Supporting Information for

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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EXPERIMENTAL

Synthetic methods. Reagents were used as received from commercial suppliers. $[Ph_4P]_2[MnN(CN)_4]\cdot 2H_2O$ was synthesised according to the method of Bendix *et al.*[1]

Synthesis of [Zn{MnN(CN)$_4$(H$_2$O)}]·2H$_2$O·MeOH. $[Zn\{MnN(CN)_4(H_2O)\}]\cdot 2H_2O\cdot MeOH$ was synthesised as a microcrystalline powder by the slow addition of $[Ph_4P]_2[MnN(CN)_4]\cdot 2H_2O$ (0.30 mmol, 250 mg) in 250 ml of 1:1 H_2O/MeOH into a solution of $Zn(NO_3)_2\cdot xH_2O$ (0.60 mmol, 178 mg) in 250 ml of 1:1 H_2O/MeOH. The yellow product was filtered, washed successively with water and methanol and dried under vacuum. IR (cm^{-1}, n = narrow, b = broad, s = strong, m = medium, w = weak): 3646, 3570 (MeOH n, s), 3351 (H_2O, b, s), 2178 (vCN, n, s), 1604 (MnN, n, w), 1606 (n, s), 554 (n, s), 455 (n, s). Yield 84%.

Single crystals suitable for diffraction were grown by the slow diffusion of a 1:1 H_2O/MeOH solution of $[Ph_4P]_2[MnN(CN)_4]\cdot 2H_2O$ into a 1:1 H_2O/MeOH solution of $Zn(NO_3)_2\cdot xH_2O$.

Single crystal X-ray diffraction (SCXRD). SCXRD measurements were made on an Oxford Supernova diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 100 K. Empirical absorption corrections were made using SCALE3 ABSPACK[2]. Structure solutions were obtained using SHELXS-97[3] and refined using SHELXL-97[4] in WinGX[5]. Atoms were refined anisotropically where meaningful, with the nitride and coordinated water oxygen sites constrained to have identical anisotropic ADPs due to their partial overlap with reflection in the *ac*-plane; atoms of the cyanide bridge were refined isotropically due to their close proximity to this mirror plane.

Based on an expectation that long-range ordering of the $MnN(CN)_4(H_2O)$ unit might be favoured by the adoption of a more regular tetrahedral geometry at the Zn centre and/or to cross-pore intraframework and framework-guest interactions, lower symmetry structural models were explored for this material, particularly those with alternating alignment of the nitride unit along the *a* and *b* axes of the parent cell so as to relieve local strain at the Zn site (requiring unit cell modulation). Reduction of the diffraction data in the $a' = \sqrt{2}a = 10.6223$, $c' = c$ supercell and examination of precession images provided no evidence for long-range modulation, with solution and refinement in $P4_2/mnm$ (in which the *ac*-mirror planes in the parent $P4_2/mmc$ cell are absent) yielding an inferior refinement to the higher symmetry disordered model in the parent cell;

50:50 disorder of the Mn site was still present in this solution. Pore volumes were calculated using a disorder-free model within this space group within PLATON.[6]

CCDC 933557 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray diffraction (PXRD). PXRD data was collected over the 5 - 80° 2θ range with a 0.02° step size and 2°/min scan rate on a PANalytical X'Pert Pro diffractometer fitted with a solid-state PIXcel detector (40 kV, 30 mA, 1° divergence and anti-scatter slits, and 0.3 mm receiver and detector slits) using Cu-Kα (λ = 1.5406 Å) radiation. Profile fits were made using the Le Bail method in Rietica.

Thermogravimetric analysis (TGA). TGA measurements were carried out on a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyser. Dry N_2 flowed through the system (0.1 L/min) during data collection. To identify the approximate temperatures of guest loss and thermal decomposition, the sample temperature was heated at 0.75 °C/min from 25 to 700 °C. Samples were loaded dry after exposure to air.

Gas adsorption. Adsorption isotherms were measured using an Accelerated Surface Area & Porosimetry System (ASAP) 2020 supplied by Micromeritics Instruments Inc. Approximately 50 mg of the sample was loaded into a glass analysis tube and outgassed for 24 h under vacuum at 90 °C prior to measurement. N_2 adsorption and desorption isotherms were measured at 77 K and data was analysed using BET models to determine the surface area.[7] CO_2 and H_2 measurements were carried out on the ASAP2020 as described above. The isosteric heat of adsorption for CO_2 was determined by interpolating carbon dioxide isotherms at 298, 308 and 318 K. Isosteric heat of adsorption calculations ($-Q_{st}$) for CO_2 at these temperatures were undertaken using the Clausius-Clapeyron equation with direct interpolation of data points.

Solid-state Fourier transform infrared (FTIR) spectroscopy. Fourier transform infrared (FTIR) spectra were collected in a potassium bromide (KBr) matrix over the range 4000-400 cm^{-1} using a Varian FTS-800 Scimitar series infrared spectrometer. KBr was heated at 400 K under vacuum for 24 h prior to analysis, with 2-4 mg of material per 200 mg of KBr used for each measurement. A KBr background scan was obtained before each new scan and subtracted from the sample scan to obtain a difference spectrum.

Diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS). *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on samples in a potassium bromide matrix over the range 4000-400 cm^{-1} using a Harrick Scientific Products, Inc. Praying Mantis attachment on a Bruker Tensor 27 FT-IR spectrometer. The Praying Mantis was mounted with a Low Temperature Reaction Chamber fitted with ZnSe windows and a Harrick Scientific Products, Inc. Temperature Controller. The sample was heated at 90 °C under vacuum for 16 h prior to analysis. High purity CO_2 (99.99%) was introduced at a range of pressures, and 1600 scans of the sample were recorded and averaged at each pressure dose.

Catalysis measurements. [Zn{MnN(CN)$_4$(H$_2$O)}]·2H$_2$O·MeOH (1 mol%), CH$_3$CN (1 ml), cyclopentene (1 mmol) and H$_2$O$_2$ (30% w/v in H$_2$O) (2 equiv.) were combined under an inert atmosphere at 23 °C. The reaction was monitored by Head Space Solid Phase Microextraction (HS-SPME) and a Finnigan PolarisQ mass spectrometer attached to a ThermoQuest trace gas chromatograph fitted with a 30 m × 0.25 mm × 0.25 mm Zebron DB5 MS column.

Table S1 Crystal data and structure refinement for [Zn{MnN(CN)$_4$(H$_2$O)}]·2H$_2$O·MeOH

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Empirical formula	C$_5$H$_{10}$MnN$_5$O$_4$Zn
Formula weight	324.49
Temperature / K	100(2)
Crystal system	tetragonal
Space group	$P4_2/mmc$
a / Å	7.51110(10)
b / Å	7.51110(10)
c / Å	13.4593(5)
α / °	90.00
β / °	90.00
γ / °	90.00
Volume / Å^3	759.33(3)
Z	2
ρ_{calc} / mg.mm^{-3}	1.419
μ / mm^{-1}	2.416
F(000)	324.0
Crystal size /mm^3	0.157 × 0.093 × 0.077
2θ range for data collection	9.78 to 52.68°
Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -16 ≤ l ≤ 16
Reflections collected	11832
Independent reflections	469 [R(int) = 0.0413]
Data/restraints/parameters	469/1/27
Goodness-of-fit on F^2	1.110
Final R indices [$I \geq 2\sigma(I)$]	R$_1$ = 0.0428, wR$_2$ = 0.1218
Final R indices [all data]	R$_1$ = 0.0446, wR$_2$ = 0.1233
Largest diff. peak/hole / e Å^{-3}	1.08/-0.24
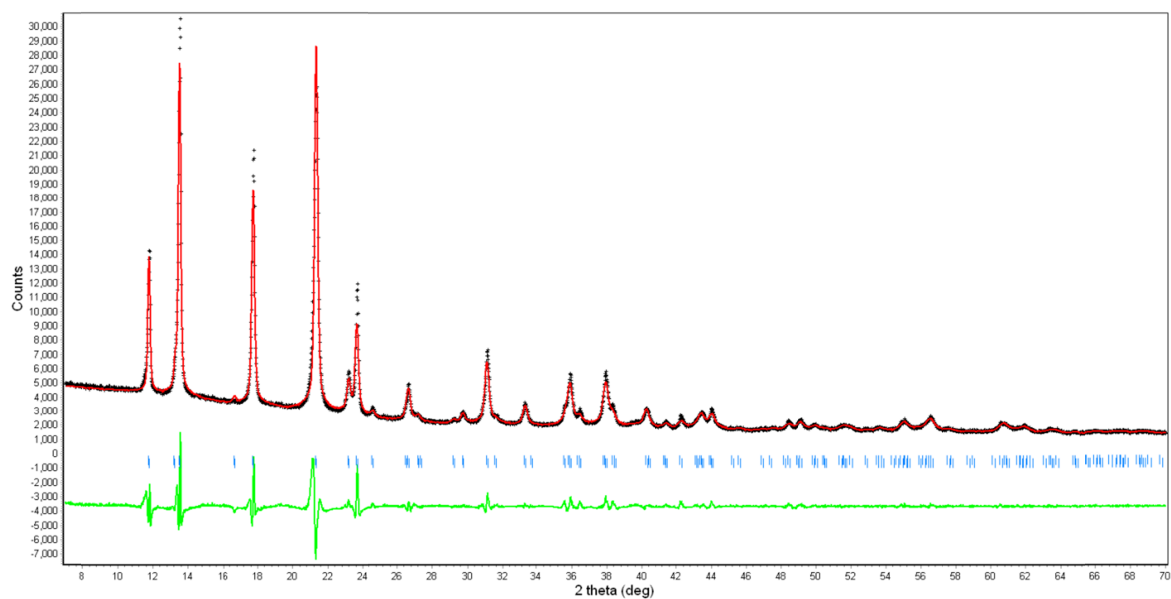
Figure S1 Le Bail extraction of the PXRD pattern for [Zn{MnN(CN)$_4$(H$_2$O)}]·2H$_2$O·MeOH at 293 K; unit cell parameters a = 7.5145(5), c =13.3846(10) Å, V = 755.82 (10) Å^3.
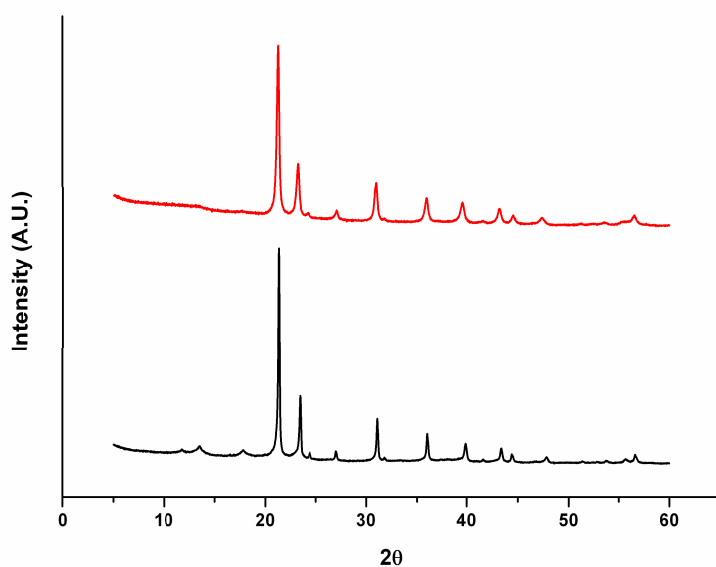

Figure S2 PXRD of [Zn{MnN(CN)$_4$(MeOH)}] before (black line) and after (red line) porosimetry measurements. Unit cells by Le Bail refinement: a = 7.6083(12), c = 13.262(2) Å, V = 767.7(2) Å^3 (black); a = 7.6340(11), c = 13.256(2) Å, V = 772.6(2) Å^3 (red).
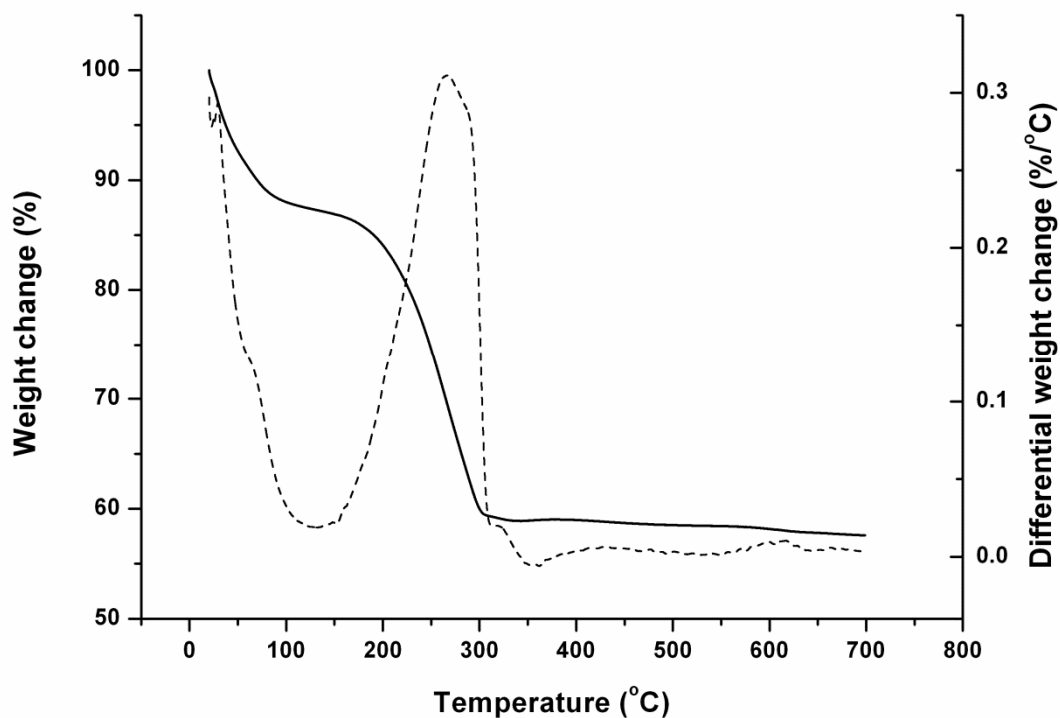
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Figure S3 TGA of an air-dried sample of [Zn{MnN(CN)$_4$(H$_2$O)}]·2H$_2$O·MeOH heated at a rate of 0.75 °C/min under a nitrogen atmosphere; solid line represents change in weight (%), broken line represents the first derivative of the solid line.

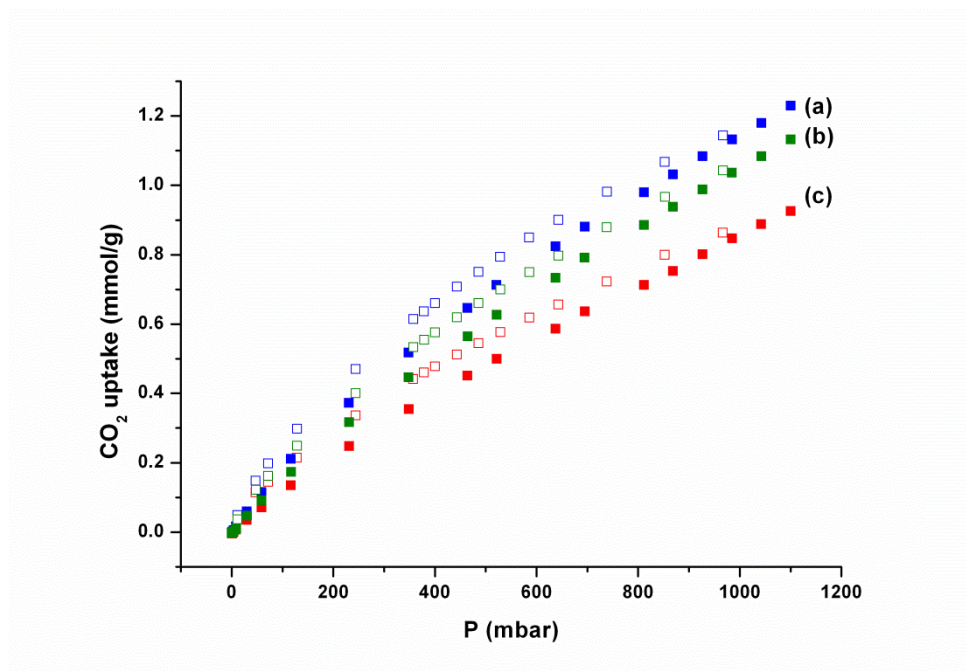**Figure S4** CO$_2$ adsorption (filled squares) and desorption (open squares) isotherms measured at (a) 298, (b) 308 and (c) 318 K for [Zn{MnN(CN)$_4$(MeOH)}].
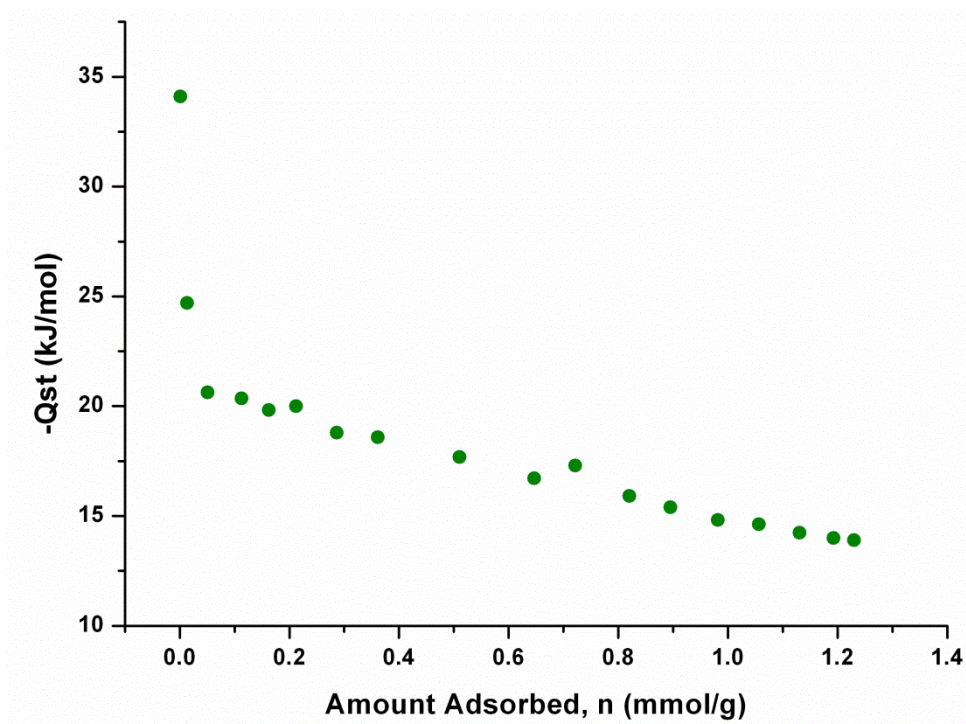
Figure S5 Calculated isosteric heat of adsorption of CO_2 in $[Zn\{MnN(CN)_4(MeOH)\}]$ as a function of coverage.
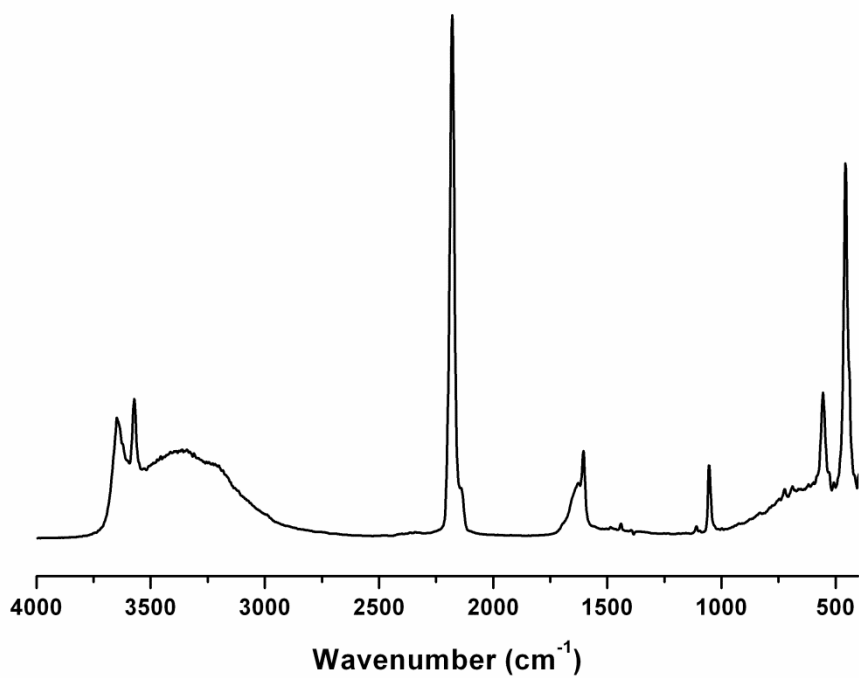

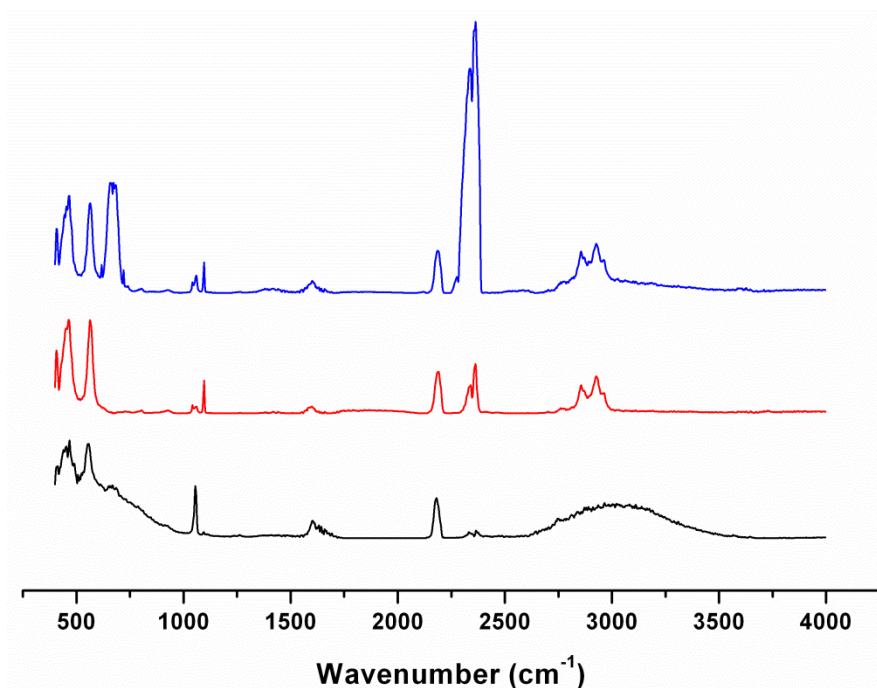**Figure S6** FTIR spectrum of $[Zn\{MnN(CN)_4(H_2O)\}]\cdot2H_2O\cdot MeOH$

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Figure S7 DRIFTS spectra of the as-made sample [Zn{MnN(CN)$_4$(H$_2$O)}]·2H$_2$O·MeOH (black);
[Zn{MnN(CN)$_4$(MeOH)}], obtained by MeOH-washing and subsequent heating of the as-made sample to 90
°C under vacuum (red), in air; and [Zn{MnN(CN)$_4$(MeOH)}] under 1 bar of CO$_2$ (blue).

Table S2 Catalysis results from the conversion of cyclopentene to cyclopentene oxide by
[Zn{MnN(CN)$_4$(H$_2$O)}]·2H$_2$O·MeOH

Reaction medium			Supernatant aliquot		
Time (hours)	[cyclopentene oxide] (M) detected	Conversion (%)[a]	Time after catalyst removed (hours)	[cyclopentene oxide] (M) detected	Conversion (%)[a]
0	0	0	0	0.0010	1
1	0.0001	0	18	0.0343	11
2.5	0.0002	0	21	0.0747	23
3	0.0010	1			
21	0.0785	25			
24	0.1688	53			

[a] Conversion (%) based on [cyclopentene] identified at time = 0 by GC–MS

REFERENCES

1. J. Bendix, K. Meyer, T. Weyhermuller, E. Bill, N. Metzler-Nolte and K. Wieghardt, *Inorganic Chemistry*, 1998, **37**, 1767-1775.

2. SCALE3 ABSPACK: Empirical absorption correction CrysAlis Software package. Oxford Diffraction Ltd.

3. G. M. Sheldrick, *SHELXS-97. Program for crystal structure solution*, University of Göttingen, Germany, 1997.

4. G. M. Sheldrick, *SHELXL-97. Program for crystal structure refinement*, University of Göttingen, Germany, 1997.

5. L. J. Farrugia, *Journal of Applied Crystallography*, 1999, **32**, 837-838.

6. A.L.Spek, *J.Appl.Cryst.* 2003, **36**, 7-13.

7. S. Brunauer, P. H. Emmett and E. Teller, *Journal of the American Chemical Society*, 1938, **60**, 309-319.