



RESEARCH ARTICLE



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Dioxygen binding at a four-coordinate cobaltous porphyrin site in a metal–organic framework: structural, EPR, and O₂ adsorption analysis†

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The study of cobalt porphyrin interactions with O₂ is important owing largely to its relevance to biological heme-mediated O₂ transport and storage. The immobilization of a metalloporphyrin site in a metal–organic framework (MOF) enables the study of these interactions without interference from solution effects such as bimolecular reactions, axial ligation, and solvent/solute interactions involving the porphyrin ligand. Here, we investigate the reaction of O₂ with the four-coordinate cobaltous porphyrin complex in the MOF PCN-224Co. Single-crystal X-ray diffraction and electron paramagnetic resonance (EPR) spectroscopy of the oxygenated form, PCN-224CoO₂ reveals a five-coordinate low-spin Co^{III} center coordinated to an $S = 1/2$ superoxo (O₂^{•−}) ligand. Moreover, O₂ adsorption measurements on PCN-224Co reveal two distinct binding sites with adsorption enthalpies of $h_{\text{ads}} = -15.2(6)$ and $-10.2(3)$ kJ mol^{−1}. The former binding event is ascribed to ligation of O₂ at the open Co site, and the obtained value is considerably lower than those observed for cobalt porphyrin units in substituted proteins and model complexes that feature axial ligands. These results provide the first structurally-characterized five-coordinate Co–O₂ species, further highlight the importance of axial ligation in biological O₂ transport and storage, and demonstrate the ability of a MOF to enable isolation and study of a species that is highly unstable in molecular form.

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Introduction

Dioxygen adducts of molecular metalloporphyrin complexes have generated much interest for decades, owing to their relevance as models of proteins that carry out biological processes such as O₂ transport and catalytic oxidation chemistry.^{1–3} In particular, porphyrin iron, or heme, complexes serve as molecular models of the O₂-binding proteins hemoglobin and myoglobin.^{4,5} In addition to hemes, cobalt porphyrin complexes have also garnered significant interest, owing largely to the fact that the doublet electronic ground state of both their deoxy- and oxy-forms lends itself to electron paramagnetic resonance (EPR) analysis.^{6–8}

Studies of molecular metalloporphyrin dioxygen adducts, in particular those involving Fe, have been limited by the propensity of these complexes to undergo deleterious bimolecular condensation reactions to form thermodynamically favored and

kinetically inert oxo-bridged dinuclear species.^{9,10} These challenges have been partially overcome through introduction of bulky substituents onto the porphyrin scaffold in order to block access to one or both axial coordination sites of the metal center. Nevertheless, even in the presence of sterically encumbered porphyrin ligands, an axial ligand such as imidazole is necessary in order to prevent bimolecular condensation or dioxygen dissociation. Consequently, the characterization of five-coordinate, base-free oxyheme^{11–14} and oxycobalt porphyrin^{15–21} complexes in molecular form has been largely limited to spectroscopic studies in frozen solvent matrices at low temperature.

We recently reported the post-synthetic metalation of the porphyrinic zirconium MOF PCN-224 with Fe^{II} to give a four-coordinate ferrous heme complex within the compound PCN-224Fe^{II}.²² Subsequent addition of dry O₂ to this species at −78 °C gave a five-coordinate heme dioxygen adduct that was characterized by single-crystal X-ray diffraction and several spectroscopic methods. Moreover, O₂ adsorption measurements on activated PCN-224Fe^{II} revealed an Fe–O₂ binding enthalpy of $-34(4)$ kJ mol^{−1}. This value is nearly half of that commonly observed in ferrous heme model complexes and in myoglobin,^{2,23–25} and demonstrates the importance of an axial ligand in biological O₂ binding. Herein, we extend this work to cobalt by examining the O₂ binding of a four-coordinate cobaltous porphyrin within PCN-224 through single-crystal X-ray

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diffraction, EPR spectroscopy, and O₂ adsorption measurements. Specifically, we show that O₂ binds the coordinatively unsaturated Co center to give a five-coordinate Co^{III} superoxo species and that O₂ binding at a four-coordinate Co^{II} center is considerably weaker than has been observed in analogues with axial ligands, in line with our previous findings regarding four-coordinate Fe^{II}.

Results and discussion

The compound PCN-224Co was reported previously, as synthesized by carrying out the MOF assembly reaction from 5,10,15-20-tetrakis(carboxyphenyl)porphyrin cobalt(II).²⁶ We synthesized PCN-224Co through a different route, by post-synthetic metalation of the free-base porphyrin-containing PCN-224.²⁶ Here, soaking cubic single-crystals of PCN-224 with excess anhydrous CoCl₂ in DMF in the presence of excess 2,6-lutidine at 150 °C for 12 h resulted in the insertion of a Co^{II} ion into the porphyrin cavity to give, after activation, the compound PCN-224Co (**1**). Quantitative Co metalation of this material was confirmed by diffuse-reflectance UV/Visible spectroscopy and trace metals analysis (see Experimental section and Fig. S1†). In addition, an N₂ adsorption isotherm collected for **1** at 77 K provided a BET surface area of 3070(70) m² g⁻¹ (see Fig. S2–S4†). This surface area is similar to other values reported for PCN-224 derivatives,^{22,26} and therefore confirms that microporosity is retained upon post-synthetic metalation. This result provides another example of post-synthetic metalation of a MOF with cobalt.^{27–32}

Upon metalation of PCN-224 with Co, the compound retains its single crystallinity, enabling characterization of **1** by single-crystal X-ray diffraction. The structure of **1** features a four-coordinate Co^{II} center that lies squarely within the N₄ plane formed by the four pyrrole nitrogen atoms of the por-

phyrin ligand, along a crystallographic four-fold rotation axis (see Fig. 1 and S5 and Table S1†). The Co–N distance of 1.936(5) Å is in the range of 1.931–1.944 Å observed for molecular four-coordinate cobalt porphyrin complexes,³³ although considerably shorter than the distance of 2.156(1) Å reported

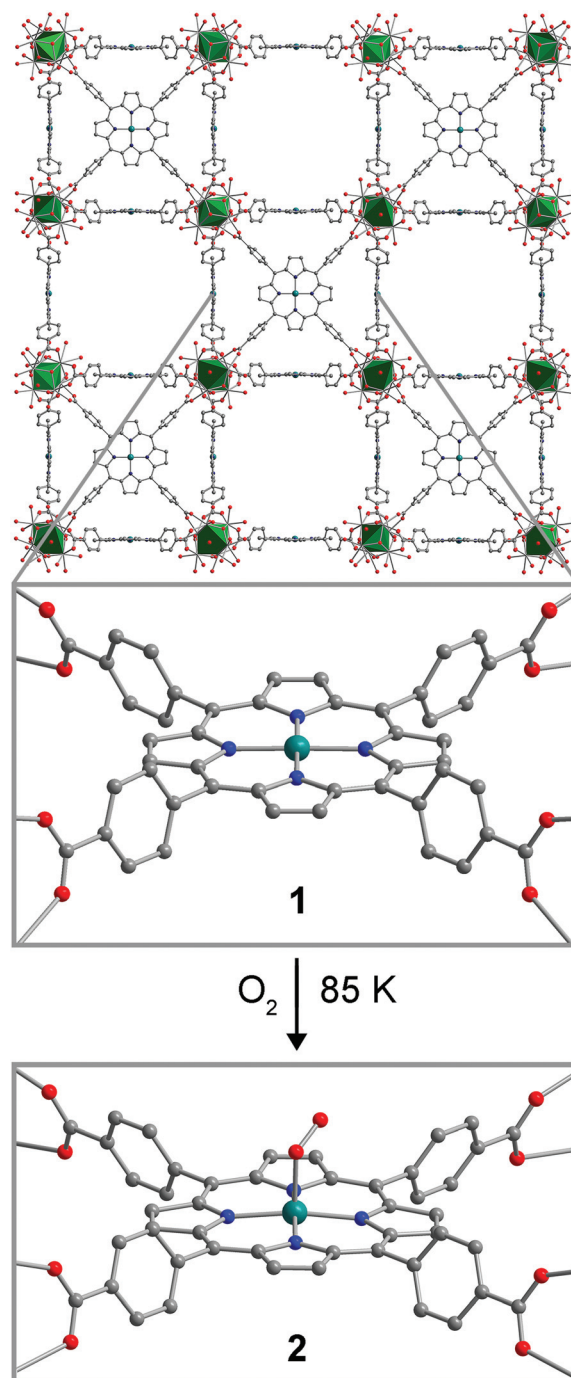


Fig. 1 Reaction of PCN-224Co (**1**) with O₂ at 85 K to form PCN-224CoO₂ (**2**). Green octahedra represent Zr atoms; teal, blue, red, and gray spheres represent Co, N, O, and C atoms, respectively; hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°) for **2**: Co–O 1.93(4), Co–N 1.974(5), O–O 1.30(4), Co...N₄ plane 0.15(4), Co–O–O 121(2).



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in the related MOF Hf-PCN-221(Co).³⁴ No significant residual electron density was present in the difference Fourier map, confirming the absence of ligation in the Co axial coordination sites.

A thin-walled boron-rich capillary containing a single crystal of PCN-224Co was exposed to 1 atm of dry O₂, cooled to 77 K and sealed under reduced pressure. Subsequent X-ray analysis of data collected at 85 K revealed the formation of a new species, PCN-224CoO₂ (2). The structure of 2 displays a five-coordinate Co center in a square-pyramidal coordination environment, with the O₂ ligand coordinated to the Co center in an η^1 , end-on binding mode (see Fig. 1, and S5 and Table S2†). The Co–O distance of 1.93(4) Å falls in the range of 1.92–1.93 Å previously reported for six-coordinate molecular Co–O₂ adducts, which have been described as Co^{III} superoxo (O₂^{•−}) species.^{35,36} The O–O distance of 1.30(4) Å and the Co–O–O angle of 121(2)° are also consistent with previously reported molecular species. Note, however, that these values should be regarded with caution owing to disorder associated with the crystallographic four-fold symmetry at the Co center. The Co^{III} center is displaced from the mean plane of the four pyrrole nitrogen atoms by 0.15(4) Å, with a corresponding elongated Co–N distance of 1.974(5) Å, and these metrics are consistent with five-coordinate, low-spin Co^{III} porphyrin species in molecular form.^{37,38} Notably, the displacement of the Co center is significantly smaller than that previously observed in the analogous MOF-based Fe species, which featured a displacement of 0.526(2) Å. This difference may be attributed to the smaller ionic radius of low-spin Co^{III} relative to low-spin Fe^{III}.³³ To our knowledge, 2 provides the first example of a structurally-characterized Co–O₂ adduct with a Co coordination number less than six.

In order to further probe the electronic structure of 1 and 2, continuous-wave X-band EPR spectra were collected on activated crystalline samples at 15 K. In a quartz tube under static vacuum, 1 exhibits an axial spectrum where each feature is split into an eight-line pattern, with this splitting arising due to hyperfine coupling of the unpaired electron to the $I = 7/2$ ⁵⁹Co nucleus (see Fig. 2, upper). To model these data, spectral simulations were carried out using the program Easyspin³⁹ and the Hamiltonian $\hat{H} = \mu_B H \cdot g \cdot S + I_{Co} A_{Co} \cdot S$, where μ_B is the Bohr magneton, H is the applied dc magnetic field, g the g -tensor, S and I_{Co} are the electronic and ⁵⁹Co nuclear spins, respectively, and A_{Co} is the tensor for hyperfine coupling to the ⁵⁹Co nucleus. The spectrum was best modeled with values of $S = 1/2$, $g_{\perp} = 3.271$, $g_{\parallel} = 1.783$, $A_{\perp Co} = 1122$ MHz, and $A_{\parallel Co} = 480$ MHz, with the parallel direction taken to be the axis normal to the porphyrin N₄ plane. Here, the $S = 1/2$ ground state and large g_{\perp}/g_{\parallel} ratio are consistent with previous reports of four-coordinate Co^{II} porphyrin complexes that were doped into solid-state diamagnetic matrices to prevent axial ligation.^{18–21} Moreover, the deviation of g_{\perp} from the free electron value of 2.0023 in cobalt porphyrin complexes is directly correlated to the axial perturbation of the Co center along the parallel direction,^{3,40–43} and the large deviation observed here for 1 corroborates the four-coordinate environment of the Co center as indicated by X-ray crystallography.

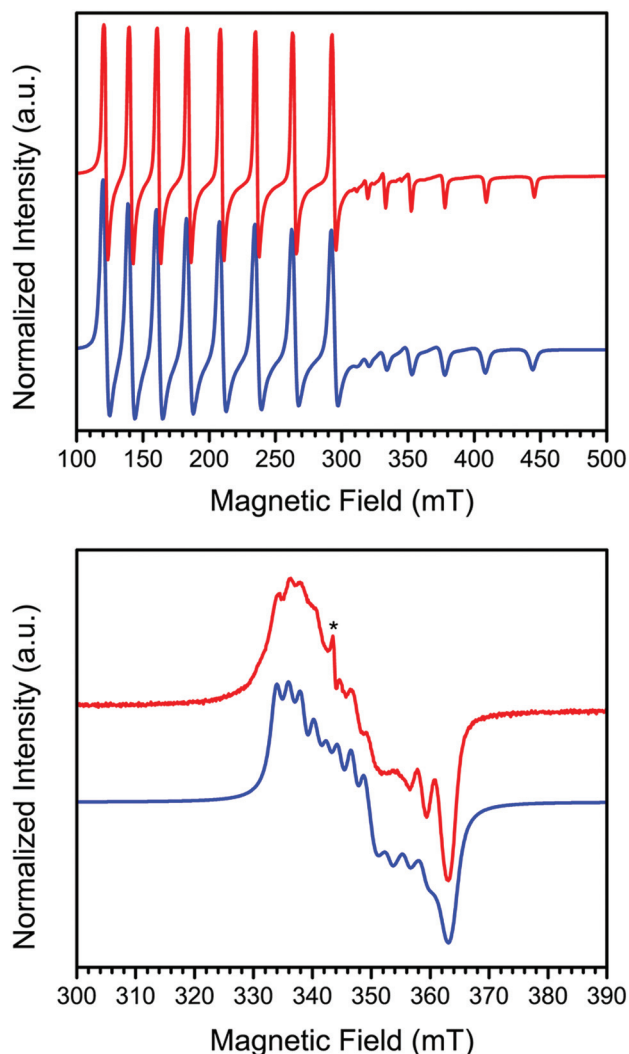


Fig. 2 X-Band EPR spectra for 1, collected at 15 K, under static vacuum (upper) and dosed with 1 atm O₂ at ambient temperature (lower). Red and blue lines correspond to experimental data and simulations, respectively, and the asterisk denotes a small amount of $S = 1/2$ impurity with $g = 2.00$. Microwave frequency = 9.632 GHz; microwave power = 6.31 mW.

The lower panel of Fig. 2 shows the spectrum of the oxygenated derivative 2, formed by dosing a sample of 1 with 1 atm of O₂ at ambient temperature followed by cooling to 15 K, which exhibits a rhombic spectrum with a significantly decreased degree of hyperfine coupling. The spectral features exist over a much smaller field range than in 1, indicative of reduced g -anisotropy. Simulating the spectrum according to the spin Hamiltonian given above provides the following parameters: $S = 1/2$, $g_x = 2.016$, $g_y = 1.973$, $g_z = 1.900$, $A_{xCo} = 60$ MHz, $A_{yCo} = 80$ MHz, and $A_{zCo} = 0$ MHz. The rhombicity of this spectrum is consistent with a bent Co–O–O angle, which precludes a symmetry rotation axis.

The significant decrease of hyperfine coupling to the Co nuclear spin suggests that the unpaired electron of the dioxygen adduct resides primarily on the oxy ligand. Accordingly, 2

is best described as containing the species $\text{Co}^{\text{III}}\text{-O}_2^{\cdot-}$, in other words a low-spin Co^{III} center bound by an $S = 1/2$ superoxo ligand. Indeed, this electronic structure is consistent with previous studies of dioxygen adducts of molecular porphyrin Co complexes that feature axial ligands at the Co center or solute and/or solvent molecules that engage in π interactions with the porphyrin ligand.⁴⁴ More specifically, one of the two singly occupied π^* orbitals of O_2 forms a σ bond with the Co d_{z^2} orbital to give a doubly occupied molecular orbital, while the other remains a singly occupied and non-bonding orbital that is predominantly an oxygen p orbital in character.^{7,45}

In order to examine the thermodynamics of O_2 binding in PCN-224Co, O_2 adsorption data were collected at selected temperatures. As depicted in Fig. 3 and S6,[†] the O_2 isotherm for **1** collected at 113 K exhibits an initial steep uptake at low pressure. As temperature is increased, the slope of this steep

region decreases until the isotherm becomes nearly linear at 195 K. In order to quantitate the O_2 binding, isotherm data at temperatures of 113, 141, 156, and 195 K were each fit to a dual-site Langmuir–Freundlich model (see Table S3[†]).^{22,46} Subsequent treatment of the variable-temperature isothermal data with the Clausius–Clapeyron equation revealed a differential enthalpy of adsorption of $h_{\text{ads}} = -15.2(6)$ kJ mol⁻¹ at low O_2 loading, followed by a gradual drop near 1:1 O_2/Co to a plateau at $h_{\text{ads}} = -10.2(3)$ kJ mol⁻¹. We respectively assign these distinct values to O_2 binding at the four-coordinate Co^{II} center and physisorption to the remainder of the MOF surface. The adsorption enthalpy of $-15.2(6)$ kJ mol⁻¹ is slightly lower than that of -17.8 kJ mol⁻¹ reported for O_2 binding at a five-coordinate $(\mu_4\text{-O})\text{Co}^{\text{II}}$ tetracarboxylate unit in PCN-9.⁴⁷

The Co– O_2 binding enthalpy of $h_{\text{ads}} = -15.2(6)$ kJ mol⁻¹ at low coverage is considerably weaker than values previously reported for cobalt porphyrins that feature axial ligands, both in Co-substituted globin proteins and in molecular model complexes.^{48–59} These values range from -33 kJ mol⁻¹ for a 1-methylimidazole-bound capped Co complex⁵⁶ to -68 kJ mol⁻¹ for cobalt octaethylporphyrin supported on a highly oriented pyrolytic graphite (HOPG) surface, where the HOPG acts as an axial ligand.⁵⁹ Indeed, the binding enthalpy of $h_{\text{ads}} = -15.2(6)$ kJ mol⁻¹ observed for **1** + O_2 falls in the range of 22–46% of these values. This difference is similar but even more pronounced than that observed for the O_2 binding of the four-coordinate heme in PCN-224Fe^{II}, which was approximately half of the values commonly observed for hemes with axial ligands,²² and further underscores the importance of axial ligand electron donation to the metal center to enable O_2 transport and storage.

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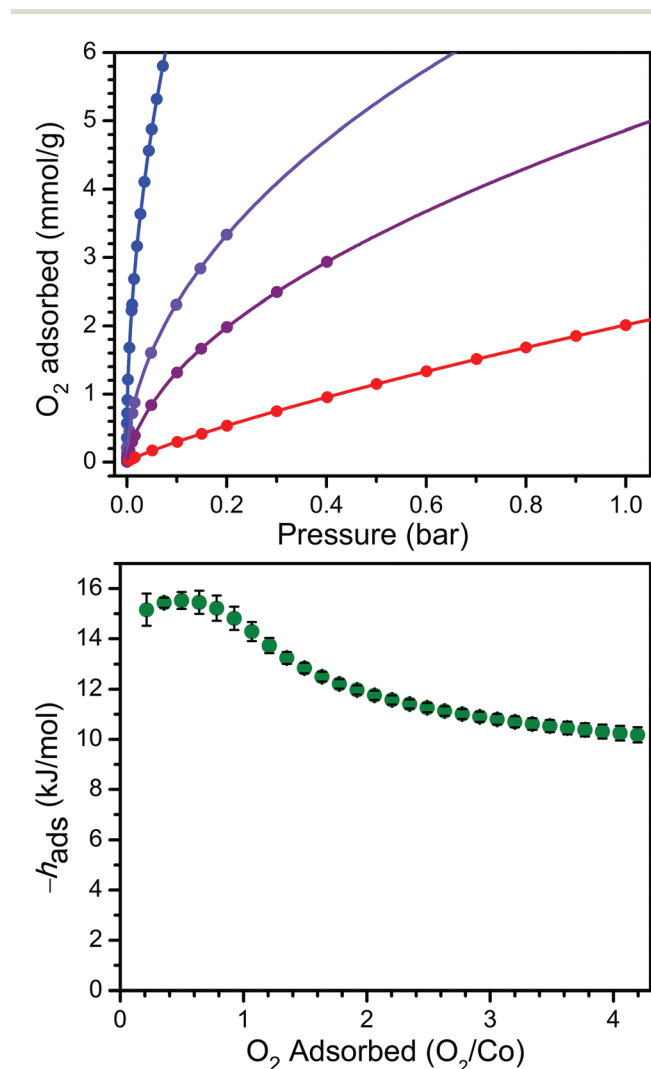


Fig. 3 Upper: O_2 adsorption data for **1** at 113, 141, 156, and 195 K (blue to red gradient). Circles represent data, and solid lines correspond to fits using a dual-site Langmuir–Freundlich model. Lower: O_2 differential enthalpy of adsorption curve for **1** as a function of amount adsorbed. Green circles represent data, and error bars are shown in black.

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