Supporting Information

Quadruple Bridged-Carbonate Supported Dodecanuclear [Ni_8Ca_4] Coordination Cluster

Kajal[a], Richa Vinayak[a], Carlos J. Gómez-García[b], Samia Benmansour[b] and Hari Pada Nayek,*[a]

[a] *Department of Chemistry & Chemical Biology, Indian Institute of Technology (Indian school of Mines), Dhanbad-826004, Jharkhand, India. E-mail: hpnayek@iitism.ac.in*

[b] *Departamento de Química Inorgánica. Universidad de Valencia. Dr. Moliner 50. 46100 Burjasot, Valencia, Spain.*

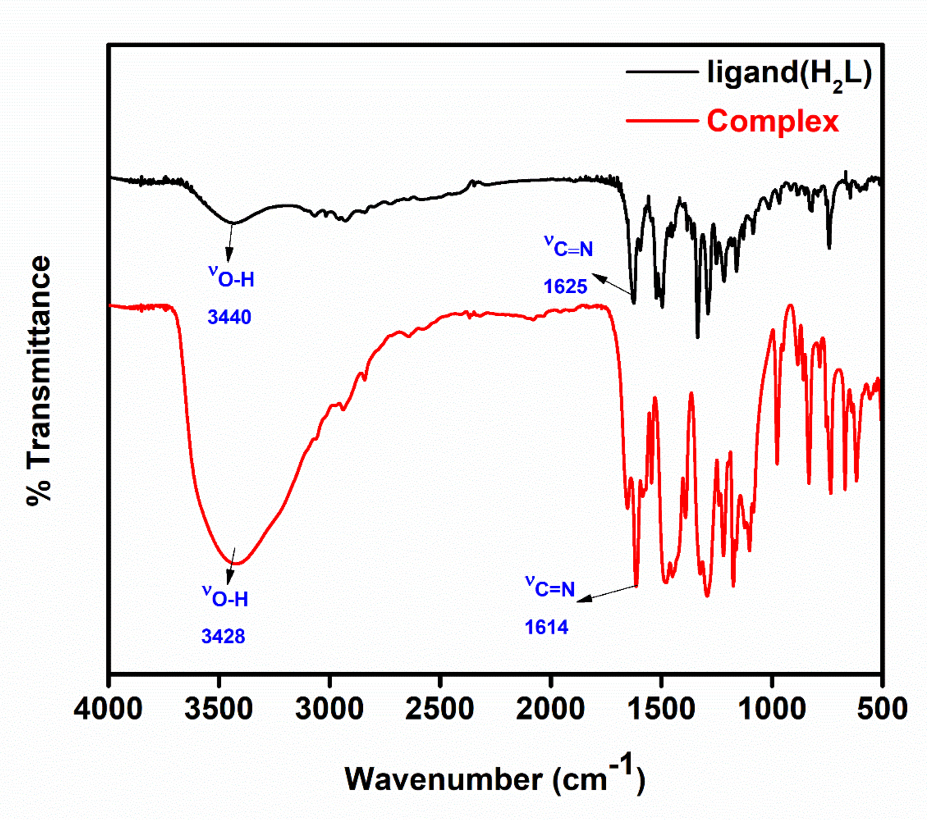

Figure S1. FT-IR spectra of the **H_2L** ligand and of compound **1**.

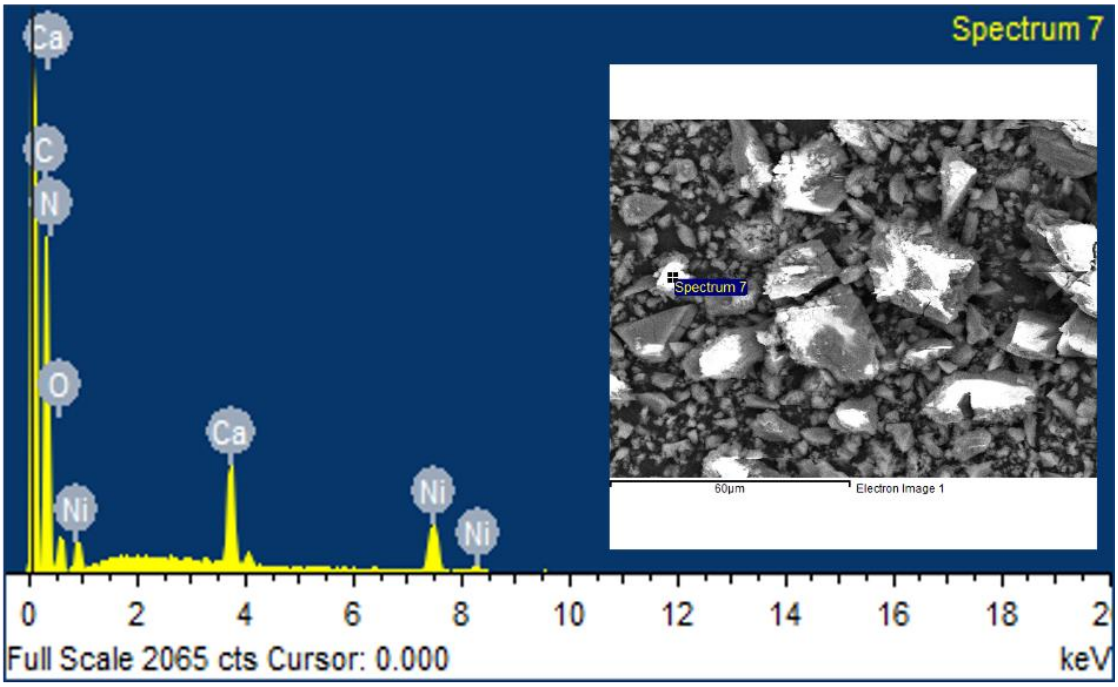

Figure S2. EDS spectrum of compound **1**.

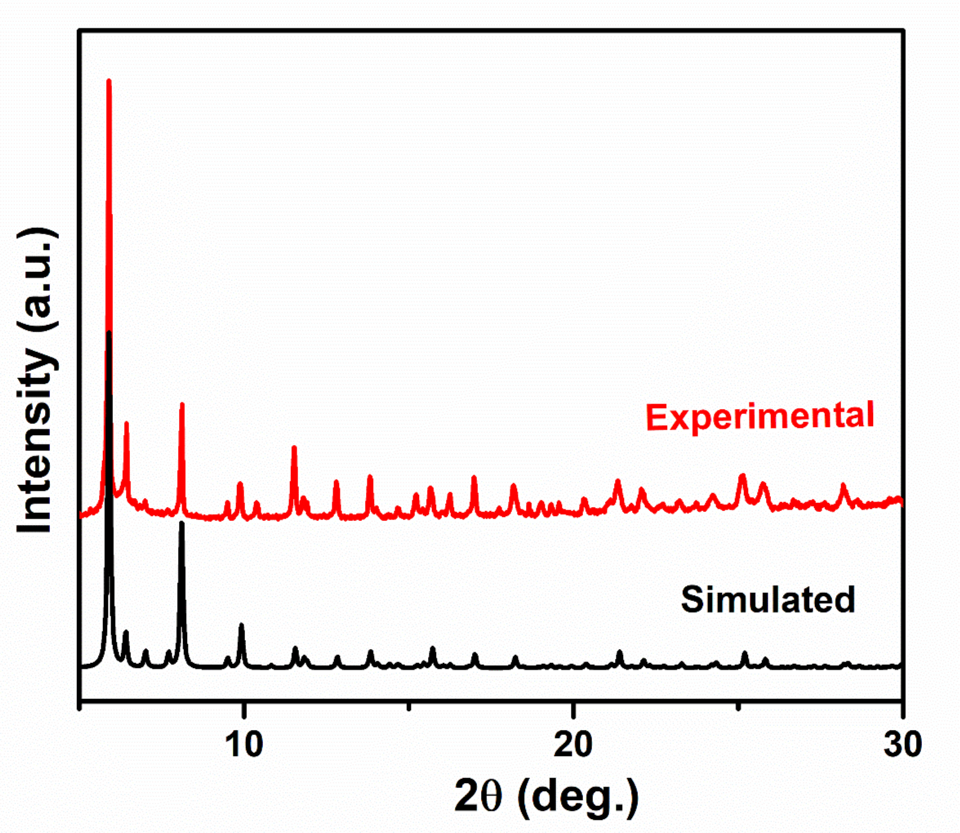

Figure S3. Experimental and simulated powder XRD pattern for compound **1**.

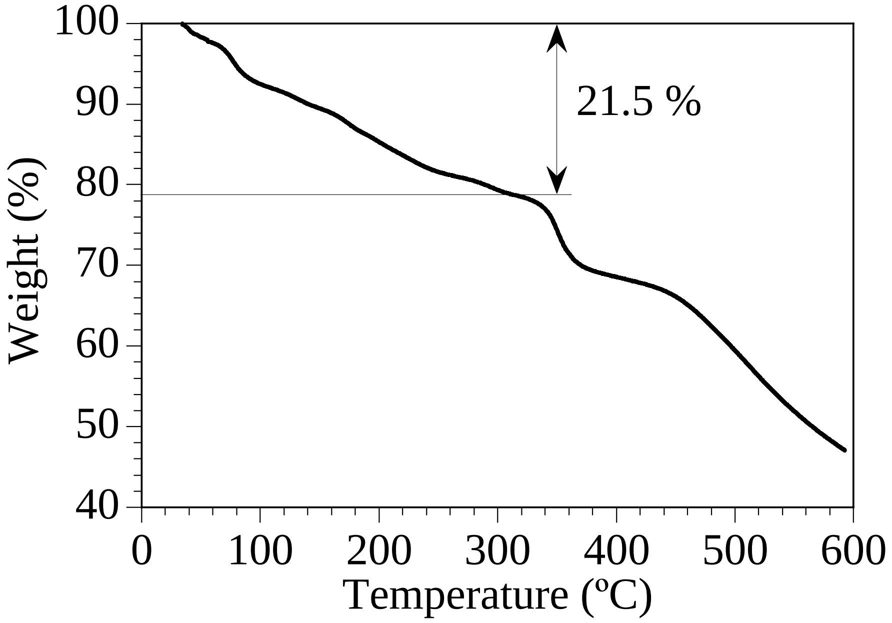

Figure S4. Thermogravimetric analysis of compound **1** in the temperature range 20-600 ºC.

X-ray crystallography

A dark brown prism-shaped single crystal of **1** with dimensions 0.20×0.15×0.12 mm^3 was mounted in a mylar loop, covered with paratone oil, on a SuperNova, Single source at offset/far, EosS2 diffractometer. Data were collected using a SuperNova, Single source at offset/far, EosS2 diffractometer operating at T = 100.00(10) K.

Data were measured using ω scans with Mo Kα radiation. The diffraction pattern was indexed and the total number of runs and images were based on the strategy calculation from the program CrysAlisPro 1.171.39.29c.[1] The maximum resolution that was achieved at Θ = 27.00° (0.78 Å).

The unit cell was refined using CrysAlisPro 1.171.39.29c on 5208 reflections, 22 % of the observed reflections.[1]

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.39.29c.[1] The final completeness is 99.91 % up to 27.00° in Θ. A multi-scan absorption correction was performed using CrysAlisPro 1.171.39.29c.[1] Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.. The absorption coefficient μ of this material is 1.065 mm^{-1} at this wavelength (λ = 0.71073Å). The minimum and maximum transmissions are 0.680 and 1.000.

The structure was solved and the space group $P4_2/n$ (# 86) was determined by the ShelXT 2014/5 structure solution program[2] using iterative methods and Olex2 1.5-dev as the graphical interface.[3] The model was refined with olex2.refine 1.5-dev[4] using full matrix least squares minimisation on F^2.

All non-hydrogen atoms were refined anisotropically. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

Absorption corrections were performed with CrysAlisPro 1.171.39.29c using spherical harmonics as implemented in SCALE3 ABSPACK.[1]

A solvent mask was calculated and 372 electrons were found in a volume of 1588 $Å^3$ in one void per unit cell. This is consistent with the presence of 16 H_2O per Asymmetric Unit which account for 320 electrons per unit cell.

There is a disorder in some parts of the ligand that results in the presence of: (i) a couple of close O atoms coordinated to Ni1 and Ni2: O6/O6a (with occupancies of 0.54 and 0.46, respectively), (ii) a couple of close N atoms connected to Ni2: N3/N3a (with occupancies of 0.54 and 0.46, respectively). Addtionally, there is a disorder in one dmf molecule coordinated to Ni1 that results in a couple of close O atoms coordinated to Ni1: O16/O16a (with occupancies of 0.75 and 0.25, respectively). There is also a disorder that affects the Ca ions bonded to a water and a dmf molecules occupying very close coordination positions (atoms O14 from a water molecule and O17, from a dmf molecule, with occupancy factors of 0.64 and 0.36, respectively).

Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 2255667. Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

SHAPE analysis of the coordination around the Ca and Ni ions.

The shape analysis clearly indicates that Ni1 and Ni2 present a slightly distorted octahedral geometry, whereas the Ca ion presents a distorted square antiprism geometry. As expected, when the water molecule (O14) is considered, the distorsion are lower than when we consider the dmf molecule (O17).

Table S1. Continuous SHAPE measurement values of the five possible coordination geometries with coordination number six for the two nickel centers in compound **1**.

Geometry	Symmetry	Ni1	Ni2
HP-6	D_{6h}	30.691	31.365
PPY-6	C_{5v}	24.410	26.886
OC-6	**O_h**	**0.881**	**0.404**
TPR-6	D_{3h}	11.929	14.112
JPPY-6	C_{5v}	28.204	30.761

HP-6 = Hexagon, PPY-6 = Pentagonal pyramid, **OC-6 = Octahedron**, TPR-6 = Trigonal prism and JPPY-6 = Johnson pentagonal pyramid J2. Lower values are indicated in bold.

Table S2. Continuous SHAPE measurement values of the 13 possible coordination geometries with coordination number eight for the Ca centre (considering O14 or O17) in compound **1**.

Geometry	Symmetry	Ca (O14)	Ca (O17)
OP-8	D8h	28.505	30.047
HPY-8	C7v	22.114	21.971
HBPY-8	D6h	14.786	12.939
CU-8	Oh	9.452	7.587
SAPR-8	**D4d**	**1.437**	**2.279**
TDD-8	D2d	2.709	3.189
JGBF-8	D2d	14.309	12.578
JETBPY-8	D3h	26.887	25.780
JBTPR-8	C2v	3.412	3.514
BTPR-8	C2v	1.828	2.808
JSD-8	D2d	5.099	5.314
TT-8	Td	9.782	7.993
ETBPY-8	D3h	22.391	22.270

OP-8 = Octagon; HPY-8 = Heptagonal pyramid; HBPY-8 = Hexagonal bipyramid; CU-8 = Cube; **SAPR-8 = Square antiprism**; TDD-8 = Triangular dodecahedron; JGBF-8 = Johnson-Gyrobifastigium (J26); JETBPY-8 = Johnson-Elongated triangular bipyramid (J14); JBTP-8 = Johnson-Biaugmentedtrigonal prism (J50); BTPR-8 = Biaugmentedtrigonal prism; JSD-8 = Snub disphenoid (J84); TT-8 = Triakis tetrahedron.

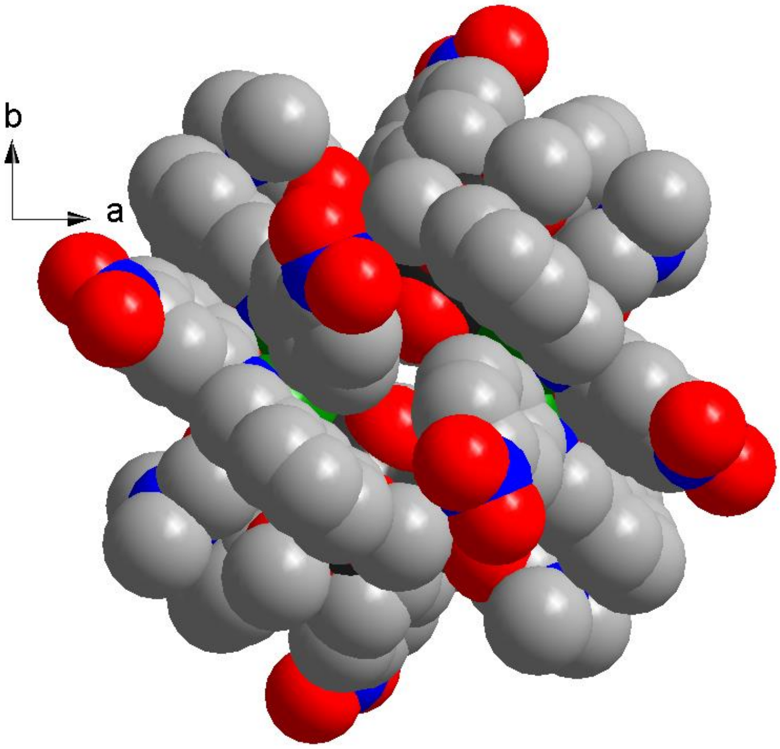

Figure S5. Space filling of compound **1**. Hydrogen atoms are omitted for clarity.

Table S3. Selected bond length (Å) for complex **1**.

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Distance (Å)
Ni1-N1a	2.013(3)	Ni2-O6[2]	2.074(19)	Ca1-O2a[1]	2.336(3)
Ni1-O1a	2.038(4)	Ni2-O6a[2]	2.05(2)	Ca1-O3a[1]	2.544(3)
Ni1-O2a	1.980(3)	Ni2-O12	2.019(2)	Ca1-O7	2.334(3)
Ni1-O6[2]	2.168(19)	Ni2-O13[1]	2.039(3)	Ca1-O8	2.669(3)
Ni1-O6a[2]	2.180(19)	Ni2-N3[3]	2.021(16)	Ca1-O11[1]	2.404(3)
Ni1-O16	2.061(5)	Ni2-N3a[3]	2.02(2)	Ca1-O12	2.388(3)
Ni1-O11	2.020(2)	Ni2-O1a	2.196(3)	Ca1-O15	2.432(3)
		Ni2-O7	1.971(3)	Ca1-O14[4]	2.492(6)
				Ca1-O17[4]	2.360(8)

(1) = y, -x + 1/2, -z + ½; (2) O6 and O6a are two very close positions due to the disorder in one L^{2-} ligand. (3) N3 and N3a are two very close positions due to the disorder in one L^{2-} ligand. (4) O14 and O17 are two very close positions due to the disorder in the H_2O (O14) and dmf (O17) coordinated molecules.

Table S4. Selected bond angles (°) for complex **1**.

Atoms	Angle (°)	Atoms	Angle (°)	Atoms	Angle (°)
O11^1-Ca1-O7	74.30(9)	O11-Ni1-O6	81.5(4)	O6-Ni2-N3	82.9(6)
O12-Ca1-O7	70.92(9)	O16-Ni1-O6	166.4(5)	O7-Ni2-N3	93.0(5)
O12-Ca1-O11^1	81.09(9)	O16-Ni1-O11	88.7(3)	O7-Ni2-O6	173.8(5)
O15-Ca1-O7	141.97(10)	O6a-Ni1-O6	6.3(8)	O12-Ni2-N3	174.3(7)
O15-Ca1-O11^1	79.84(9)	O6a-Ni1-O11	87.5(5)	O12-Ni2-O6	96.9(4)
O15-Ca1-O12	77.98(9)	O6a-Ni1-O16	168.0(6)	O12-Ni2-O7	86.73(11)
O14-Ca1-O7	74.70(17)	N1a-Ni1-O6	95.4(4)	O13-Ni2-N3	95.6(7)
O14-Ca1-O11^1	143.37(17)	N1a-Ni1-O11	175.27(12)	O13-Ni2-O6	88.7(5)
O14-Ca1-O12	70.69(16)	N1a-Ni1-O16	94.9(3)	O13^1-Ni2-O7	96.40(11)
O14-Ca1-O15	115.09(15)	N1a-Ni1-O6a	89.5(5)	O13^1-Ni2-O12	90.08(10)
O17-Ca1-O7	90.5(2)	O1a-Ni1-O6	87.5(5)	N3a-Ni2-N3	7.4(11)
O17-Ca1-O11^1	163.5(2)	O1a-Ni1-O11	100.76(10)	N3a-Ni2-O6	87.9(6)
O17-Ca1-O12	87.9(2)	O1a-Ni1-O16	85.0(3)	N3a-Ni2-O7	88.5(5)
O17-Ca1-O15	110.0(2)	O1a-Ni1-O6a	84.5(6)	N3a-Ni2-O12	175.3(5)
O17-Ca1-O14	20.46(19)	O1a-Ni1-N1a	82.64(12)	N3a-Ni2-O13^1	90.2(7)
O2a^1-Ca1-O7	117.54(10)	O2a-Ni1-O6	95.8(5)	O6a-Ni2-N3	76.7(6)
O2a^1-Ca1-O11^1	70.08(9)	O2a-Ni1-O11	85.75(11)	O6a-Ni2-O6	6.6(8)
O2a^1-Ca1-O12	144.89(10)	O2a-Ni1-O16	92.9(3)	O6a-Ni2-O7	167.6(6)
O2a^1-Ca1-O15	77.59(10)	O2a-Ni1-O6a	98.2(6)	O6a-Ni2-O12	102.8(5)
O2a^1-Ca1-O14	143.46(16)	O2a-Ni1-N1a	90.99(13)	O6a-Ni2-O13^1	91.5(6)
O2a^1-Ca1-O17	124.2(2)	O2a-Ni1-O1a	173.09(10)	O6a-Ni2-N3a	81.9(7)

1 = y, -x + 1/2, -z + ½

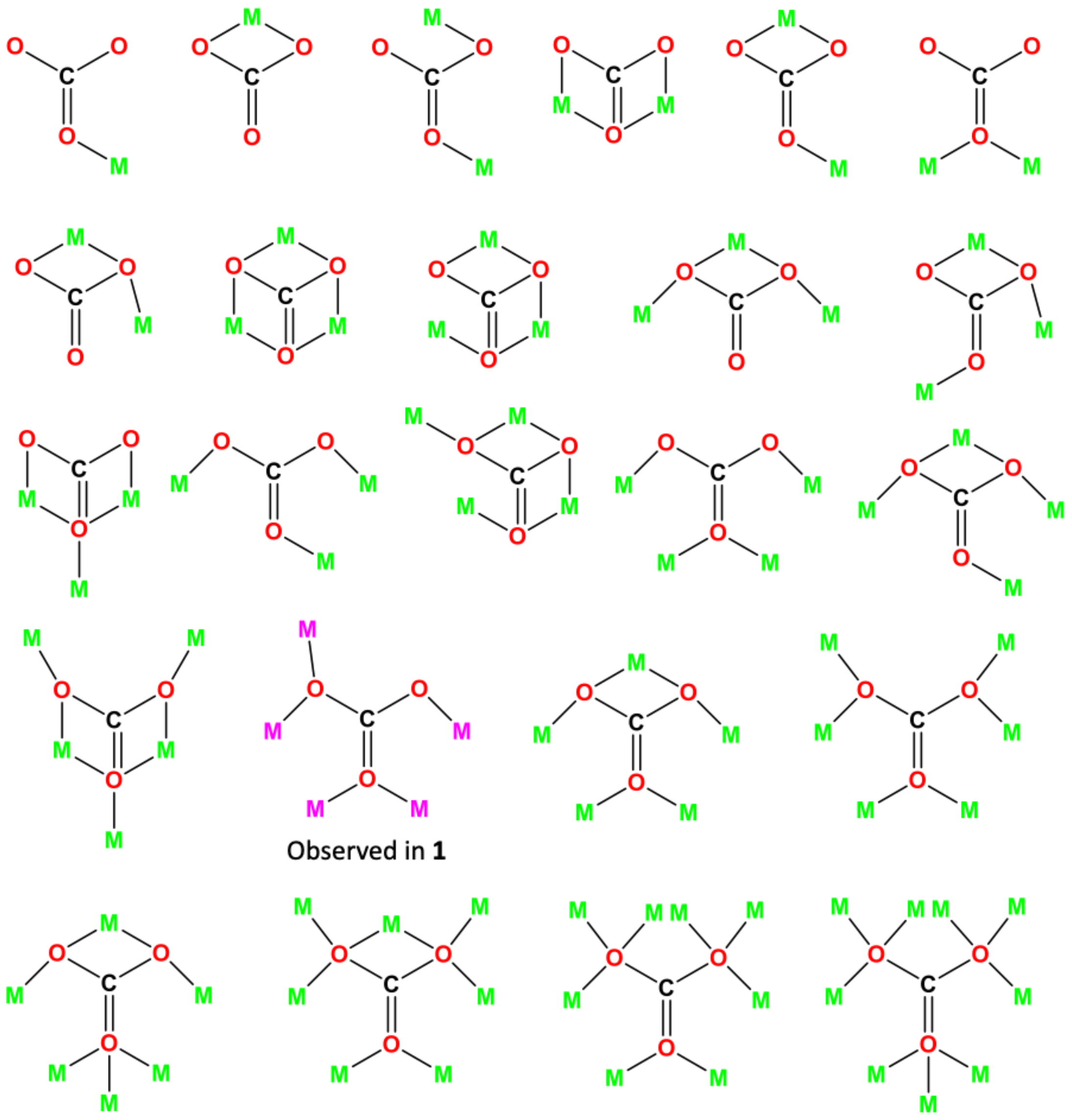

Figure S6. Various coordination modes of the carbonate anion reported in the literature.

Magnetic measurements. Variable temperature magnetic susceptibility measurements, in the temperature range 2-300 K, were performed with an applied magnetic field of 100 mT on a polycrystalline sample with a mass of 23.124 mg using a Quantum Design MPMS-XL-5 SQUID susceptometer. The isothermal magnetization was performed on the sample at 2K with magnetic fields up to 5 T. The susceptibility data were corrected for the sample holder previously measured using the same conditions and for the diamagnetic contribution of the sample, as deduced by using Pascal's constant tables.[5]

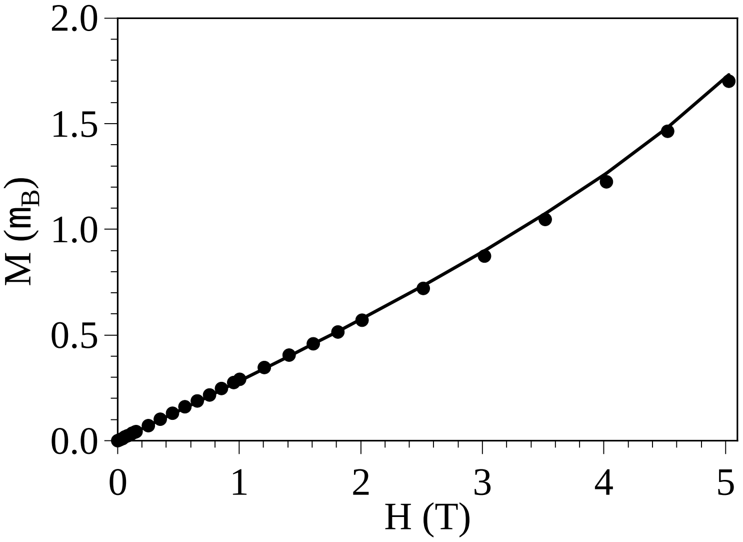

Figure S7. Isothermal magnetization of compound **1** at 2 K. Solid line is the best fit to the model (see text).

References

1- CrysAlisPro Software System, Rigaku Oxford Diffraction, (2017).

2- Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

3- O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

4- L.J. Bourhis and O.V. Dolomanov and R.J. Gildea and J.A.K. Howard and H. Puschmann, The Anatomy of a Comprehensive Constrained, Restrained, Refinement Program for the Modern Computing Environment - Olex2 Disected, *Acta Cryst. A*, (2015), **A71**, 59-71.

5- G. A. Bain, J. F. Berry, Diamagnetic Corrections and Pascal's Constants *J. Chem. Educ.*, 2008, **85**, 532-536.