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A porous Mn(V) coordination framework with PtS topology: assessment of the influence of a terminal nitride on CO_2 sorption†

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A new coordination framework material, $[Zn\{MnN(CN)_4(H_2O)\}]\cdot 2H_2O\cdot MeOH$, has been characterised crystallographically and the effect of a terminal nitride on the N_2, H_2 and CO_2 sorption capacities of the material assessed through porosimetery measurements and DRIFTS.

Coordination frameworks have increasingly been investigated as materials for CO_2 capture and storage due to their high internal surface areas and large pore volumes and to the tuneable nature of their structures.[1] Current research has identified coordinatively unsaturated metal sites and pendant functional groups as features that lead to enhanced uptake or selectivity of CO_2 over other guest molecules, due in part to their electrostatic interactions with the quadrupole moment of CO_2.[2–5] The inclusion of nitrogen-containing groups within coordination frameworks, for example *via* the grafting of amine groups onto unsaturated metal sites, has primarily been aimed at mimicking the acid–base interactions of the alkanolamines that are currently used to chemically absorb CO_2.[6–9] The incorporation of these functionalities can result in significant increases in CO_2 adsorption compared with non-grafted materials at the low partial pressures relevant to flue gas capture.

In the present study, the influence of a terminal nitride ligand on N_2, H_2 and CO_2 sorption in a new cyanido-based coordination framework, $[Zn\{MnN(CN)_4(H_2O)\}]\cdot 2H_2O\cdot MeOH$, with PtS topology, has been assessed. The secondary building unit (SBU) $[MnN(CN)_4]^{2-}$ possesses interesting catalytic[10] and electrochemical[11] properties in the solution state by virtue of the active Mn(V) centre, and is known to give rise to unique thermal expansion[12] and gas sorption properties[13] when incorporated into framework materials. Frameworks with the PtS topology contain both square planar and tetrahedral nodes, and have been of interest for heterogeneous catalysis due to the presence of coordinatively unsaturated metal sites within their structures, examples of which have incorporated metalloporphyrins and post-synthetically modified ligands.[14–16] On this basis, a preliminary assessment of the catalytic performance of $[Zn\{MnN(CN)_4(H_2O)\}]\cdot 2H_2O\cdot MeOH$ for the epoxidation of cyclopentene was performed.

The crystal structure of the solvated framework was solved and refined in the tetragonal space group $P4_2/mmc$ with unit cell dimensions a = 7.51110(10) and c = 13.4593(5) Å at 100 K (Fig. 1–3).‡ The asymmetric unit consists of Mn(V) and Zn(II) centres bridged by a cyanido ligand (Fig. 1). The Mn(V) site forms a distorted octahedron, with four bridging C-coordinated cyanides in the equatorial plane and with terminal nitride ($Mn\equiv N$ distance = 1.64(3) Å) and water ($Mn–OH_2$ distance = 2.20(2) Å) bound axially. The entire $MnN(CN)_4(H_2O)$ unit is 50 : 50 disordered about the *ac*-mirror plane, with there being no evidence for long-range ordering of its orientation despite an expectation that the distorted tetrahedral coordination geometry of the Zn(II) centre might favour this (see ESI†). The crystalline framework contains a 3D PtS-type pore network that occupies 56% of the crystal volume; the narrowest pore windows in the *ab* plane have dimensions 3.7 × 4.4 $Å^2$ and in the *c*-direction 5.2 × 5.2 $Å^2$ (Fig. 2 and 3). The axial Mn(V) sites project directly into this pore space.

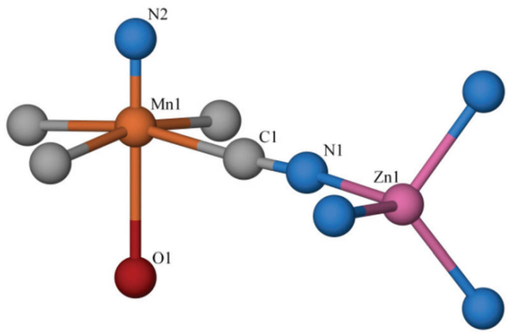

Fig. 1 The coordination spheres of the Mn(V) and Zn(II) centres of $[Zn\{MnN(CN)_4(H_2O)\}]\cdot 2H_2O\cdot MeOH$.

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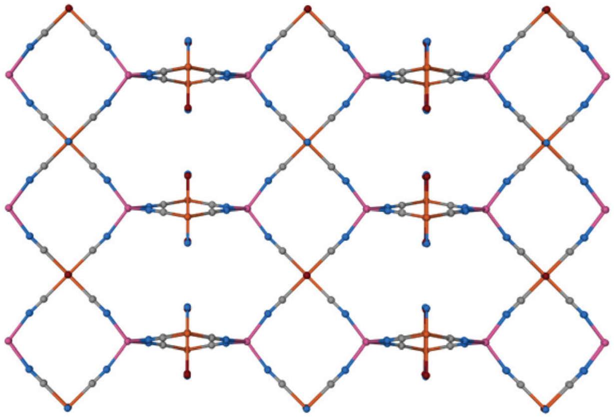

Fig. 2 Extended crystal structure of $[Zn\{MnN(CN)_4(H_2O)\}]\cdot 2H_2O\cdot MeOH$ viewed parallel to the *a*-axis. Framework disorder and pore solvent have been removed for clarity.

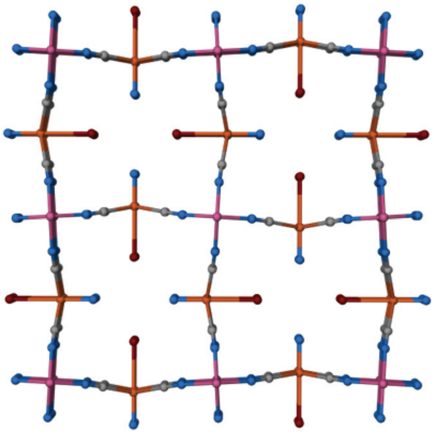

Fig. 3 Extended crystal structure of $[Zn\{MnN(CN)_4(H_2O)\}]\cdot 2H_2O\cdot MeOH$ viewed parallel to the *c*-axis. Framework disorder and pore solvent have been removed for clarity.

A N_2 sorption isotherm was measured at 77 K on a methanol-washed sample of the framework that had been desolvated at 90 °C for 24 h under vacuum to produce $[Zn\{MnN(CN)_4(MeOH)\}]$ (see Fig. 4). Interpretation of the reversible type I isotherm using the Brunauer–Emmett–Teller (BET) equation yielded an estimated surface area of 537.3 ± 0.6 $m^2\ g^{-1}$. This is comparable to other cyanide-based frameworks such as Prussian blues, $[M_3\{Co(CN)_6\}_2]$ (M = Mn, Fe, Co, Ni and Cu), and tetracyanido-based frameworks, which have surface areas in the ranges of 560–870 $m^2\ g^{-1}$,[17,18] and 127–398 $m^2\ g^{-1}$, respectively.[19] In comparison, the closest structurally related framework, $Zn[Ni(CN)_4]$, which is reported to contain two interpenetrated networks, is effectively non-porous, with a surface area of 8.32 $m^2\ g^{-1}$.[20] The saturation uptake of 6.5 mmol g^{-1} corresponds to 1.8 molecules of N_2 per formula unit.

The 298 K CO_2 isotherm (Fig. 5) shows a reversible uptake of 5.0 wt% (1.14 mmol g^{-1}) at 298 K and 1 bar, corresponding to 0.3 molecules of CO_2 per formula unit. This uptake is broadly comparable with those of frameworks with similar pore volumes, such as Prussian blues (8–12 wt% CO_2 uptake at 1 bar).[21,22] The hydrogen sorption capacity of $[Zn\{MnN(CN)_4(MeOH)\}]$ at 77 K (Fig. 4) is 0.84 wt% at 1 bar, which is also in the range observed for Prussian blues.[17,18]

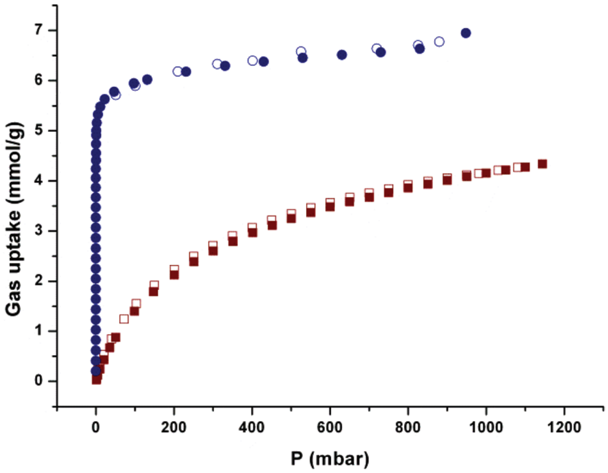

Fig. 4 Adsorption and desorption isotherms for N_2 (filled and open circles) and H_2 (filled and open squares) at 77 K for $[Zn\{MnN(CN)_4(MeOH)\}]$.

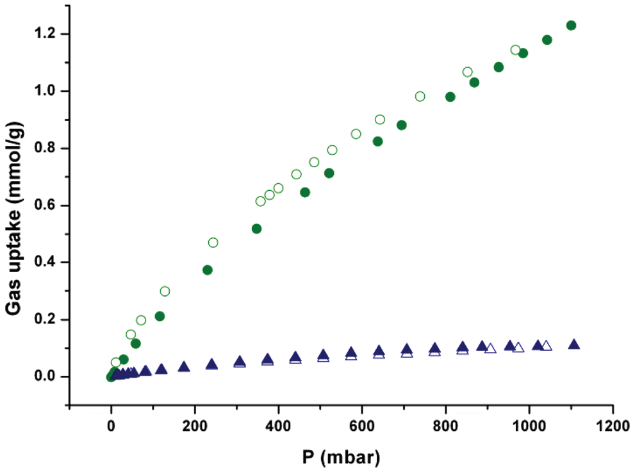

Fig. 5 Adsorption and desorption isotherms for N_2 (filled and open triangles) and CO_2 (filled and open circles) at 298 K for $[Zn\{MnN(CN)_4(MeOH)\}]$.

The isosteric heat of adsorption ($-Q_{st}$) for CO_2 was calculated from the Clausius–Clapeyron equation using adsorption isotherms collected at 298, 308 and 318 K (see ESI†). At low coverage, $-Q_{st}$ was 34 kJ mol^{-1}, which is indicative of a physisorptive interaction between CO_2 and the framework, possibly to a small proportion of coordinately unsaturated Mn(V) sites. With increasing coverage, $-Q_{st}$ declined rapidly to 21 kJ mol^{-1}, then more gradually to 15 kJ mol^{-1} at higher loadings, which is consistent with the physisorption of CO_2 onto itself.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was employed to probe the interaction of CO_2 with adsorption sites in the framework (see ESI†). A methanol-washed sample of $[Zn\{MnN(CN)_4(H_2O)\}]\cdot 2H_2O\cdot MeOH$ was activated *in situ* at 90 °C for 16 h whereupon the broad peak centred at 3000 cm^{-1} disappeared, indicating the removal of the occluded water solvent; however, the peaks at 2856 and 2926 cm^{-1}, which are indicative of coordinated MeOH,[23,24] were retained. Activation of the framework under vacuum at temperatures above 110 °C resulted in an amorphous powder with reduced surface area (*ca.* 230 m^2 g^{-1}), indicative of framework collapse. Consequently, it was postulated that the 6-coordination of the Mn(V) site is important to the structural integrity of the framework upon guest desorption.

To investigate whether the terminal nitride ligands interacts strongly with the guest CO_2 molecules, the ν(MnN) stretch at 1090 cm^{-1} in the DRIFTS spectrum of $[Zn\{MnN(CN)_4(MeOH)\}]$ was monitored at various loadings of CO_2 (see ESI†). As the concentration of CO_2 increased, no change in ν(MnN) was observed, indicating that the nitride ligand is not sufficiently nucleophilic to interact strongly with CO_2.

The complex $[Ph_4P]_2[MnN(CN)_4]\cdot 2H_2O$ has previously been shown to catalyse the epoxidation of alkenes and the oxidation of alcohols to aldehydes.[10] Preliminary investigations into the ability of $[Zn\{MnN(CN)_4(H_2O)\}]\cdot 2H_2O\cdot MeOH$ to catalyse the epoxidation of cyclopentene by H_2O_2 indicated some limited degree of conversion to cyclopentene oxide; however, this conversion was still observed in samples where the catalyst was removed from the reaction medium after several hours, suggesting that some degree of leaching of the active metal complex from the framework had occurred (see ESI†).

In summary, a new porous coordination framework, $[Zn\{MnN(CN)_4(H_2O)\}]\cdot 2H_2O\cdot MeOH$, based upon the functional $[MnN(CN)_4]^{2-}$ subunit, has been synthesised and characterised. A coordinated solvent molecule on the Mn(V) centre is integral to the structural integrity of the desolvated framework. The material exhibits a preference for CO_2 over N_2 at temperatures and pressures relevant to flue gas separation. However, the terminal nitride functionality exhibits a weak affinity towards CO_2 compared with other pendant nitrogen-based moieties in frameworks (*e.g.*, alkylamines). This type of fundamental understanding of host–guest chemistry in porous coordination solids paves the way towards the design of multifunctional materials with potential industrial applications.

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Notes and references

‡Crystal data for $C_5H_{10}MnN_5O_4Zn$ (M = 324.49): tetragonal, space group $P4_2/mmc$ (no. 131), a = 7.51110(10), c = 13.4593(5) Å, V = 759.33(3) $Å^3$, Z = 2, T = 100(2) K, μ(Mo-Kα) = 2.416 mm^{-1}, ρ_{calc} = 1.419 g mm^{-3}, 11 832 reflections measured (9.78 ≤ 2θ ≤ 52.68), 469 unique (R_{int} = 0.0413). R_1 = 0.0429 ($I \geq 2\sigma(I)$) and wR_2 = 0.1233 (all data). CCDC 933557 contains the supplementary crystallographic data for this paper.

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