Supporting Information

A Perception of Ferro- and Antiferromagnetic Interaction in a Two Dimensional Ni(II) Heterochiral Coordination Polymer Showing Unusual CO_2 Uptake behavior

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Materials and Methods

All the solvents and reagents were purchased from commercial sources and used as received. Acetyl pyridine, $NaN(CN)_2$, (Aldrich, USA); 2-hydroxybenzaldehyde, $NiCl_2 \cdot 6H_2O$, hydroxylamine hydrochloride and Zn dust (Merck India Ltd) and solvents were used as received without further purification. (R,S) phenyl(2-pyridyl)methaneamine and (R, S) 2-((phenyl(2-pyridyl)methylimino)methyl)phenol (LH) were prepared using our earlier reported procedures.[1]

Physical Measurements

Magnetic measurements were performed using a Quantum Design SQUID VSM magnetometer. The measured values were corrected for the experimentally measured contribution of the sample holder, while the derived susceptibilities were corrected for the diamagnetism of the samples, estimated from Pascal's tables.[2] Elemental analysis was performed on an Elementar vario Micro Cube instrument. IR spectrum was recorded on a Perkin-Elmer spectrometer from KBr pellets. Thermogravimetric analyses of both the complexes were recorded on a Perkin-Elmer TGA 4000 instrument in the temperature range of 30 – 900 °C under N_2 flow with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data were collected on a PANalytical EMPYREAN instrument using Cu-Kα radiation.Gas adsorption measurements were performed by using BelSorpmax (BEL Japan) automatic volumetric adsorption instrument. All the gases used were of Ultra-pure research grade (99.999%). Before every measurement sample was pretreated for 24 hrs at 373 K under 10^{-2} KPa continuous vacuum using BelPrepvac II and purged with N_2 on cooling. CO_2, CH_4 isotherms were measured at 195 K (Dry ice-MeOH cold bath) and 273 K (Julabo chiller with Ethylene glycol-water mixture as a coolant).

X-ray Crystallography

Suitable single crystals of complex 1 was mounted on a Bruker SMART diffractometer equipped with a graphite monochromator and Mo–Kα (λ = 0.71073 Å, 296 K) radiation. Data collection was performed using φ and ω scan. The structure was solved using direct methods followed by full matrix least square refinements against F^2 (all data HKLF 4 format) using SHELXTL.[3] Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms.

Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and multi–scan absorption correction were applied. Non-hydrogen atoms were refined with independent anisotropic displacement parameters and hydrogen atoms were placed geometrically and refined using the riding model. All calculations were carried out using SHELXL 97,[4] PLATON 99,[5] and WinGX systemVer-1.64.[6]

Synthesis of complex 1:

To a methanol (10 mL) solution of $NiCl_2 \cdot 6H_2O$ (0.948 g, 4.0 mmol) was added LH (1 g, 4.0 mmol) dissolved in methanol (30 mL). To this mixture Et_3N (0.404 g, 4.0 mmol) was added and the resulting mixture was stirred for 2h. Solid sodium dicyanamide (0.356 g, 4.0 mmol) was added and the solution heated at reflux for 1h. The solvent was removed and the green residue was washed with ice-cold methanol. Yield: 1.04 g (69%). Single crystals of 1 suitable for X-ray diffraction study were obtained by layering the CH_3CN solution of the crude green solid over dichloromethane. Anal. Calc. for $C_{32}H_{26}N_{10}O_2Ni_2$: C, 54.91; H, 3.74; N, 20.01%. Found: C, 54.67; H, 3.46; N, 19.65%. Selected IR (KBr, cm^{-1}) bands: 3432, 2274, 2165 (dicyanamide), 1623, 1598, 1412, 1327, 1050, 902, 764, 754.
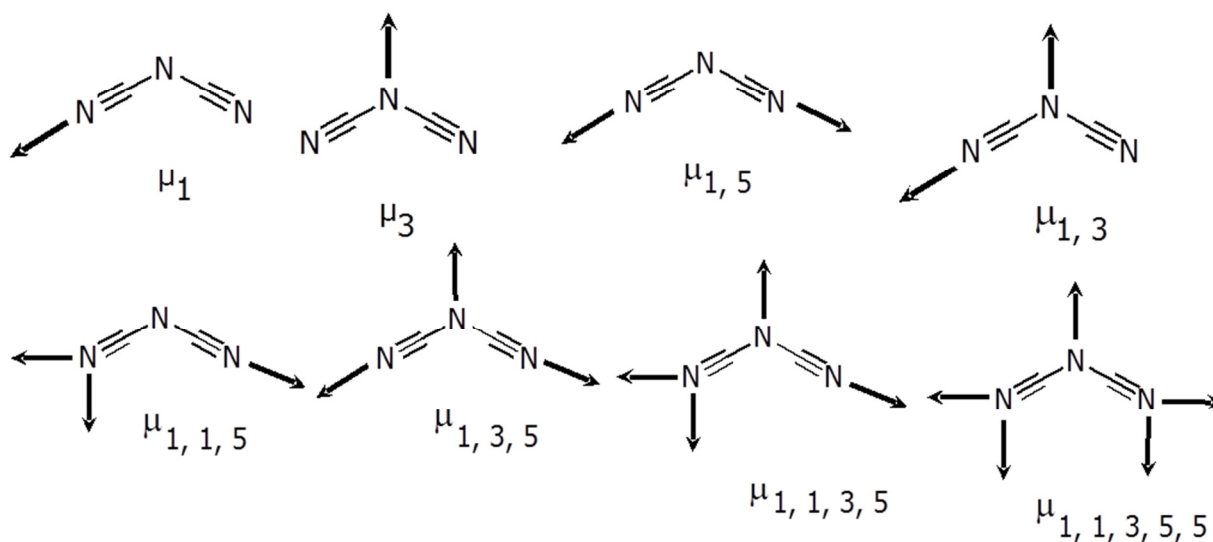
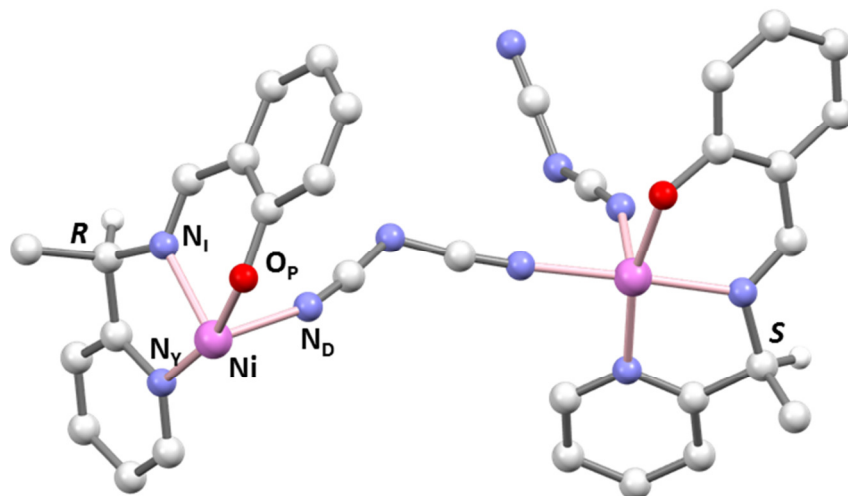**Scheme 1.** Illustration of different bridging modes of dicyanamide ion.

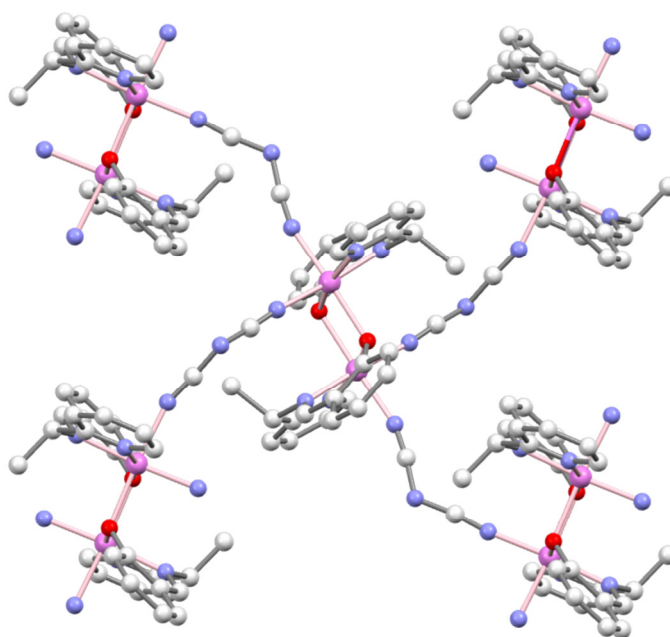**Fig. S1.** Asymmetric unit of the complex **1.** Colour Codes: Ni(magenta), O(red), C(gray), N(blue).

Fig. S2. Illustration of a single heterochiral dimer linked to four other dimers by dicyanamide bridge found in complex 1. Colour codes same as Fig. S1.
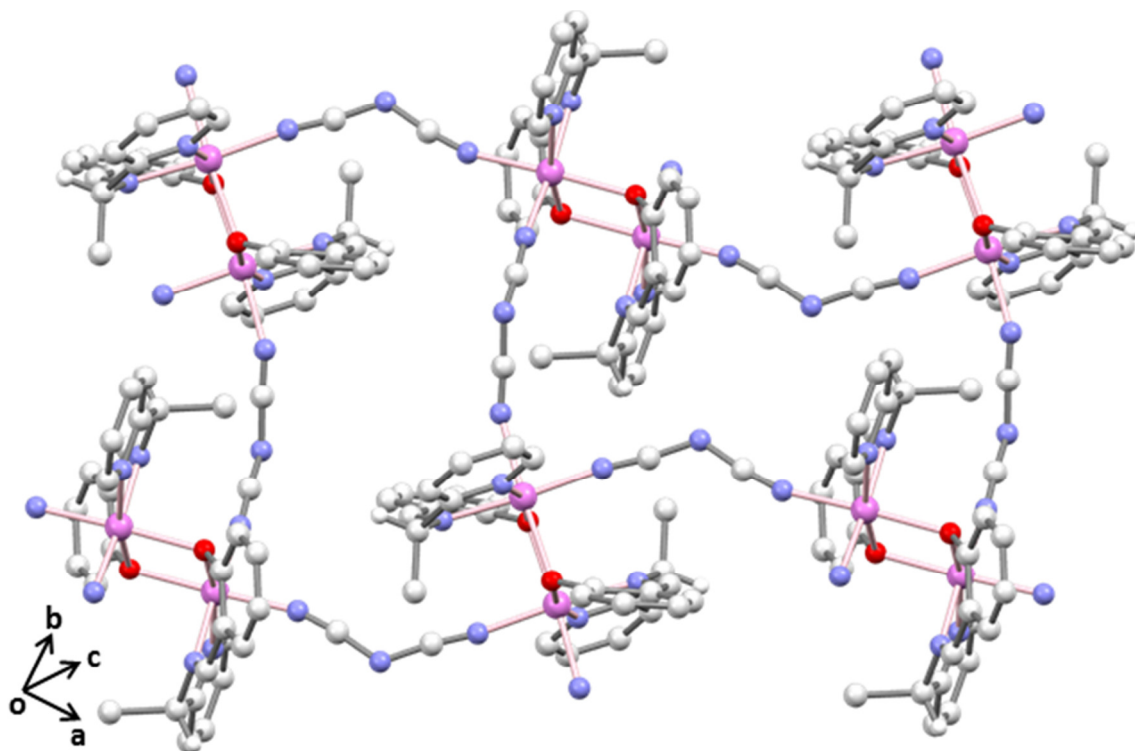
Fig. S3. Illustration of a two dimensional coordination polymer found in complex 1. Colour codes same as Fig. S1.
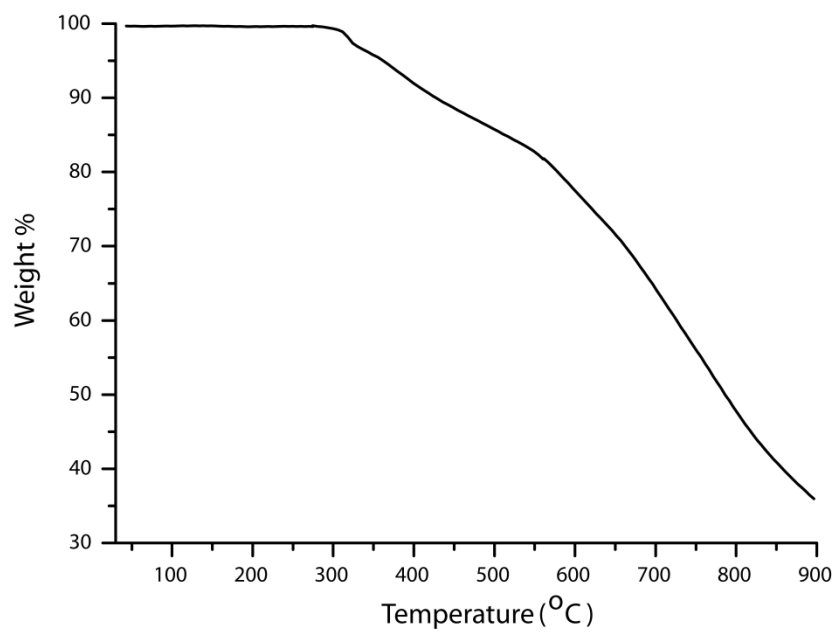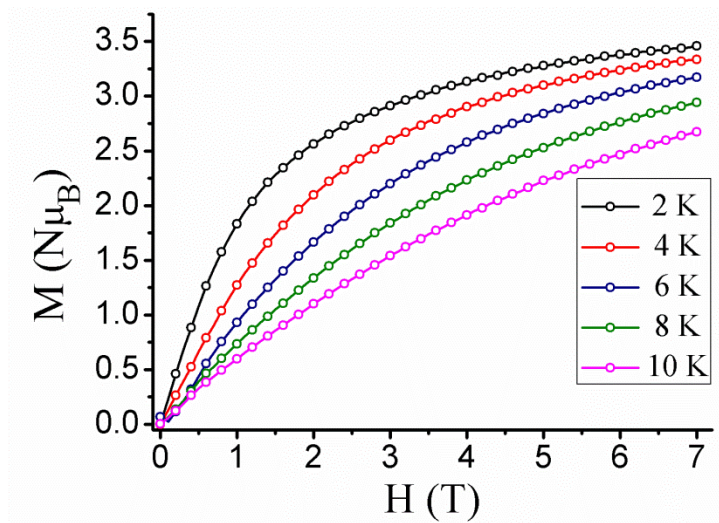

Fig. S4. TGA profile of complex **1**.

Fig. S5. Field-dependencies of isothermal magnetization plots for complex 1.
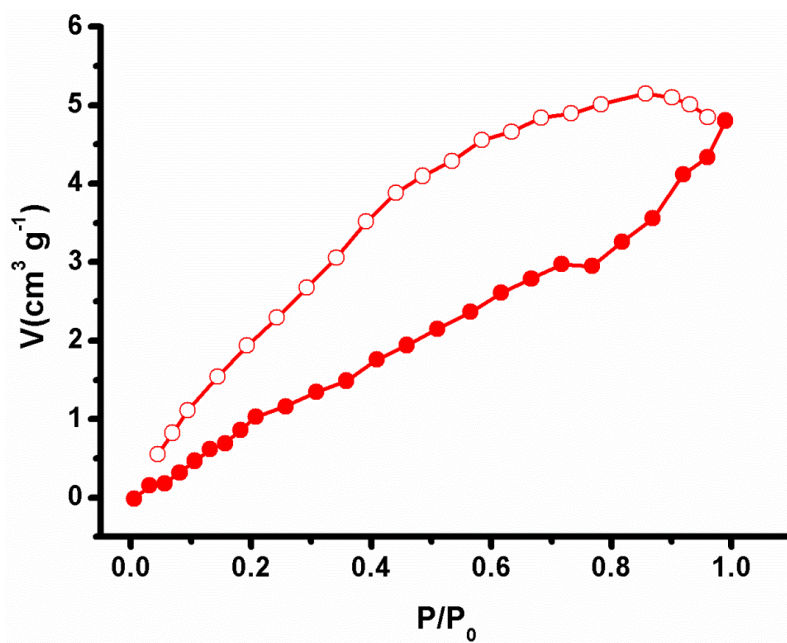

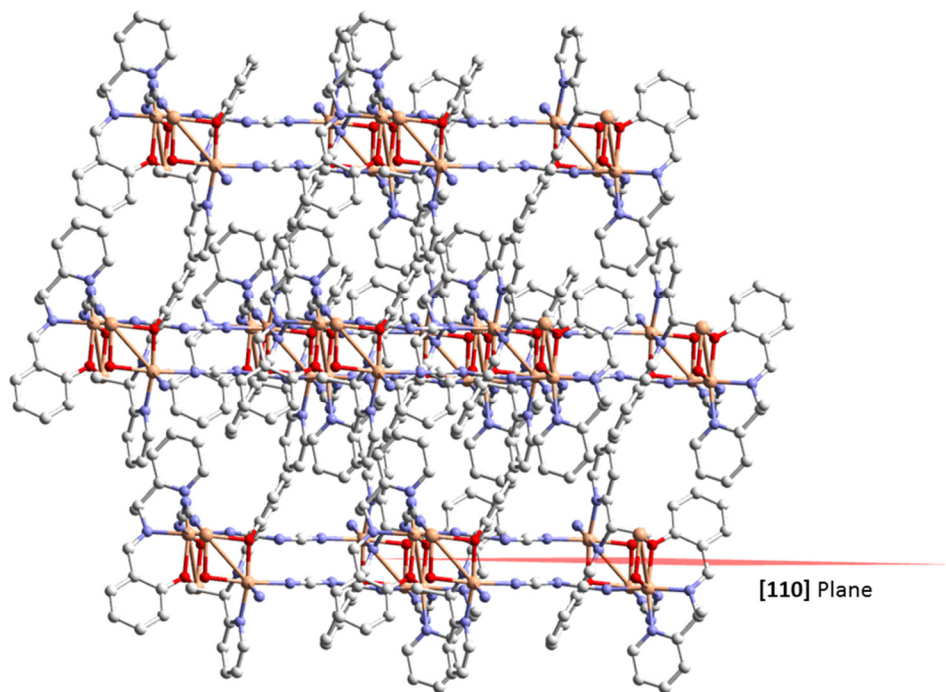**Fig. S6.** N_2 adsorption isotherms of complex 1 at 77 K.
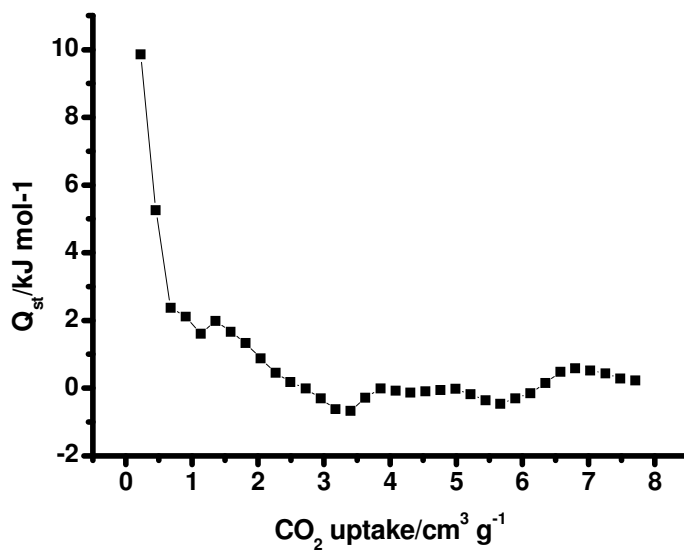
Fig. S7. Illustration of [110] plane found in complex 1.

Fig. S8. Isosteric heat of adsorption for complex **1** obtained from CO_2 sorption data at 273 K and 298 K.
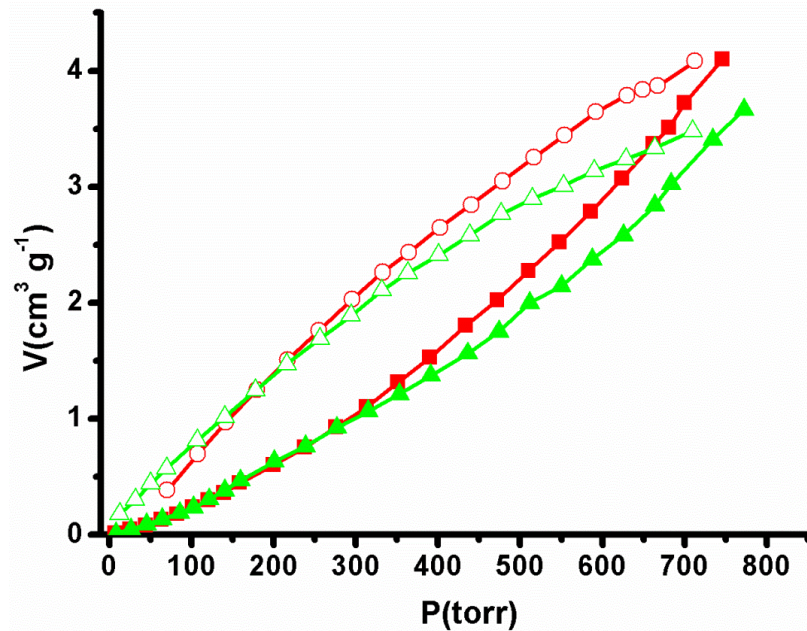
Fig. S9. CH$_4$ adsorption isotherms of complex 1 at 298 K (red), 273 K (green).
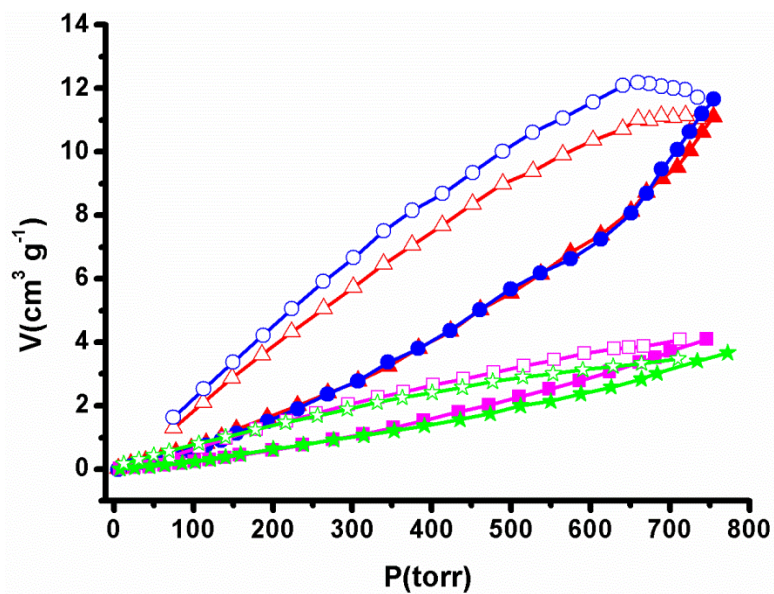

Fig. S10. Gas sorption isotherms at around room temperature, CO$_2$ at 273 K (red), 298 K (blue) and CH$_4$ at 273 K (green), 298 K (magenta).
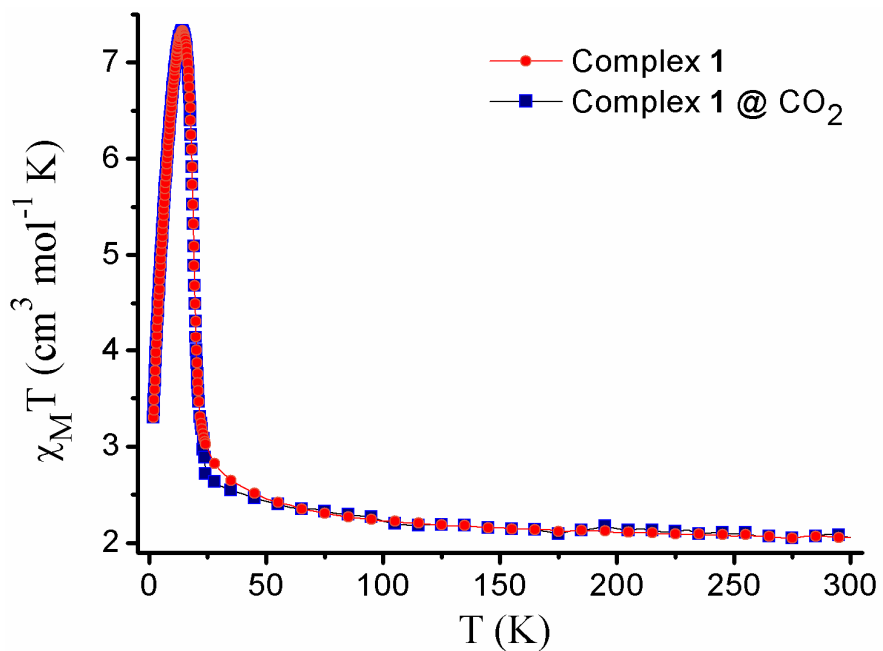
Fig. S10. Temperature dependence of the DC susceptibility for complex **1** and CO_2 loaded complex **1** (complex **1@CO₂**).
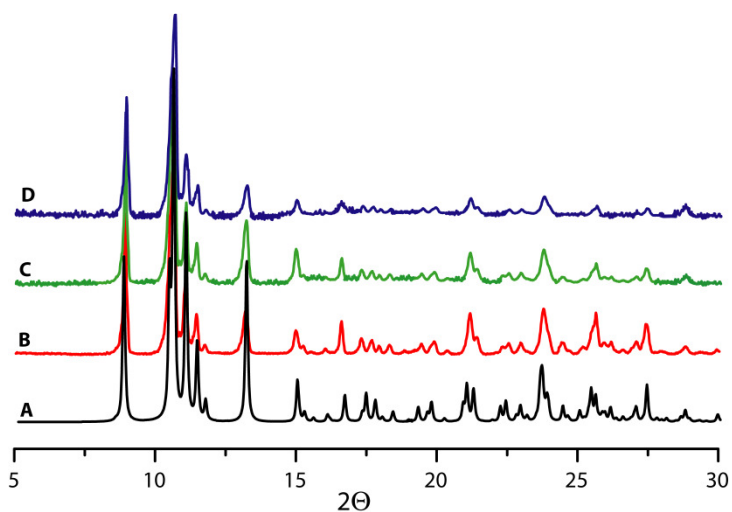

Fig. S11. PXRD patterns of complex **1** at 298 K; (A) as-synthesized, (B) Activated, (C) CO_2 loaded complex 1 and (D) after CO_2 desorption.

Table 1. Summary of X-ray Crystallographic Data for complex 1.

CCDC number	1014355
Molecular Formula	$C_{32}H_{26}N_{10}Ni_2O_2$
Formula Mass (g/M)	700.01
Wavelength (Å)	0.71073
Temperature (K)	296(2)
Crystal system	Triclinic
Space group	P-1
a /Å	11.4696(4)
b /Å	11.6432(5)
c /Å	13.4883(5)
α (°)	84.488(2)
β (°)	82.801(2)
γ (°)	61.108(2)
V/ A^3	1563.33(10)
Z	2
D_C/ gcm^{-3}	1.487
μ (Mo-K$_\alpha$)/mm^{-1}	1.252
F(000)	720.0
Total reflection	7832
Unique reflection	6258
GOOF on F^2	1.003
R1^a[I>2σI]	0.0510
wR2^b[I>2σI]	0.1172
[a]R1=Σ||Fo|-|Fc||/Σ|Fo| & [b]wR2 =|Σw(|Fo|^2 - |Fc|^2)|/Σ|w(Fo)^2|$^{1/2}$	

Table 2. Selected bond distances (Å) and angles (˚) found in complex 1.

1			
Ni1–N1	2.089(4)	Ni2–N3	2.083(4)
Ni1–N2	2.021(4)	Ni2–N4	2.029(3)
Ni1–N5	2.037(4)	Ni2–N7	2.090(4)
Ni1–N8	2.110(3)	Ni2–N10	2.057(4)
Ni1–O1	2.037(4)	Ni2–O2	2.029(4)
Ni1–O1A	2.147(3)	Ni2–O2A	2.140(3)
Ni1···Ni1A	3.182(1)	Ni2···Ni2A	3.148(1)
N1–Ni1–N2	79.3(1)	N3–Ni2–N4	79.6(1)
N1–Ni1–N5	96.1(2)	N3–Ni2–N7	92.3(2)
N1–Ni1–N8	88.6(2)	N3–Ni2–N10	95.3(2)
N1–Ni1–O1	166.9(1)	N3–Ni2–O2	166.2(1)
N1–Ni1–O1A	94.8(1)	N3–Ni2–O2A	92.5(1)
N2–Ni1–N5	174.6(2)	N4–Ni2–N7	86.8(2)
N2–Ni1–N8	90.9(2)	N4–Ni2–N10	174.0(1)
N5–Ni1–N8	86.1(2)	N4–Ni2–O2	88.0(1)
N2–Ni1–O1	88.4(1)	N4–Ni2–O2A	92.8(1)
N2–Ni1–O1A	93.2(1)	N7–Ni2–N10	90.3(2)
N5–Ni1–O1	96.4(2)	N7–Ni2–O2	93.1(2)
N5–Ni1–O1A	90.1(2)	N7–Ni2–O2A	175.1(2)
N8–Ni1–O1	96.4(2)	N10–Ni2–O2	97.4(1)
N8–Ni1–O1A	175.1(2)	N10–Ni2–O2A	90.5(1)
O1–Ni1–O1A	81.0(1)	O2–Ni2–O2A	82.0(1)
Ni1–O1–Ni1A	99.0(1)	Ni2–O2–Ni2A	98.0(1)

Reference:

(1) H. S. Jena, J. Subramanian, V. Manivannan, *Inorg. Chim. Acta* 2011, **365**, 177.

(2) O. Kahn, Molecular Magnetism, VCH, New York, 1993.

(3) G. M. Sheldrick, SHELXTL, *Program for the Solution of Crystal of Structures*, University of Göttingen, Göttingen, Germany, 1993.

(4) G. M. Sheldrick, SHELXL 97, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.

(5) A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7.

(6) L. J. Farrugia, *J. Appl. Crystallogr.* 1999, **32**, 837.