Dalton
Transactions

COMMUNICATION

Self-assembly of a $[Ni_8]$ carbonate cube incorporating four μ_4-carbonato linkers through fixation of atmospheric CO_2 by ligated $[Ni_2]$ complexes†

Cite this: *Dalton Trans.*, 2014, **43**, 1970

Received 24th October 2013,
Accepted 18th November 2013

DOI: 10.1039/c3dt52999a

www.rsc.org/dalton

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The communication reports the synthesis, characterization, and magnetic behavior of a novel μ_4-carbonato supported and imidazole capped ligated nickel cage $[Ni_8(\mu\text{-}H_2bpmp)_4(\mu_4\text{-}CO_3)_4(ImH)_8](NO_3)_4\cdot 2H_2O$ (1) through self-assembly of ligand bound ferromagnetic Ni_2 building blocks. Structural analysis indicates newer geometrical features for the coordination cage formation and dominant interdimer antiferromagnetic coupling resulting in a diamagnetic ground state.

The self-assembly of dinuclear transition-metal complexes to high nuclearity supramolecular aggregates through control of reaction conditions has become an exciting area of research in synthetic coordination chemistry because of the observation that several of these compounds show single-molecule magnet (SMM) behavior.[1–11] Over the past two decades, the field has been enriched by the synthesis and characterization of a large number of polymetallic entities of first-row transition metals, lanthanides, and actinides having diverse and exciting structures.[12] Several aesthetically pleasing architectures (*e.g.*, squares,[13] rectangles,[1] and pentagons[14]) have been assembled in recent years. These are discrete polynuclear coordination compounds assembled from mono-, bi- or trinuclear building blocks. In several known phenoxido bound dinuclear nickel(II) complexes the Ni^{II} ions are coupled ferromagnetically to yield $S = 2$ states.[15–17] These ferromagnetically coupled dinuclear entities can be assembled into larger magnetically coupled systems by means of bridging ligands capable of mediating magnetic exchange interaction. In particular, such an endeavor may be accomplished during fixation of atmospheric CO_2 by a mildly basic aqueous methanolic reaction mixture of Ni(II) ions and co-ligands, due to the *in situ* generation of carbonato linkers. The geometry of the ensuing multinuclear edifices is dictated by the nature of the co-ligands used in the reaction.

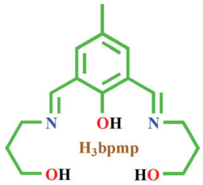

Chart 1

A multidentate ligand 2,6-bis-[(3-hydroxy-propylimino)-methyl]-4-methyl-phenol (H_3bpmp,[18] Chart 1) has been successfully utilized in the isolation of many d-block transition-metal clusters.[19]

We have recently isolated mono- and trinuclear Zn complexes of H_3bpmp and its close congener for varying aggregating performances.[18] To proceed with paramagnetic metal ions, we have chosen a mixed-ligand approach *via* the reactions of H_3bpmp with a variety of co-ligands, in this case with ImH and *in situ* generated CO_3^{2-}. The reaction of $Ni(NO_3)_2\cdot 6H_2O$, H_3bpmp, imidazole, and NEt_3 in a methanolic solution led to the isolation of a green block like solid after slow evaporation after 9 days. This resulted in a novel octanuclear nickel cluster of the general formula $[Ni_8(\mu\text{-}H_2bpmp)_4(\mu_4\text{-}CO_3)_4(ImH)_8](NO_3)_4\cdot 2H_2O$ (1) in 74% yield (eqn (1)) [see the ESI† for full experimental details].

$$\begin{aligned} &4H_3bpmp + 8Ni(NO_3)_2\cdot 6H_2O + 8ImH + 4CO_2 + 4NEt_3 \\ &\quad \rightarrow [Ni_8(\mu\text{-}H_2bpmp)_4(\mu_4\text{-}CO_3)_4(ImH)_8](NO_3)_4\cdot 2H_2O \\ &\qquad + 4(HNEt_3)(NO_3) + 8HNO_3 + 42H_2O\ldots \end{aligned} \tag{1}$$

Direct addition of CO_3^{2-} as potassium carbonate can also provide **1** in an equivalent yield reported above. Complex **1** (Fig. 1, below) forms prismatic green crystals and crystallizes

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† Electronic supplementary information (ESI) available: Detail synthesis procedure, characterization data, and crystallographic data in CIF. CCDC 869968. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52999a

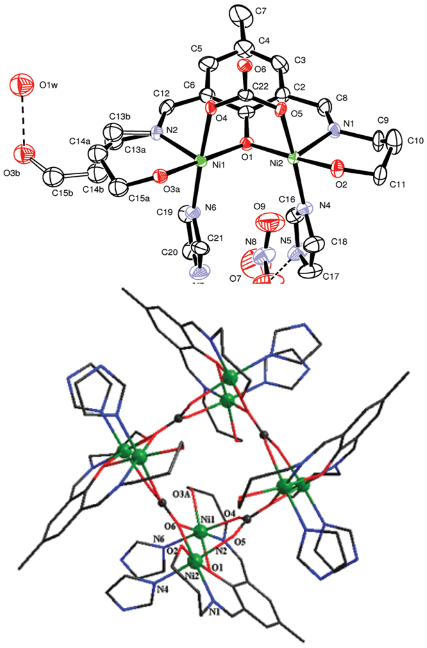

Fig. 1 (above) ORTEP[20] view of the asymmetric unit and (below) ball and stick presentation of the octanuclear unit $[Ni_8(\mu\text{-}H_2bpmp)_4(\mu_4\text{-}CO_3)_4(ImH)_8](NO_3)_4{\cdot}2H_2O$ in **1**. Color code: Ni, light and dark green; N, blue; O, red; C, black.

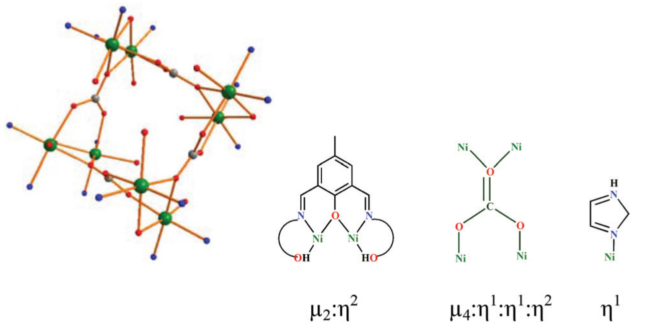

Fig. 2 (left) Side view of coordination environments around Ni atoms in **1** and (right) observed ligand bonding modes.

in the tetragonal space group $P42_1c$, with the asymmetric unit (Fig. 1, below) containing the Ni_2 repeating unit as well as a nitrate counter anion and solvent H_2O molecule. The structure displays disorder on the propanol chain C13–C14–C15–O3 which was refined over two sites (Fig. 1, below).

The complex consists of eight Ni^{II} ions, with the metallic core displaying a cubic motif (Fig. S1†). It may best be described as μ-H_2bpmp^- bound two Ni^{II} ions (Ni1 and Ni2) occupying two corners of the cube and repeated *via* bridging of carbonato groups in a cyclic manner (ESI, Fig. S2†). Complex **1** is formed by four dinuclear $[Ni_2(H_2bpmp)]^{3+}$ units linked covalently by four μ_4-carbonate ligands generated *in situ* through fixation of atmospheric CO_2 into the supramolecular $[Ni_2(\mu\text{-}CO_3)]_4$ aggregate. It was found that at the four faces of the cube four carbonato groups were present, which adopt a μ_4-η^1:η^1:η^2-bonding mode (Fig. 2) ([4.211] in Harris notation[21]), binding to four Ni_2 fragments present, and it appears to be directing the positions of these fragments. The eight Ni(II) ions are thus positioned in vertices of a distorted cube compressed along the 4-fold axis.

Recently we have shown the formation of a Co_5 cluster which had been seen to encapsulate bridging CO_3^{2-} ligands in the absence of any carbonate addition.[6–8,22] Similar to this earlier report, in the present case the CO_3^{2-} ligand is most probably derived from the fixation of atmospheric CO_2, which results in the fascinating Ni_8 coordination cage. The CO_3^{2-} ion (*vis-à-vis* NO_3^-) was identified *via* charge balance consideration, solution molar conductivity determination[23] and cautious consideration of the X-ray diffraction data (ESI†). The FTIR spectrum of **1** displays strong absorptions at 1548 and 1331 cm^{-1} due to $\bar{\nu}_{asym}(CO_2)$ and $\bar{\nu}_{sym}(CO_2)$ vibrational modes of the carbonate ligand, respectively.[24] The transformation of atmospheric CO_2 to CO_3^{2-} is similar to the function of carbonic anhydrase, forming HCO_3^- in animal tissues at high CO_2 concentration. Four such carbonato ligands provide appropriate binding geometry along the four faces of the cube to support the formation of the cluster cube.

Around the four faces of the carbonate-stabilized metallic core lie organic blocking groups made up of singly deprotonated H_3bpmp and imidazole ligands. The former displays bridging [3 + 3] mode of bonding, while the latter functions as a terminal ligand. The crystallographically unique atoms Ni1 and Ni2 are six-coordinate with distorted octahedral geometries, with a *cis*-N_2O_4 coordination environment (ESI, Fig. S3 and S4†). The remaining six Ni atoms of the cube display the same symmetry related geometry. The average Ni–O and Ni–N bond lengths are 2.070 Å and 2.060 Å, respectively. The Ni–OH bonds from the alcohol ends are longer at 2.080 (av) Å. The corresponding lengths for the carbonato ligand range from 2.030 to 2.101 Å. The bond angles are within the normal range for the octahedral coordination environment. Within the Ni cube, the distance between adjacent metal centers along one edge of the cube, within the dimer, is 3.012 Å. The average distance along the other edges, across the CO_3^{2-} bridge, is 5.322 Å.

While the CO_3^{2-} bridging modes present in this complex are quite common, the coordination driven supramolecular assembly of cubic cluster **1** is rather exceptional. Intermolecular void spaces between the clusters are occupied by solvation water molecules and nitrate ions (ESI, Fig. S5†). There are intermolecular hydrogen bonds formed between the cluster cube and the water molecules and counter ions *via* the protonated alcohol terminals of the H_2bpmp^- ligands. In one case the disordered arm is not coordinated to the Ni^{II} ion, but is engaged in a hydrogen bonding interaction with one solvent water molecule. Terminal imidazole groups were also engaged in hydrogen bonding interactions with O atoms of the nitrate groups (ESI, Fig. S6†). Selected bond lengths and angles are given in Table S1 in the ESI.†

Magnetic properties were investigated on a polycrystalline sample of **1**. The temperature dependence of inverse magnetic susceptibility ($1/\chi$) is nearly linear in the 50–300 K range

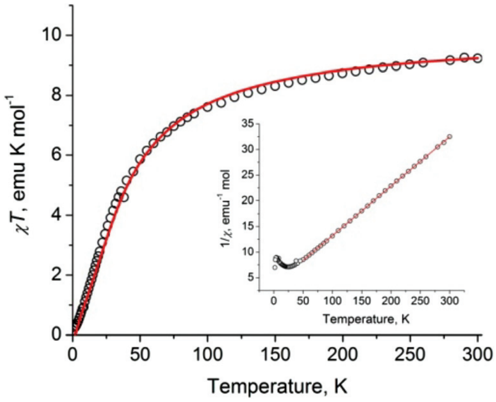

Fig. 3 Temperature dependence of χT for **1**. The solid red curve represents the best simulation of the experimental data. Inset: temperature dependence of inverse magnetic susceptibility of **1**, with the Curie–Weiss fit shown as a solid red line.

(Fig. 3, inset). Fitting this part of the data to the Curie–Weiss law resulted in the Curie constant of 10.39(2) emu K mol^{-1} per cubic cluster, *i.e.* ~1.30(2) emu K mol^{-1} per Ni^{2+} ion. This value is larger than the spin-only value of 1.00 emu K mol^{-1} expected for the $S = 1$ Ni^{2+} ion, indicating orbital contribution to the total magnetic moment, as is well known for Ni(II) complexes.[25] The Weiss constant obtained from the linear fit is negative, $\theta = -37.3(3)$ K, suggesting the presence of dominant antiferromagnetic interactions between Ni^{2+} ions. Nevertheless, the magnetic exchange coupling in this cluster is far more complicated. This conjecture can be made based on the earlier detailed work by Fondo *et al.*[15] on the magnetic properties of a tetranuclear carbonato-bridged Ni(II) complex with bonding topology that essentially represents one face of the Ni_8 cubic cluster discussed herein. According to the report on the tetranuclear complex and using the high symmetry of our complex, we can identify three magnetic exchange pathways: a ferromagnetic exchange within each Ni_2 dimer ($J_1 > 0$), a ferromagnetic exchange along the long cube edge ($J_2 > 0$), and an antiferromagnetic exchange along the face diagonal of the cube ($J_3 < 0$). The latter two interactions are mediated by the CO_3^{2-} bridge. Consequently, the temperature dependence of χT was modeled with the three magnetic exchange constants restrained to have the corresponding signs. The simulation of the χT *vs.* T curve (Fig. 3) was performed with Magpack,[26] resulting in the values of $J_1 = 3.0(2)$ cm^{-1}, $J_2 = 0.4(1)$ cm^{-1}, and $J_3 = -7.5(3)$ cm^{-1}, with $g = 2.24(1)$. The magnitude of the exchange constants is well comparable to the values reported by Fondo *et al.* for the tetranuclear Ni(II) complex mentioned above. The antiferromagnetic exchange (J_3) acting along the face diagonal of the cube appears to dominate the magnetic behavior of the Ni_8 cluster, resulting in the $S_T = 0$ ground state. This notion is additionally confirmed by field-dependent magnetization measurements performed at 1.8 K. The magnetization value observed in low fields is rather low, but the magnetization curve is non-linear, suggesting that some crossing of magnetic states takes place at higher fields, as could be expected from the relatively low and competing values of the magnetic exchange constants.

In summary, this work is one of the notable examples of utilizing *in situ* generated carbonato linkers to form a discrete cubic coordination cluster of fascinating magnetic behavior, revealing the flexibility and utility of this linker for future synthesis and magnetic material applications. A new octanuclear cubic coordination cluster type has been prepared through the assembly of H_2bpmp^- chelated Ni(II) ions and imidazole capping ligands. The four faces of the cubic cluster contain four μ_4-carbonato ligands, which are derived from atmospheric CO_2 fixation. Magnetic studies indicate the presence of competing magnetic interactions mediated by the carbonate bridge. The antiferromagnetic exchange across the face diagonal of the cubic cluster dominates the magnetic behavior, resulting in the spin-singlet ground state.

Acknowledgements

AKG is thankful to the Council of Scientific and Industrial Research, New Delhi, India for financial support. The authors also thank DST, New Delhi, for providing the Single Crystal X-ray Diffractometer facility in the Department of Chemistry, IIT Kharagpur under its FIST program. VB acknowledges the Italian Ministry of University and Scientific Research (MIUR, Rome). MS is grateful to the National Science Foundation for the partial support of this work (award CHE-0911109).

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