through an end-on interaction with a Co–N(N2) distance of 2.236(6) Å (Fig. 1). This distance is comparable with the Fe–N(N2) distance of 2.30(1) Å obtained from the powder neutron diffraction structure of N2 in Fe2(dobdc).32 Deviation of the Co–N–N angle (170.2(9)°) from 180° also suggests minimal π-back donation from CoIII to N2. Of the cobalt dinitrogen complexes reported in the CCSD,41 none have Co–N(N2) distances greater than 2.0 Å and only one of these features cobalt in its +2 oxidation state.42 The long Co–N(N2) distance in Co2(dobdc)-3.8N2 indicates a much weaker interaction between N2 and the high-spin cobalt(n) centers in Co2(dobdc) compared to the Co–N2 bonds formed in typical cobalt dinitrogen complexes.86–88 The Co–N2 bonds in these complexes are strengthened by significant Co–N2 π back-donation, whereas N2 can be thought to interact mainly through σ donation to cobalt(n) in Co2(dobdc). The secondary N2 binding sites in Co2(dobdc)-3.8N2 (Fig. 3 and S1†) display van der Waals interactions between N2 and the oxygen atoms of dobdc⁻, with N–O contacts ranging from 3.44(2) to 3.77(1) Å (Fig. S2†). These sites are nearly identical to those located in the powder neutron diffraction structure of N2 in Fe2(dobdc).32 Full population of both binding sites to give four N2 molecules adsorbed per formula unit in Co2(dobdc) corresponds surprisingly well to the estimated number of N2 molecules adsorbed as a monolayer in the framework, which is ~4.3 based on a Brunauer–Emmett–Teller (BET) fit to 77 K N2 adsorption isotherm data.29

To determine the structure of O2 in Co2(dobdc), data was collected on a single crystal dosed with 0.5 bar of O2 in a sealed capillary at 100 K. In the structure of Co2(dobdc)-5.9O2 (Fig. 3), O2 is found to bind end-on with a Co–O(O2) distance of 2.216(5) Å (Fig. 1). Disorder of the O2 molecule results in two bent orientations with Co–O–O angles of 127.3(10)° and 128(3)° and relative occupancies of 73(3)% and 27(3)%, respectively (Fig. S8†). The Co–O distance in Co2(dobdc)-5.9O2 is unusually long. Structures of cobalt dioxygen complexes in the CCSD and recently reported dioxygen adducts formed in other cobalt metal–organic frameworks,50,52 all show Co–O distances that fall below 2.0 Å. This again suggests significant disparity between the Co–O2 interaction in Co2(dobdc) and those in molecular cobalt complexes, where O2 binding is characterized by electron transfer from one or two cobalt(n) centers to form superoxo or peroxo complexes, respectively.99,99 In addition to the long Co–O–O distance, no significant difference in the average Co–O distances is apparent between cobalt(n) and dobdc⁻ in Co2(dobdc) (2.035(5) Å) and in Co2(dobdc)-5.9O2 (2.036(5) Å). This further implies that partial oxidation of cobalt(n) does not occur upon O2 binding, which is in contrast to partial oxidation of the iron(n) centers in Fe2(dobdc) to form either iron-superoxo species at 211 K or iron-peroxo species at...
298 K.\textsuperscript{35} Like in Co$_2$(dobdc)$\cdot$3.8N$_2$, the secondary bindings sites in Co$_2$(dobdc)$\cdot$3.9O$_2$ feature O$_2$ interacting with the dobdc$^{4-}$ oxygen atoms, with O$\cdots$O contacts that range from 3.39(17) Å to 3.88(2) Å. Remarkably, tertiary binding sites for O$_2$ can also be identified in the structure, where O$_2$ interacts only with other O$_2$ molecules adsorbed on the primary and secondary sites. Similar sites were also observed by powder neutron diffraction in the structure of O$_2$ in Fe$_2$(dobdc).\textsuperscript{35} Experimental observation of these sites is particularly helpful to computational efforts focused on understanding the contribution of gas–gas interactions to adsorption in metal–organic frameworks and other porous materials.\textsuperscript{40,65,68,91,92}

The structure of Co$_2$(dobdc)$\cdot$2.0CH$_4$ (Fig. 3) was obtained by cooling a single crystal of Co$_2$(dobdc) under 1 bar of CH$_4$ to 100 K in the gas cell. Although methane hydrogen atoms could not be located in the structure due to disorder and the difficulty in locating hydrogen atoms by X-ray diffraction, electron density corresponding to a methane carbon atom could be distinctly resolved above the framework cobalt sites with a Co$^{II}$$\cdots$C$_{CH_4}$ distance of 2.941(19) Å (Fig. 1). Significantly, this is the first M–CH$_4$ interaction that has been characterized by single-crystal X-ray diffraction. The Co$^{II}$$\cdots$C$_{CH_4}$ distance is comparable to distances characterized for metal–methane interactions in other metal–organic frameworks, which are generally close to 3 Å. The most relevant of these are from structures determined by powder neutron diffraction for CD$_4$ in Fe$_2$(dobdc) (Fe$^{III}$$\cdots$C$_{CD_4}$ distance of 2.98(1) Å)\textsuperscript{166} and in Mg$_2$(dobdc) [Mg$^{II}$$\cdots$C$_{CD_4}$ distance of 3.04 Å].\textsuperscript{35} The long M$^{II}$$\cdots$C$_{CH_4}$ distances in all of these structures are indicative of weak non-covalent interactions that stem from polarization of CH$_4$ by the partial positive charge on the metal center. These distances contrast with the relatively short M$^{II}$$\cdots$C distances (around 2.4–2.5 Å) in alkane $\sigma$-complexes, which involve donation from the alkane C–H $\sigma$ bond to the metal center.\textsuperscript{164,168} Although the Co$^{II}$$\cdots$CH$_4$ interaction in Co$_2$(dobdc) and analogous noncovalent M–CH$_4$ interactions should clearly be distinguished from the bonds formed in true metal–alkane $\sigma$-complexes, characterization of such weak M–CH$_4$ interactions has become increasingly important in the evaluation of materials for natural gas storage.\textsuperscript{35}

The inherent chemical stability of the noble gases has been thoroughly exploited for maintaining an inert environment for highly reactive species. As a result of this stability, isolation of molecular metal–noble gas species is exceedingly difficult. While no molecular metal–noble gas species other than metal–Xe\textsuperscript{94,95} have been characterized crystallographically, computational methods and experimental techniques such as photo-dissociation spectroscopy and mass spectrometry have been employed to study these species.\textsuperscript{95,100} Encouraged by the preceding results, attempts were made to characterize metal–Ar interactions, which have never been crystallographically observed, in Co$_2$(dobdc). Under a pressure of 1.14 bar of Ar in the gas cell, no significant electron density could be observed over the cobalt(n) sites in Co$_2$(dobdc) at 100 K. Upon cooling to 90 K, however, two binding sites for Ar were resolved, one directly above the metal center and another at a location similar to the secondary binding sites of N$_2$ and O$_2$ (Fig. 2 and S1†). It is highly improbable that Ar occupies these adjacent sites simultaneously, because the distance between Ar molecules in the two sites (2.71(3) Å) is much shorter than twice the van der Waals radius of Ar (3.76 Å). In agreement with this, refinement of the Ar site occupancies results in site occupancies of 60.6(1.3)% for Ar interacting with cobalt(n) and 39.3(1.6)% for the second site, which give an overall formula of Co$_2$(dobdc)$\cdot$2.0Ar. These observations suggest that both sites have comparable affinities for Ar, resulting in an equilibrium between the two. Similar adsorption behavior has been observed for Kr and Xe in Ni$_2$(dobdc) and Mg$_2$(dobdc).\textsuperscript{40,46} The interaction of Ar with the cobalt(n) centers in Co$_2$(dobdc) is characterized by a Co–Ar distance of 2.932(9) Å (Fig. 1), which represents the first metal–Ar interaction observed by crystallography. This distance compares well with M–Kr and M–Xe distances in Ni$_2$(dobdc) and Mg$_2$(dobdc) [Ni–Kr = 3.03(3) Å and 3.26(15) Å, Mg–Kr = 3.23(3) Å, Ni–Xe = 3.01(2) Å and 3.395(7) Å, Mg–Xe = 3.14(2) Å] obtained by powder X-ray diffraction.\textsuperscript{46,47} The long distances between Ar, Kr, and Xe and the exposed metal sites in these frameworks is attributed to polarization induced by the partial positive charge on the metal centers. Like N$_2$ and O$_2$, Ar interacts with the dobdc$^{4-}$ oxygen atoms in its second binding site (Fig. S2†). Interactions between Ar and other noble gases with the linker oxygen atoms in other metal–organic frameworks have also been observed by both single-crystal\textsuperscript{95,104} and powder X-ray diffraction.\textsuperscript{46,47}

Motivated by previous work demonstrating the confinement of white phosphorus within a supramolecular cage\textsuperscript{102} and a coordination solid,\textsuperscript{103} we envisioned that Co$^{III}$$\cdots$P$_4$ species could be stabilized by leveraging the site-isolation of the open cobalt(n) coordination sites in Co$_2$(dobdc). Heating activated single crystals of Co$_2$(dobdc) in the presence of white phosphorus in a sealed vial at 80 °C resulted in adsorption of P$_4$ molecules to give Co$_2$(dobdc)$\cdot$1.3P$_4$ as determined by single-crystal X-ray diffraction. Initial refinement of the structure revealed clearly resolved P$_4$ tetrahedron exhibiting $\eta^1$-coordination to the cobalt(n) sites of the framework, with a Co$^{III}$$\cdots$P$_4$ distance of ~2.6 Å. The P$_4$ moiety, however, displayed highly prolate anisotropic displacement parameters and unusual P–P bond distances, long P$_{apical}$–P$_{basal}$ bonds (~2.6 Å) and short P$_{basal}$–P$_{basal}$ bonds (~2.0 Å), compared to the P–P bond distances in the crystal structure of P$_4$ (2.190(5)–2.212(5) Å).\textsuperscript{104} Given the relatively long Co$^{III}$–P bond distance and large displacement parameters, the apparent distortion of the coordinated P$_4$ likely resulted from disorder of the P$_4$ molecule rather than activation by the cobalt(n) center. Thus, the P$_4$ molecule was modelled to be disordered over two positions with all P–P distances restrained to be similar. The revised structure reveals that P$_4$ binds to only 45.5(10)% of the cobalt(n) sites with a long Co$^{III}$$\cdots$P$_4$ distance of 2.625(10) Å (Fig. 1 and 3). The relative distance between P$_4$ molecules coordinated to adjacent cobalt(n) sites suggests that P$_4$ cannot coordinate to each cobalt(n) center because this would lead to P–P contacts (2.53(3) Å) that are much shorter than twice the van der Waals radius of P (3.90 Å). Consequently, the rest of the adsorbed P$_4$ populates a second site (20.6(10)% occupancy) 3.88 Å away from the cobalt(n) center (Fig. S10†), where steric congestion prevents closer approach of the P$_4$ molecule to cobalt(n). Although rare, several molecular $\eta^1$–P$_4$ complexes have been prepared by employing
transition metal precursors with an agostic interaction or weakly coordinated ligand that can be displaced by P₄ under mild reaction conditions. In contrast to the long Co⁻⁻⁻P₄ distance in Co₂(dobdc)-1.3P₄, molecular η¹-P₄ complexes reported in the CCSD³ possess much shorter metal–P₄ distances that range from 2.162(8)–2.464(3) Å and contain electron-rich metals capable of π backbonding to P₄. These comparisons imply that, similar to the Co⁻⁻⁻CO and Co⁻⁻⁻N₂ interactions characterized in Co₂(dobdc), the longer Co⁻⁻⁻P₄ bond in Co₂(dobdc)-1.3P₄ arises from the inability of the high-spin cobalt(n) centers to effectively support π back-donation to P₄. Notably, the weaker cobalt(n)–P₄ complexes in Co₂(dobdc) can be prepared and remain stable at much higher temperatures whereas most molecular η¹-P₄ complexes readily decompose at room temperature. This thermal stability is attributed to the site-isolation of these Co⁻⁻⁻P₄ species and their inability to decompose through oxidative addition of P₄, due to the high-spin state and coordinative saturation of the framework cobalt(n) centers.

**Gas adsorption**

Low-pressure gas adsorption isotherms at different temperatures were collected for CH₄, N₂, O₂, and Ar, while the isotherms for CO and CO₂ were obtained from previous work to relate the adsorption properties of these gases to the corresponding structures (Fig. 4 and S11–S18). To provide a quantitative comparison, the differential enthalpies of adsorption (Δhₐd), a measure of the average binding energy for an adsorbate at a specific surface coverage, were calculated from isotherm data at low coverage of each gas (Table 1). In agreement with the crystal structures, the differential enthalpies of adsorption, which range from ~48.8(2) (for CO) to ~17(1) kJ mol⁻¹ (for Ar), indicate relatively weak Co–gas interactions compared to those characterized in molecular complexes. To place these values into context, η ad for CO in Co₂(dobdc) is about one third of the bond dissociation energy for the first CO in CpCo(CO)₂ (148(2) kJ mol⁻¹; Cp⁻⁻⁻cyclopentadienyl)⁴⁸

The trend in η ad values, CO > CO₂ > N₂ > CH₄ > O₂ > Ar, shows no clear correlation with the Co-Xgas distances obtained by single-crystal X-ray diffraction. As an approximate method to account for differences in the van der Waals radii among coordinated atoms, the sum of the ionic radius for high-spin cobalt(n) and the van der Waals radius of the coordinated atom (Δd) was calculated for CH₄, because the Co–C distance is between Co and the central atom of CH₄, not the coordinated hydrogen atoms, which makes it difficult to compare rigorously with the other gases. Although the structure of CO₂ in Co₂(dobdc) was collected at a higher temperature (150 K) compared to the other structures (90 and 100 K), the Co–OCO distance (2.23(4) Å) obtained at 10 K from powder neutron diffraction data shows that the Co–OCO distance does not shorten significantly at lower temperatures.

### Table 1

<table>
<thead>
<tr>
<th>Gas</th>
<th>d(Co–Xgas) (Å)</th>
<th>Δhₐd (Å)</th>
<th>Δhₐd (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2.215(6) (Co–C)</td>
<td>~0.230(6)</td>
<td>~48.8(2)⁴⁰</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.261(9) (Co–O)⁴⁹</td>
<td>~0.004(9)</td>
<td>~33.6(1)²⁹</td>
</tr>
<tr>
<td>N₂</td>
<td>2.236(6) (Co–N)</td>
<td>~0.059(6)</td>
<td>~20.3(6)</td>
</tr>
<tr>
<td>O₂</td>
<td>2.216(5) (Co–O)⁵⁰</td>
<td>~0.049(5)</td>
<td>~18.5(6)</td>
</tr>
<tr>
<td>CH₄</td>
<td>2.941(19) (Co–C)</td>
<td>~0.192(9)</td>
<td>~19.2(6)</td>
</tr>
<tr>
<td>Ar</td>
<td>2.932(9) (Co–Ar)</td>
<td>~0.307(9)</td>
<td>~17(1)</td>
</tr>
</tbody>
</table>

| Δd = the Co-Xgas distance minus the sum of the ionic radius for high-spin cobalt(n)⁵⁷ and the van der Waals radius of the coordinated atom. Δd was not calculated for CH₄ because the Co–C distance is between Co and the central atom of CH₄, not the coordinated hydrogen atoms, which makes it difficult to compare rigorously with the other gases. 

a Low-coverage differential enthalpies of adsorption were calculated at a loading of 0.5 mmol g⁻¹ using independent Langmuir fits to low-pressure adsorption isotherms. Although the structure of CO₂ in Co₂(dobdc) was collected at a higher temperature (150 K) compared to the other structures (90 and 100 K), the Co–OOC distance (2.23(4) Å) obtained at 10 K from powder neutron diffraction data shows that the Co–OOC distance does not shorten significantly at lower temperatures.²⁹

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![Fig. 4](image-url)  
**Fig. 4** Low-pressure gas adsorption isotherms for CO (yellow),⁴⁰ CO₂ (green),⁴⁹ CH₄ (gray), N₂ (dark blue), O₂ (red), and Ar (light blue) at 298 K (left). High-pressure gas adsorption isotherms for CO (yellow),⁴⁰ CO₂ (green), CH₄ (gray), N₂ (dark blue), and Ar (light blue) at 298 K (right). The filled circles and solid lines represent experimental data and corresponding Langmuir fits, respectively.
a $\text{CO}_2$–O distance of 3.29(7) Å. This indicates that both direct interaction of $\text{CO}_2$ with the metal site and weak secondary interactions contribute to its enthalpy of adsorption. Conceivably, these additional interactions cause $\text{CO}_2$ to be an outlier in the trend between $\Delta d$ and $-\Delta H_{\text{ad}}$. Care should be exercised, however, in inferring relative binding strengths by comparing crystallographic distances. Overall, these results show that multiple factors contribute to the binding energy of a molecule and that interaction distances alone cannot adequately represent all of these factors, especially when considering different molecules. More reliable correlations can be drawn if distances are compared between the same molecule interacting with the same metal center.

The high-pressure adsorption isotherms for $\text{CO}$, $\text{CO}_2$, $\text{CH}_4$, $\text{N}_2$, and $\text{Ar}$ at 298 K (Fig. 4) show that secondary adsorption sites become relevant at higher pressures, as the uptake for all gases eventually exceeds one gas molecule per cobalt site with increasing pressure. Qualitative comparison of the isotherms suggests that the secondary adsorption sites for $\text{CO}_2$ have the highest binding affinity with an uptake of \( \sim 2 \) $\text{CO}_2$ molecules per $\text{Co}$ at 40 bar. This likely results from the favorable interaction between the partial positive charge on the $\text{CO}_2$ carbon atom with linker oxygen atoms in the framework and intermolecular interactions between neighboring $\text{CO}_2$ molecules (Fig. S2†). In contrast, $\text{CO}$, $\text{CH}_4$, $\text{N}_2$, and $\text{Ar}$ have less pronounced adsorption at high pressures, with each showing an uptake of less than 1.5 molecules of gas per $\text{Co}$ at 40 bar. Perhaps the most striking comparison lies between $\text{CO}$ and $\text{CO}_2$. As a polar molecule, $\text{CO}$ has a stronger interaction with the cobalt(II) sites in the framework, which is clearly evident in its steeper low-pressure isotherm and more negative differential enthalpy of adsorption determined from low-pressure gas adsorption isotherms (Fig. 4). The result of site occupancies for multiple molecules. More reliable correlations can be drawn if distances are compared between the same molecule interacting with the same metal center.

Conclusions

The foregoing results highlight the unique advantages of metal–organic frameworks as robust crystalline matrices that facilitate unhindered access of guest molecules, enabling for example the study of guest interactions with open metal coordination sites within the framework pores. Rigorously air-free gas-dosing methods were developed to overcome the challenges associated with studying weakly binding gases in single crystals. Through these methods, the interaction of $\text{CO}$, $\text{CH}_4$, $\text{N}_2$, $\text{O}_2$, $\text{Ar}$, and $\text{P}_4$ with the metal–organic framework $\text{Co}_2(\text{dobdc})$ were directly observed by single-crystal X-ray diffraction. The resulting structures reveal the location of the primary, secondary (for $\text{N}_2$, $\text{O}_2$, and $\text{Ar}$) and tertiary (for $\text{O}_3$) binding sites for these gases within the framework. Moreover, examination of the CoII–gas distances shows that these CoII–gas interactions are distinctly weak compared to those found in molecular complexes. These unique interactions arise from the square pyramidal coordination geometry and the high-spin electronic configuration enforced by the framework on cobalt(II). As a result, this work represents the first report of the structural characterization of such species by single-crystal X-ray diffraction. Finally, differential enthalpies of adsorption determined from low-pressure gas adsorption isotherms corroborate the weak binding affinities inferred from the relatively long CoII–gas distances observed in the single-crystal structures, while high-pressure gas adsorption isotherms at 298 K show significant contribution from secondary binding sites at pressures beyond 1 bar. Altogether, these results establish in situ single-crystal X-ray diffraction as a valuable technique, which imparts not only a practical understanding of gas adsorption in porous materials, but also new insights into the underlying interactions that give rise to their adsorption behavior.

Ongoing efforts are focused on developing in situ single-crystal X-ray diffraction methods that can be routinely employed in the evaluation of metal–organic frameworks for specific applications, such as gas separations and gas storage. In particular, techniques are being explored to enable (i) mounting crystals that decompose in air, (ii) systematic determination of the dependence of site occupancies for multiple binding sites on guest loading, (iii) collection of diffraction data at lower temperatures to lessen thermal disorder, and (iv) structural assessment of the absorptive properties of these materials in the presence of gas mixtures. Furthermore, it can be envisioned that these techniques can be used to isolate and observe reactive intermediates in metal–organic frameworks, providing a way to determine the structures of species that have only been amenable to characterization by spectroscopy.

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Notes and references