On the elusive nature of Oxygen binding at coordinatively unsaturated 3d transition metal centers in metal-organic frameworks

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Abstract

Using gas sorption measurements at ambient temperature and *in situ* neutron powder diffraction methods, we have studied the interaction strengths and coordination geometries of O₂ and N₂ near the non-occupied coordination site (open metal site) in the isostructural MOF structures of the CPO-27-M/M-MOF-74 series (with M=Co, Ni, Mn and Cu). Our experimental observations are compared to periodic quantum chemical model calculations. Contrary to recent computational studies, our results, both experimental and theoretical, unequivocally suggest rather weak interactions between the M(II) coordinatively unsaturated centers and the adsorbate molecules, being mainly dispersive and electrostatic in nature, and excluding significant orbital charge transfer effect that could lead to superoxide/peroxide formation. The calculated binding energies appear in good agreement to the measured isosteric heats of adsorption in the range of 10-20 kJ/mol. These, relatively weak host-guest interactions, lead to a tilted end-on geometry in all of the investigated M(II)-guest molecule adducts.

Introduction

Binding, activation, transport, and controlled release of molecular oxygen are of vital importance for aerobic organisms where the processes typically operate assisted by metalloenzymes^{1,2}. Not less important is the role of adsorbed molecular oxygen in its electron

scavenging role at the surface of photo catalysts such as CeO_2 ³, the TiO_2 allotropes anatase and rutile^{4,5}, as well as $\text{CeO}_2/\text{TiO}_2$ hybrid nanomaterials⁶. Direct oxidation of light hydrocarbons to alcohols is another quite tempting and attractive catalytic application of bound O_2 .⁷ In addition, solid state gas storage via molecular adsorption has recently attracted scientific attention.⁸ Another related and not less important issue is the separation of molecular oxygen from other molecules that are similar in weight and size, such as N_2 . Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), attract continuously growing attention due to their highly crystalline, porous structures, associated with high specific surface areas. MOF compounds that remain intact after removal of the solvent have generated a lot of interest for their potential applications in fields such as catalysis, gas storage, and gas separation.⁹⁻¹¹ The permanently porous isostructural MOF series CPO-27-M (Figure 1), also denoted $\text{M}_2(\text{dhtp})$, $\text{M}_2(\text{dobdc})$ ($\text{dhtp} / \text{dobdc} = \text{C}_8\text{H}_2\text{O}_6^{4-}$) or M-MOF-74, where $\text{M} = \text{Co}$,¹² Ni ,¹³ Mg ,¹⁴ Mn ,¹⁵ Zn ,¹⁶ Fe ,^{17,18} Cu ,¹⁹⁻²¹ and Cd ,²² has particularly useful properties in adsorption related applications due to the large number of coordinatively unsaturated metal centres which are present in the desolvated form.²³ This leaves the metal centre with a non-occupied coordination site (open metal site) available for interaction with adsorptives, and renders them potentially interesting for separation of O_2 from air.^{12,23} Intriguingly, two bound O_2 species have been recently detected in the Fe member of the CPO-27 (MOF-74) family.¹⁷ A reversible superoxido -complex with thermal stability about 40-60 kJ/mol has been anticipated below 200 K, while an irreversible Fe-peroxide, associated with oxidation change of the Fe from +2 to +3, is the stable form near room temperature.^{17,18} Recent computational studies on the binding of O_2 and N_2 , as well as their separation, including the other members of the CPO-27 MOF family^{26,27} suggested very strong binding of O_2 on the open metal sites at the M(II) metal centers, with an intriguing trend in the O_2 binding energies increasing in the following order: $\text{Zn} < \text{Cu} < \text{Ni} < \text{Co} < \text{Fe} < \text{Mn}$. The computed binding energy for N_2 in the same structure was found to be much lower, which would point towards great potential for application of the material in O_2/N_2

separation by O₂ gettering. The binding energy for N₂ was reported to be a dramatic 5 times lower than that of O₂ in the case of Mn(II). In fact, such a large binding energy, of the order of ca. 100 kJ mol⁻¹ O₂ and a significantly elongated O₂ bond of 1.4 Å suggests facile oxidation of Mn(II) to Mn(III) and the formation of a side-on Mn(III)-O₂²⁻ peroxido complex which could offer some particularly interesting applications in heterogeneous catalysis. The experimental and theoretical findings mentioned above motivated us to explore the capability for binding and activation of molecular oxygen by several open shell 3d metal ions in square pyramidal coordination. The family of isostructural porous MOFs CPO-27-M, with its rigid, thermally relatively stable structure, offers an excellent experimental frame for such studies. To determine the corresponding O₂ and N₂ isosteric heats of adsorption, Q_{st}, in the Mn, Co, Ni, and Cu and Zn materials, we performed adsorption isotherm measurements at a series of ambient temperatures. On a microscopic level, the corresponding O₂ adducts were investigated by means of *in situ* neutron powder diffraction, which is compared to the adsorption behavior at 87 K. Additionally, the O₂ and N₂ binding energies and corresponding adsorbate complex stereochemistry were elucidated with the aid of DFT based computational studies.

Methods

Sample synthesis and characterisation. CPO-27-M (M=Mn, Co, Ni, and Cu and Zn) were synthesized and pre-treatment for gas adsorption studies was performed according to already published procedures¹²⁻²¹ (details are available in the Supplementary Information). The identity and purity of the materials were ascertained by powder x-ray diffraction measurements in Bragg-Brentano geometry using monochromatic Cu K_{α1} radiation on a Bruker AXS D8 Advance instrument. Gas adsorption measurements were performed using a BELSORP-max instrument equipped with a low pressure transducer and a turbomolecular pump, allowing measurements with high precision, beginning from very low pressures ($p/p_0 = 10^{-8}$).

Figure 1. The empty structure of CPO-27-M. The metal cation originally coordinated to a solvent molecule in the solvated form changes on desolvation from octahedral to square pyramidal environment. The now available coordination site can interact with a variety of guest molecules.

The samples were prepared under inert conditions and transferred to the sample cell in a glove box. Prior to the measurements the samples were pre-treated at 453 K (Zn), 423 K (Ni, Mn and Co) and 393 K (Cu) for 24 hours in a dynamic vacuum. Textural information was obtained from N₂ measurements at 77.35 K. For measurements in the range 273–298 K, the temperature was controlled by immersion of the sample cell in an external water bath whose temperature was controlled using a Julabo F25-ME refrigerated/heating circulator with external temperature sensor.

Neutron Diffraction. A desolvated CPO-27-Mn sample (0.80 g) was measured on the HRPT²⁸ instrument (neutron wavelength 1.886 Å). The same material was subsequently measured on the DMC²⁹ instrument (neutron wavelength 2.45 Å) dosed *in situ* with 0.33, 1, and 2 O₂ per Mn ion. CPO-27-Co (0.80 g) was measured on the HRPT instrument in desolvated state and loaded *in situ* with 0.5, 1 and 2.4 O₂ per Co center. Both instruments are installed at the SINQ neutron source, PSI, Villigen, Switzerland. Samples of CPO-27-Cu and CPO-27-Ni dosed with 1 O₂ per Cu, and with 0.5, 1, 1.8, and 2.6 O₂ per Ni, as well as 1 N₂ per Ni, were measured on the E9 instrument³⁰, at the HZB, Berlin, Germany. Desolvated CPO-27-Ni (1.02 g) and desolvated CPO-27-Cu (0.40 g) were each loaded in vanadium sample containers of 8 mm diameter and attached to a centre stick

equipped with a gas capillary, using a He-filled glove bag. Prior to the neutron measurements all samples were additionally evacuated at 453 K for Mn and Ni, 473 K for Co, and 393 K for Cu, for 12 hours in dynamic vacuum with the use of a turbomolecular pumping unit. The O₂/N₂ dosing procedures were performed between 200 and 80 K. Adsorption equilibration periods of minimum 30 min were applied for each loading. The neutron diffraction patterns were measured at around 20 K and below as indicated further in the text. After the end of the final neutron measurement, the adsorbed oxygen was desorbed into a calibrated volume at room temperature. The system was monitored for about 30 min in each case to check for possible stronger reaction at room temperature, due to possible temperature activated chemisorption. However, there was no observable irreversible binding in any of the tested materials, in contrast to the previously reported peroxide formation in the Fe-material.^{17,18} Crystal structure refinements, based on the collected powder diffraction data, were performed with the use of the Fullprof suite of programs.³¹ The refinement of the CPO-27-Mn wide angle data collected on the HRPT instrument was used as a starting point for the DMC data refinements, in which the atomic displacement parameters of the framework atoms were kept fixed. All other parameters, including all atom coordinates and guest molecule atoms thermal factors, as well as peak shape parameters were refined for all DMC data. The resulting Rietveld refinement plots are shown in Figures S58-S72 and the variation of the corresponding lattice cell parameters, as functions of the guest loading, are depicted in Figure S73.

DFT Calculations: Quantum chemical model calculations on the structure and thermodynamics of the different species adsorbed on CPO-27 materials were performed within the frame of the Density Functional Theory (DFT) and the Generalized Gradient Approximation (GGA), Perdew-Berke-Ernzerhof (PBE) functional with the Projector Augmented Wave (PAW) formalism, as implemented in the ABINIT v.7 software.^{32,33} To prevent self-interaction related errors in the description of the open-shell 3d electrons, we included a standard amount of 25% Hartree-Fock exchange energy in the functional form,

as implemented in ~~Abinit~~ABINIT, only on the metal ion 3d and N and O atoms 2p electrons. Full geometry optimisations of the corresponding 54 atom primitive unit cells of the desolvated materials were carried out, retaining only the translational symmetry of the original space group. The primitive cells were selected so as to be able to efficiently model the corresponding low temperature magnetic structures, containing a chain of 3 metal centers, one with two metal centers and another with one for the desolvated materials³⁴, as shown in Figure 2, and the same plus one guest molecule (1/6 per M(II) ion) per primitive unit cell for modelling the adsorbates. A 2×2×2 supercell representation of this structure is shown in Figure 3, clearly indicates there was no significant deviation from the R-3 symmetry due to the geometry optimisation in the P1 space group. In each case we used a 900 meV energy cut off on the plane wave basis. Total energies were computed only at the Brillouin zone centre. The calculations were checked for convergence with respect to the guest molecule binding energy which appeared of the order of 0.5 to 1 kJ mol⁻¹ for the different metals and with respect to plane wave cut off and k-sampling (compared to 1000 eV on the cut off energy and for a 2×2×2 shifted k point grid). Spin polarized calculations were performed for all cases, starting with the AFM1 magnetic order in the case of Fe, Co, and Ni, and AFM2 state for the Mn- and Cu-materials^{11,34}. The AFM1 structure has ferromagnetically ordered spins within one –O–M(II)–O– helical chain, but ions from neighbouring chains are antiferromagnetically ordered. The AFM2 order stands for both intra and interchain antiparallel spin orientations.^{11,34} In all cases the magnetic moments were aligned along the helical chain direction coinciding with c-axis of the unit cell in the present primitive cell choice. Geometry convergence criteria were set to 0.01 eV/Å during each structure optimisation. The corresponding energy convergence was of the order of 10⁻⁸ eV. The desolvated cells were fully relaxed with no symmetry restrictions, i.e. in space group P1 (Figure 2), while the ones with guest species attached to one of the metal centres

were isotropically relaxed i.e. the lattice vectors were allowed to change their magnitudes while angles between them were kept fixed at the values of the corresponding relaxed desolvated cell. All atomic coordinates were relaxed at each step. This strategy was adopted to model random adsorption, that is no ordering allowed for low adsorbate loadings, at the otherwise crystallographically equivalent metal centres, which should anticipate only some rather small and isotropic (i.e. cell angles kept fixed) unit cell deformation. The total energy of each guest species, with geometry relaxed under the same conditions as above, was evaluated in a box of $16 \times 16 \times 16 \text{ \AA}^3$ size. Dispersion interactions were taken into account during all geometry optimisation procedures, using the empirical correction of Grimme³⁵, denoted as GD2 further in the article. In selected cases, for the Co and Ni-compounds, we also performed the calculations for the conventional 54 atom rhombohedral cell, in space group R-3, as in previous works,²¹ applying the same chemistries and convergence criteria as above, on a $2 \times 2 \times 2$ Monkhorst-Pack shifted k-point grid. These were extended to higher loadings corresponding to 1, 2, and 3 O_2 molecules per Co (or Ni) ion to be able to compare to the corresponding experimental neutron diffraction structures. In all investigated cases the triplet ground state of the O_2 molecule remained lower in energy than the first excited singlet state in the corresponding adsorbed states as in the free state, along with the unchanged (with respect to the guest free compound) high spin state of the adsorbent structure. For N_2 only the ground singlet molecular state was used in all initial guesses.

Figure 2. The CPO-27-M(II) primitive unit cell used with no symmetry restrictions. Adsorption of guest molecules was probed at the central ion in the chain containing three metal centers.

Figure 3. DFT, PBE0 optimized structure of CPO-27-Ni + 1/6 O₂ per Ni in a 2x2x2 super cell representation for a better visualization of the complete porous MOF structure. There is one O₂ molecule at every three Ni(II) ions in a chain, at every other chain.

Results and Discussion

O₂ and N₂ Gas sorption

We performed gas sorption measurements of nitrogen at 77 and 87 K and of oxygen at 87 K to determine the maximum uptake of the materials. Measurements in the temperature range 273-298 K were used to derive the isosteric heat of adsorption for oxygen and nitrogen.

The nitrogen sorption isotherms at 77 K and 87 K show the characteristic trend of the CPO-27 series compounds with their large number of coordinatively unsaturated metal sites. The first molecule of the adsorptive is adsorbed at the metal centre at significantly lower pressures than the second molecule which is visible in the form of steps in the adsorption isotherm (Fig. 4). Analogous steps have been observed for other adsorptives, such as H₂, CH₄, and CO₂.^{11,35,36} All of the CPO-27 compounds investigated here have a maximum uptake of 2.2-2.3 molecules nitrogen per formula unit, except for CPO-27-Mn, for which another step occurs at p/p_0 corresponding to ~2.2 molecules

adsorbed per formula unit, with a final uptake of ~ 2.6 molecules N_2 per formula unit. The unit cell volume of the empty structure of CPO-27-Mn is 5-8 % larger than that of CPO-27-Ni and Co, and a small change in unit cell parameters at this p/p_0 apparently allows more nitrogen molecules to occupy the centre of the channel in CPO-27-Mn than in the other compounds. (See below for structural details of the different adsorption sites in CPO-27.)

We observe a larger number of molecules of oxygen adsorbed in all CPO-27 compounds investigated here at 87 K, compared to the nitrogen uptake (at the same temperature and at 77 K). This correlates to the size of the adsorptive molecules. The kinetic diameter of the dioxygen molecule is slightly smaller than that of dinitrogen. The maximum uptake is in the range 2.9-3.3 molecules O_2 per formula unit for CPO-27-Ni, Co, and Mn, and ~ 2.25 and ~ 2.6 molecules O_2 per formula unit for CPO-27-Cu and Zn, respectively. Intriguingly, the O_2 isotherms for the cobalt, nickel, and manganese compound actually show three well-defined steps. Apparently, the ~ 3 molecules O_2 are adsorbed in consecutive order, which indicates a clear separation in adsorption enthalpies of the three different adsorption sites. The difference between the second and third step is still observable, but much less pronounced for CPO-27-Zn and Fe. In contrast, CPO-27-Cu shows no significant difference in slope of the isotherm for the first and second oxygen molecule adsorbed, indicating energetic equivalence for the two adsorption sites. This is in good agreement with the observation that there is no essential thermodynamic effect of the coordinatively unsaturated metal site on hydrogen adsorption in the copper compound.²¹ Note, however, that there is a step in the nitrogen isotherms at 77 and 87 K. In any case, it is significantly less pronounced than in the other homologues.

The O_2 and N_2 isotherms at 87 K reveal that the adsorption of the first two molecules per formula unit of either gas occurs at almost the same pressure for CPO-27-Co, Ni, and Mn, and only small differences are observed for Zn and Cu. This observation is already an indication that there is no significant difference in interaction strengths between O_2 or N_2 and the respective CPO-27

compound at 87 K. This picture changes somewhat around ambient temperature. In the temperature range 273-298 K all five compounds adsorb to varying degrees more nitrogen than oxygen at a given temperature and pressure (Figures S1-S5), opening up for the possibility that CPO-27-M (M = Co, Ni, Mn, Zn and Cu) might preferentially bind N₂ over O₂. The difference in uptakes is largest for CPO-27-Ni and -Co, whereas the difference is much less for both CPO-27-Mn and -Zn, while for CPO-27-Cu there is hardly any difference observed. Overall, CPO-27-Ni has the largest uptake of both N₂ and O₂.

Figure 4. Nitrogen and oxygen sorption isotherms for a) CPO-27-Co, b) CPO-27-Mn, c) CPO-27-Ni, d) CPO-27-Cu, e) CPO-27-Zn (circles: N₂ at 77 K, squares: N₂ at 87 K, diamonds: O₂ at 87 K); f) Comparison of the oxygen sorption at 87 K for the CPO-27 series (data for CPO-27-Fe was taken from ref. 18).

The overall uptake of both nitrogen and oxygen is low for all samples at these temperatures and pressures, but it is particularly low for CPO-27-Cu and Zn, for which the sorption data is not of excellent quality, despite using a larger amount of sample. The data for all the five members of the series and for both nitrogen and oxygen adsorption were fitted using the single-site Langmuir-

Freundlich model (Equation 1, Figures S6-S55, and Tables S1-S13 in the Supplementary Information). The fitting results were then used in the calculation of the isosteric heat of adsorption. The experimentally derived isosteric heats of adsorption, Q_{st} , for O₂ and N₂, averaged for loadings in the range 0–0.1 guest molecule per metal center are presented in Table 1. There is little data in the literature available for comparison: For the case of Cu(II) in HKUST-1, detailed O₂ adsorption data has been measured and the corresponding Q_{st} estimated as 9.7 kJ/mol⁸, which is slightly less than the value of 13.5 kJ/mol determined here for CPO-27-Cu (Table 1). It is of course not certain that the measured energetics at ambient temperatures, taking into account the low Q_{st} values, correspond to adsorption only on the metal ions. More likely, they reflect the isosteric heat of adsorption averaged over all adsorption sites the adsorbate molecule can dynamically occupy at these temperatures. Thus, binding at the secondary site, predominantly due to interaction with oxygen atoms from the organic linker, and at a potential tertiary site, presumably represented by the phenyl ring of the organic linker, also might contribute significantly to the adsorption state in the case of CPO-27, and the measured isosteric heats reflect the respective contribution of the three main sites. The magnitude of each interaction may be estimated by comparison with similar interactions in the literature. It has been reported that isosteric heat of adsorption of O₂ at room temperature in activated carbon is in the range 11-13 kJ/mol³⁸, which might be indicative for the binding affinity at the phenyl ring linker sites. Somewhat lower, at 12 kJ/mol O₂, is the more recently measured Q_{st} in Faujasite type zeolite NaX⁴⁰. A value of only 10 kJ/mol for low coverage isosteric heat of adsorption of O₂ at room temperature has been reported recently for a highly porous Al-soc-MOF-1 material⁴¹.

Table 1. Low adsorbate concentration average, ambient temperature isosteric heats of adsorption of O₂ and N₂ in CPO-27-M(II), M(II) = Mn, Fe, Co, Ni, and Cu. Distances, where available, are obtained from analysis of the neutron diffraction measurements.

Metal Guest Molecule	Mn	Co	Ni	Cu	Zn
	exp., RT Q_{st} , kJ/mol, d_{M-X} , Å				
O ₂	13.3(4), 2.80(4)	15.6(3), 2.46(1)	17.0(4), 2.23(3)	14(1), 3.06(6)	9(1), -
N ₂	16.1(3), -	21.2(5), -	23.7(5), 2.30(1)	13.5(3), -	13(1), -

Table 2.

Computed guest molecule binding energies and M(II) – nearby guest molecule atom distances
For CH₄ the distance between the metal center and the carbon atom is given.

Guest Metal ion	O ₂	N ₂	NO	CO	CH ₄
	E_b , kJ/mol, d_{M-X} , Å				
Mn	35.7, 2.105	18.4, 2.630	57.9, 2.103	37.4, 2.350	27.0, 3.022
Fe	28.9, 2.200	16.3, 2.494	78.5, 1.908	44.9*, 2.225	27.3, 2.960
Co	19.9, 2.264	18.4, 2.547	53.1, 2.156	43.4, 2.163	25.4, 3.003
Ni	20.1, 2.235	18.8, 2.449	58.4, 2.107	49.1, 2.104	26.2, 2.988
Cu	12.6, 2.932	13.6, 2.829	17.1, 2.289	26.2, 2.309	21.7, 3.014
Zn	16.6, 2.614	17.6, 2.701	39.0, 2.329	36.4, 2.278	27.0, 2.973

*Values calculated assuming AFM1 magnetic order on the Fe(II) ions in the desolvated framework, but. AFM2 order in the CO adsorbed material as suggested by experimental studies.⁴¹ See text for details.

Table 3. Computed guest species intramolecular bond distances and metal centre-diatomic species bond angle. Only the average C-H distance is given in the case of CH₄. Intramolecular PBE0(GD2) bond lengths and the corresponding experimental values for each guest molecule in the free state are given in the last row of the table.

Guest Metal ion	O ₂	N ₂	NO	CO	CH ₄
	X-X bond length, Å M-X-X angle, deg.				
Mn	1.290, 122.1	1.140, 141.7	1.291, 122.1	1.147, 149.7	1.13
Fe	1.283, 123.7	1.140, 146.0	1.225, 143.9	1.150, 157.0	1.10
Co	1.270, 122.1	1.139, 143.3	1.202, 122.1	1.149, 154.1	1.10
Ni	1.272, 120.8	1.140, 142.3	1.202, 120.4	1.148, 152.5	1.10
Cu	1.255, 119.0	1.139, 137.8	1.198, 119.5	1.147, 146.1	1.10
Zn	1.263, 109.0	1.140, 141.1	1.198, 124.6	1.146, 150.9	1.10
Free state	1.254, 1.207*	1.140, 1.098*	1.192, 1.150*	1.149, 1.128*	1.091, 1.087*

* *Tables of Interatomic Distances and Configuration in Molecules and Ions*, L.E. Sutton, ed., London: The Chemical Society, 1958.

A higher value of 16.3 kJ mol⁻¹ has been measured for O₂ adsorption in silicalite³⁹, which may be used as a reference for O₂ adsorption at the oxygen atom environment – the secondary O-sites in our case. The isosteric heats determined in this way, are indicative of the physisorption nature of the

binding of both N₂ and O₂ in the presently and previously^{8,41} studied porous MOF materials, which is also consistent with the theoretical and neutron scattering results presented below. Their magnitudes are comparable to the corresponding latent heats of O₂ and N₂ of 6.8 and 5.6 kJ/mol, respectively.

Computational Results

Computed binding energies and geometries for the adsorption of guest molecules at the M(II) centers in the CPO-27 framework are listed in Tables 1 – 3. For Mn(II), at a 2×2×2 k-point grid the computed binding energy decreased only by a negligible fraction from 35.7 to 35.2 kJ mol⁻¹ for the corresponding Gamma point calculation presented in Table 1. Hence, the binding energies at the other M(II) ions were calculated only at the Gamma point. As seen in the data in Table 1, for all measured materials, the interactions between the corresponding coordinatively unsaturated metal center and the guest are either stronger for N₂ than O₂, or very similar, contrary to the previous theoretical DFT, PBE results.^{26,27} Using both pure GGA, PBE and GGA+U corrected PBE functional in our study to calculate binding energies for O₂ at the Mn(II) site also lead to values in excess of 100 kJ mol⁻¹. We therefore attempted a different approach by introducing 25% Hartree-Fock exchange in the energy functional, acting only on the 3d electrons of the corresponding metal ion and the 2p electrons of both O₂ and N₂. This resulted in a significant reduction in the computed binding energies, especially for O₂, but did not completely remove the known DFT associated electron delocalization and self-interaction effects, which are particularly strong in open shell systems.⁴² Within the same theoretical model frame as for oxygen and nitrogen, we also estimated the interactions at the M(II) centres of the CPO-27 (MOF-74) framework with NO, CO, and CH₄ guest species, Tables 2, and 3. In the case of CO adsorbate at Fe(II), even at the low concentration of 1CO per 6 Fe(II), probed in our model, the minimum energy structure becomes the one with AFM2 order as suggested by in situ magnetic measurements.⁴³ It should be noted that in the desolvated state, the AFM1 order is more stable by about 7.5 meV/Fe(II) than the FM order. Somewhat counterintuitively, with the other strong ligand, NO, the AFM1 order remained in the minimum energy state. The magnetic order for desolvated and loaded structures remained always AFM1 for Co(II) and Ni(II), and AFM2 for Mn(II) and Cu(II), with negligible energy difference to the AFM1 order for the later, indicating that the framework would not show magnetic ordering at very low temperatures. As for the low fractional loading results obtained in space group P1, for the stoichiometric loadings of 1 guest molecule per 1 metal center, probed for the Co- and Ni-

frameworks, where the R-3 primitive cell was used, the O₂ moments aligned again antiferromagnetically with respect to the neighbouring M(II) ion moment.

Table 5. Computed magnetic moments on Co(II) and Ni(II) ions for the desolvated and loaded with different amounts of O₂ in the CPO-27 structure in its conventional R-3 space group rhombohedral setting. Magnetic moments on the O atoms of the O₂ molecule are listed as well. Negative sign stands for antiparallel alignment of the O atom magnetic moment with respect to the neighboring Co or Ni ion magnetic moment.

Metal ion	empty	+1O ₂	+2O ₂	+ 3O ₂
	μ_{Bohr} for M(II) and on each O-atom of the O ₂ at sites I, II, and III			
Co	2.73	2.71;	2.71;	2.71;
O ₂ on Co		-0.79, -0.65	-0.79, -0.65;	-0.79, -0.64;
O ₂ on O-ligands			0.82, 0.82	0.82, 0.82
O ₂ in pore inter.				0.82, 0.82
Ni	1.70	1.78;	1.78;	1.78;
O ₂ on Ni		-0.81, -0.69	-0.81, -0.69;	-0.81, -0.69;
O ₂ on O-ligands			0.82, 0.82	0.82, 0.82;
O ₂ in pore inter.				0.82, 0.82

The second and third O₂ guest molecule atom magnetic moments, adsorbed near secondary and tertiary sites were both found antiparallel to the ones in the first O₂ molecule at the primary site, Table 5. Although the computational accuracy of our model may not be high enough to reliably predict such tiny energetic effects, in the case of Fe(II) it has been experimentally observed, via macroscopic magnetic measurements, that strong ligands do alter the magnetic order, while weak ligands only reduce the magnetic coupling constants.⁴⁴ With respect to the focus of the present work, namely the adsorption thermodynamics of the investigated guest species, and related guest – M(II) adduct structure, although GGA functionals with exchange part closely matching exact exchange such as revPBE⁴⁵ and RPBE⁴⁶ would be also interesting to test due to their relatively low computational cost, hybrid functionals, such as the traditionally used for adduct thermochemistry computations B3LYP⁴⁷, on the other hand, might give better agreement to experiment, but remain outside our computational resources at present. The deficiency of pure DFT functionals in predicting binding energies of adduct molecules at metal centers, however, is well known and is due to underestimation of the HOMO – LUMO gap of the resultant system. This leads to a false hybridization of the guest molecule frontier orbitals with metal 4s and 3d states, with the later particularly strong in open shell systems, and especially on undercoordinated metal centers such as in porous MOFs and zeolites. The problem is usually tackled by adding a certain portion exact exchange to the density functional as in the hybrid functional e.g. B3LYP, PBE0. The triplet ground state molecule O₂ bound to an open shell 3d metal ion constituent structure investigated here seems like a prominent example. However, despite the use of 25% HF exchange in the energy functional

on frontier metal ion and guest species orbitals, the overestimation of the binding energy on metal ions with unpaired electrons in the d shell is still observable in the dependence of the experimental Q_{st} and the computed E_b on the M(II) ion (Figure 5). As can be seen in the same figure, we have obtained quite good agreement for N_2 , where ca. 90 % of the computed binding energy is due to dispersive interactions, represented by the Grimme D2 term.

Figure 5. Isosteric heat of adsorption, Q_{st} , and computed binding energy, E_b , for N_2 on the left block, and O_2 , right block, vs. M(II) in the CPO-27 structure. GD2 is the Grimme D2 dispersion component in the binding energy.

On the other hand, the computed binding energy for O_2 on the half filled 3d shell Mn(II) is overestimated by more than a factor of 2, with all the error due to an obviously artificial chemical interaction, leaving the dispersive term below 50 % of the total binding (Fig. 5). It would be of some fundamental and practical interest to compare the results of these in part PBE0⁴⁸ hybrid functional results, being already reasonably close to the experimental results, to those of all electron hybrid DFT and higher level ab initio calculations. When such specific open shell complex cases are not treated with care, errors in the pure DFT estimated binding energies may amount to an order of magnitude²⁷ as compared to experimental data. Notably, non-periodic cluster methods, combined with the meta GGA local functionals M06-L and M11-L provide reasonable agreement to experiment with best match for the hybrid version (27% HF exchange) M06, in the case of the Fe(II)-based material.⁴⁹ However, no test has been made for the Mn(II) analogue, for instance, where the measured isosteric heat of O_2 adsorption is much smaller to the one measured in the

Fe(II) case, which is difficult to rationalize if we assume that in both cases the hosts always remain in their high spin states, no change in the corresponding oxidation states occurs, neither significant charge transfers processes are evident, with the guest O₂ also remaining in its triplet ground state as in the free state. One would then expect that the interactions at the pentacoordinated Fe(II) center would also be dominated by electrostatic and dispersive contributions which are unlikely to exceed the binding at Co(II) or Ni(II) by much. However, it should be pointed out that, in contrast to the O₂ sorption energetics, DFT+U studies on CO adsorption at M(II) centers in the CPO-27 structure have achieved quite accurate binding energies.⁴⁹ Our computed PBE0-like values match their experimental values⁵⁰, with the largest deviation of a few kJ/mol for Mn(II), possibly due to the more rigid approach used by us, adding a fixed amount of HF exchange in all of the tested cases. Going further to the NO molecule with doublet ground electronic state, we observed stronger binding at all studied M(II) ions with respect to CO, except for Cu(II), for which the order is reversed with a substantial preference for CO, by 9 kJ mol⁻¹. This is yet another peculiar property of the CPO-27-Cu analogue in the series. NO is a well known probe molecule for Cu(II) species in zeolites⁵⁰, where, as a rule of thumb, it binds to various Cu(II) species much stronger than CO. Nearly constant binding energy with respect to the metal center is computed for CH₄ adsorption, in line with earlier experimental and computational studies.¹¹ The computed binding energy reported herein appeared to be entirely dominated by the dispersion Grimme D₂ term, ranging between 26 kJ mol⁻¹ CH₄ for Mn(II) to 27 kJ mol⁻¹ CH₄ for Zn(II). For the weaker Cu(II) ion,²¹ the Grimme D2 term is slightly larger than the total binding energy, 22.4 kJ mol⁻¹ CH₄ compared to 21.7 kJ mol⁻¹ (Table 2), probably due to a significant mismatch between the minimum position of the potentials of the pure PBE and the dispersive potential curves. Clearly, one needs a precise description of the involved, often dominating, dispersive interactions to accurately predict the thermochemistries and geometries of the investigated small molecule adsorbates, and they must be incorporated in a

functional form able to take care of spin effects and correct band gap description of the whole complex system.

Neutron Powder Diffraction

A direct microscopic insight into the sorption phenomena discussed above was accomplished with the use of in situ gas adsorption neutron diffraction techniques. These provided further evidences of a rather weak interaction between the N_2 and O_2 guest molecule and the metal centers in the CPO-27 structures. In all tested cases ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{and Zn}$), the observed M(II) –guest molecule distances, ranging between 2.3 Å on Ni(II) and 3.1 Å on Cu(II) , do not indicate chemical bonding between host and O_2 guest, but rather that physisorption is responsible for the corresponding host-guest adduct formation of relatively low stability. The neutron diffraction results at low loadings, up to 1 adsorbate molecule per formula unit (f.u.), are listed in Table 1. As expected, the largest deviation from the computed values is observed in the case of the half-filled shell of Mn(II) ion – by about 0.5 Å in our model and 0.8 Å in an earlier DFT study.²⁶ Notably, as the number of unpaired electrons in the 3d shell of the M(II) center decreases, the errors in both binding energy and M(II) – O_2 adduct distance are reduced to just a few kJ mol^{-1} and about 0.1 Å (Table 1 and 2).

Figure 6. Top: Neutron powder diffraction structures of CPO-27-Ni loaded with 1 molecule O_2 per Ni(II) , on the left, and the same material loaded with 1 molecule N_2 per Ni -site on the right. Bottom: Same structures as resulting from the simulations.

While no accurate value for the bond lengths of the adsorbed O₂ and N₂ species could be derived from the neutron diffraction data, probably due to a too large orientational disorder of the adsorbate molecules, we can conclude with moderate accuracy that an end-on coordination is preferred in all the cases studied herein, in agreement with our DFT simulations. As also predicted by the computational models, the O₂ molecule, being in an end-on configuration with respect to the nearby M(II) centre, is tilted so as to lie nearly parallel to one of the phenyl rings of the organic ligand, while N₂ points almost radially towards the pore interior (Figure 6). We attempted to refine the diffraction data by modeling the adsorbed O₂ molecule as a single O atom and shaping it through the corresponding anisotropic thermal parameters. The refinements (crystal structure data is available as cif files as part of the Supporting information) converged to only marginally worse fit quality parameters, while the corresponding adsorbate molecule thermal ellipsoids again indicated an end-on coordination mode (Figure 7). The corresponding metal center-to-O atom distances, now being 2.59(4), 2.50(1), 2.43(2), and 3.32(4) Å at Mn, Co, Ni, and Cu accordingly, were consistent with the ones in Table 1, correctly following the trend in the measured Q_{st}.

Figure 7. Crystal structure of CPO-27-Co loaded with 1 O₂ molecule per f.u. from Rietveld refinement of neutron diffraction data. The adsorbed O₂ molecule was modelled as a single atom with anisotropic thermal parameters. Allowing for double site occupancy, a refined O-loading of 1.93(3) was obtained.

At higher O₂ loadings between 1 and 2 O₂ molecules per formula unit, which correspond to the second plateau in the corresponding adsorption isotherm (Figure 3), the space between the primary adsorption sites at the pore corners is occupied with guest molecules, and a chain like adsorbate

structure is formed (Figure 8). Oxygen atoms from the carboxylate units of the linker ligand mainly constitute the adsorbent surface defining the secondary adsorption sites.

To further test our computational model predicting a maximum of 3 guest molecules of O₂ adsorbed in both CPO-27-Co, and Ni, we tried to load as much oxygen as possible in both frameworks, at temperatures as low as 90 K.

Figure 8. Structural excerpt of CPO-27-Ni loaded with 1.8 O₂/f.u. representing the secondary O₂ sites inserted between the primary sites at the metal cation, as obtained from the neutron diffraction structure refinement.

The maximum loadings attained were 2.4 and 2.6 O₂ per Co(II) and Ni(II), respectively, comparing favorably to the maximum uptakes measured in the oxygen adsorption experiments at 87 K. Unfortunately, the corresponding Rietveld refinement results suffer from unphysically large mean square displacements of the guest atoms.

Figure 9. Crystal structure of CPO-27-Ni loaded with 2.6 O₂ molecules per f.u. from Rietveld refinement of neutron diffraction data (left) and the same material modelled with 3 O₂/f.u. after full geometry relaxation as explained in the text (right). In both cases the molecules were forced into three crystallographically distinct positions.

They are most likely due to a large static disorder of the adsorbate molecules in the pore interiors and are particularly large in the Co material. Figure 9 shows the resulting structures for the Ni compound, along with the same from the periodic PBE0 simulations. It is worth pointing out that in the case of water and hydrogen, near the corresponding boiling points of the two adsorbates, much larger capacities of ca. 5 guest molecules per formula unit are attained.²¹ In contrast to H₂(D₂) adsorbates of CPO-27,²¹ for which a third adsorption site at the phenyl ring is available, this site is now blocked by the larger, farther lying, and tilted O₂ molecules at the metal site. Thus, increasing the loading above 2 guest molecules per f.u. already leads to filling of the pore interiors. Such adsorbate molecules are not directly in contact with the host surface, i.e. they effectively form a second molecular layer. For these adsorbate molecules, the adsorbate-adsorbate interactions are expected to become significant and at a certain point even exceed the adsorbate-host interactions. Consequently, pore interior molecular structures may not necessarily be described within the same symmetry as the host structure. Thus, enforcing the same structural model on these interior structures may not be justified. In fact, spreading the adsorbate into just three crystallographically distinct sets of adsorption sites for total loadings of 3 guest molecules per f.u. as in Figure 9, leads to very low computed by the DFT simulations binding energies. For the molecules in the pore center of the Ni- and Co-frameworks the computed binding energies are below 2 kJ mol⁻¹. Although these stoichiometric model structures lead to Rietveld fits of good quality, with corresponding computed binding energies that are about a factor of three lower than the corresponding latent heats of bulk O₂ and N₂, they do not seem to be physically correct. It is likely that allowing for some nonstoichiometricity on the guest site occupation in the pore may help to achieve more flexible and optimal packing. Introducing a fourth site clearly produces a better fit of the experimental data for CPO-27-Co dosed with 2.4 O₂ per f.u. The corresponding cif file is provided in the Supplementary information. This nonstoichiometric manner of pore filling with relatively large thermal parameters indicates that we are already at the onset of disorder with respect to the host structure symmetry.

While accurate guest atom position determination was impossible from our high loadings above 2 guest molecules per f.u. data sets, the fits were good enough to output the dependence of the corresponding lattice cell parameters on the guest loading. For all measured materials, loading with O₂ clearly leads to a decrease of the **a** lattice cell parameter, which means the pore diameter contracts, and a small increase of the **c** lattice parameter. For CPO-27-Co and Ni this behavior can be traced to the highest attainable loadings of 2.4 and 2.6 O₂ molecules per f.u., and could be attributed to significant long range attractive adsorbate-adsorbate interactions, supporting the arguments above and further indicating that the computational model with 3 crystallographic positions is inadequate. The opposite seems to happen for N₂, for which even at 1 N₂ per Ni ion, both cell parameters increase. This is reflected in the lower maximum uptake of N₂ compared to O₂ in the corresponding low temperature sorption isotherms of these materials, shown in Fig. 3.

Conclusions

Using experimental thermodynamic and neutron scattering methods as well as theoretical quantum chemistry computational models, we have studied the interactions of O₂ and N₂ with coordinatively unsaturated divalent open shell metal ions, which are an essential structural part of the CPO-27 porous coordination polymers. Adsorption isotherms near the boiling points of the adsorbates show three steps corresponding to three groups of adsorption sites with different adsorption energetics. Neutron diffraction experiments identified these sites as: 1) at the coordinatively unsaturated M(II) ions, 2) in the vicinity of O atoms of the linker ligands, between primary sites at the metal ions, 3) pore interiors. The magnitudes of the measured isosteric heats of adsorption of O₂ and N₂ at ambient temperatures and pressures, and the host-guest structures determined from neutron diffraction experiments at low temperatures as well as hybrid DFT simulations, indicate rather weak binding even at the open metal sites, typical for electrostatic and dispersive interactions. Around ambient temperature, CPO-27-Ni has the highest heat of adsorption for both nitrogen and oxygen in

the series, successively followed by Co and then Mn. Intriguing differences in trends are observed for CPO-27-Mn, Cu and Zn. The isosteric heat of adsorption for O₂ in CPO-27-Cu is very similar to that observed for CPO-27-Mn, and significantly larger than that for CPO-27-Zn. The isosteric heat of adsorption of N₂ in both CPO-27-Cu and -Zn are almost identical and the value for CPO-27-Mn is slightly larger.

No superoxide or peroxide complex formation was found for any of the studied structures, neither at low nor ambient temperatures. Although our experimental data represent a good reference frame for testing theoretical models, especially valuable in the case of open shell systems like interactions with molecular oxygen, the observed O₂/N₂ sorption thermodynamics and geometries do not imply great potential use of the investigated materials for O₂/N₂ separation or efficient high density storage. In contrast to pure DFT, GGA functionals supplying our density functional with 25 % Hartree-Fock exchange (PBE0) on the frontier lone pair electrons, helps to correctly identify the structures and magnitudes of the corresponding interactions at a qualitative level, but it still does not seem to be able to accurately predict the trend in the oxygen binding with respect to each divalent 3d transition metal ion in the series. Its accuracy towards binding of small singlet molecules like CO₂ and CH₄ is, on the other hand, preserved. At the very final stages of this manuscript preparation we noticed that other authors have also measured O₂ and N₂ adsorption at high loadings in one of the investigated here frameworks, namely the CPO-27-Co⁵¹, using single crystal X-ray diffraction techniques. Their results, being similar to ours, also suggest that both species are in a physisorption regime at the Co(II) site with the N₂ molecule in a nearly straight *end on* geometry and the O₂ molecule in a tilted geometry. Notably these authors also observed orientational disorder in the guest species, precluding accurate intramolecular bond length determination.

Supporting Information.

Materials synthesis procedures, N₂ and O₂ sorption isotherms, details of the Q_{st} calculation, Rietveld refinement plots and obtained lattice parameters, DFT total density of states plots, cif files of the refined structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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