A one-pot synthesis of a paramagnetic high-nuclearity nickel(II) cluster: an octadecanuclear $Ni^{II}_{16}Na^{I}_{2}$ metal aggregate†

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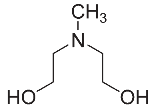
An unusual $Ni^{II}_{16}Na^{I}_{2}$ cluster which features formate as a bridging clamp between two octanuclear nickel cages is reported; preliminary magnetic studies exhibit paramagnetic low-lying states resulting from dominating antiferromagnetic interactions between the nickel(II) centers.

The current interest in the synthesis of high-nuclearity 3d-metal complexes has been sparked due to their relevance to various fields, ranging from metallobiochemistry[1] to molecular magnetic materials.[2,3] However, there is no obvious and deliberate synthetic routes to high nuclearity clusters.[4] Thus, polymetal cages are often self-assembled, the assembling process being sometimes facilitated by alkali metal[5] templates. Consequently, the search for ligands containing good bridging groups, thus fostering formation of polynuclear products, has become an active research area. In this field we have been exploring the feasibility of OH-group containing ligands[6] to influence the nuclearity and topology of metal complexes. Since nickel(II) is known to have a large single-ion zero-field splitting and often gives rise to ferromagnetic coupling, we have especially focussed our attention on polynuclear nickel(II) complexes[6] with the aim of obtaining "high-spin" molecules. Although polynuclear nickel(II) complexes containing up to four metal ions are not rare,[6a,7] but the assembles with more nickel(II) ions still remain a matter of curiosity.

Here we report an interesting example of self-assembly exhibiting how metal–ligand frameworks can be successfully templated about a substrate alkali metal cation. Thus, the synthesis and preliminary magnetic properties of an octadecanuclear supracage $Ni^{II}_{16}Na^{I}_{2}$ in which four star-shaped Ni^{II}_{4} triangular units are linked through two octahedral sodium cations and two bridging formate ligands. There are only a very few magnetically characterized nickel complexes with more than sixteen metal centers reported in the literature.[8] Noteworthy is the presence of the smallest carboxylate, formate, as a bridging ligand. Such molecular nickel–sodium metal aggregates are potential candidates for SMMs (single molecule magnets). *N*-Methyldiethanolamine[8c,9] has been reported in the literature to influence the nuclearity and topology of metal complexes. In the present work we report some other interesting developments.

Reaction of $Ni(CH_3COO)_2{\cdot}4H_2O$ with *N*-methyldiethanolamine (H_2L) and $NaOCH_3$ (ratio 4 : 3 : 6) in methanol yielded a green solution, which was refluxed for 2 h. The solvent methanol was removed *in vacuo* to obtain a green solid, which was recrystallized from acetonitrile; X-ray quality crystals in 70% yield grew over two days. X-Ray diffraction studies show formation of $[(LH)_{12}Ni_{16}(OOCCH_3)_{20}(\mu\text{-}Na)_2(\mu_2\text{-}OOCH)_2]{\cdot}3CH_3CN{\cdot}21H_2O$ **1**.‡ To check whether the isolated crystals consist of a single compound, we have compared the powder-diffraction pattern of the bulk material with the diffraction pattern of the single crystal. In this way we have confirmed the isolation of a compound **1** of single composition. Use of other bases such as Et_3N, CH_3COO^-, NaOH did not yield **1**. Presumably OCH_3^- ion gets oxidized to $HCOO^-$ during the aerial aggregation process and the bridging formate does not originate from carbon dioxide of the air. The yield of **1** did not increase by additional formate ion from outside. The electronic absorption spectrum of **1** in dry methanol exhibits d–d bands.[10] As the mass spectrometry in different solvents, *viz.* CH_3OH, CH_3CN, CH_2Cl_2 indicates the presence of a tetranuclear unit in solution, we assign the d–d bands to the tetranuclear core.



$= H_2L$

$$3\,H_2L + 4\,Ni(CH_3COO)_2 \xrightarrow[CH_3OH]{NaOCH_3} [Na_2\{Ni^{II}_4(HL)_3(OOCCH_3)_5\}_4(HCOO)_2]$$

The structure of **1**, $Ni^{II}_{16}Na^{I}_{2}$, consists of four trigonal-pyramidal building blocks, $[Ni^{II}_4(LH)_3(OOCCH_3)_5]$, which are connected to each other by two sodium cations and two formate anions. Each of the three tridentate ligands (HL^-) connects two nickel centers from the base of the pyramid with the apical nickel center through a μ_3-O ethanolate donor. In addition, one nitrogen atom and one μ-OH donor from the alcohol ligand are bound to a nickel cation in the base. Moreover, the three nickel centers in the base are coordinated to non-bridging monodentate acetate ions and one formate anion, which bridges the two halves of the structure **1**. Three additional acetate ions each bridge the nickel centers at the base with the fourth nickel center at the apex of the trigonal pyramid, thus satisfying the hexa-coordination of all four nickel centers of the building block $[Ni^{II}_4(LH)_3(OOCCH_3)_5(HCOO)_{0.5}]$. A sodium ion connects two such building blocks and is thus coordinated to six oxygen atoms of the said acetate ions originated from the building blocks. The nickel pyramids are thus apex-linked and rotated by approximately 180° relative to each other, thus resulting in a dimer $[Na^{I}\{Ni^{II}_4(HL)_3\,(OOCCH_3)_5(HCOO)_{0.5}\}_2]$. Two such dimers are bridged by two formate anions thus resulting in the neutral molecule **1** $[Na^{I}_2\{Ni^{II}_4(HL)_3(OOCCH_3)_5(HCOO)_{0.5}\}_4]$ whose ORTEP view is shown in Fig. 1.

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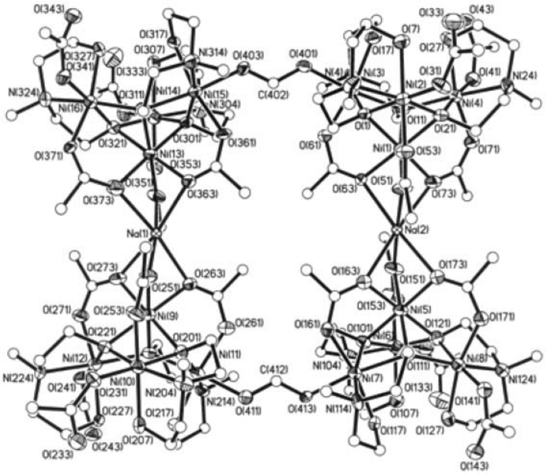

Fig. 1 An ORTEP plot of $[Na^{I}_2\{Ni^{II}_4(HL)_3(OOCCH_3)_5(HCOO)_{0.5}\}_4]$ (40% ellipsoids).

The building block containing the tetranickel(II) center is shown in Fig. 2 while Ni(1) occupying the apex of the trigonal pyramid Ni^{II}_4 is in a Ni(1)O_6 coordination environment, Ni(2), Ni(3) and Ni(4) are in an NO_5 environment and form a nearly equilateral triangle of the pyramidal base. The Ni(2) and Ni(4) are coordinated to one amine nitrogen, two μ_3-O alkoxo oxygens, two acetate oxygens and one protonated oxygen atom of the alcohol ligand. On the other hand, Ni(3) differs from Ni(2) and Ni(4) in the carboxylate coordination; instead of two acetate, Ni(3) is coordinated to one acetate oxygen and one oxygen of the bridging formate. Ni(1) is bonded to three μ_3-O of the alkoxo groups and three acetate oxygen atoms. Table 1 (ESI†) summarizes selected bond lengths and angles of complex **1**. Strong hydrogen bondings between the μ_3-alkoxo oxygen atoms, protonated alcohol oxygen and the oxygen atom of the acetate groups with the O···H···O separation in the range 2.547–2.979 Å are presumably responsible for building up of the supramolecular structure for complex **1**.

The magnetic susceptibility data for a polycrystalline dried sample of **1** were collected in the temperature range 2–290 K in an applied magnetic field of 1 T, and a plot of μ_{eff} (magnetic moment) *vs.* *T* (temperature) is displayed in Fig. 3. The effective magnetic moment μ_{eff} = 11.81 μ_B ($\chi_M T$ = 17.430 cm^3 mol^{-1} K) at 290 K decreases monotonically with decreasing temperature to reach a value of μ_{eff} = 7.50 μ_B ($\chi_M T$ = 7.023 cm^3 mol^{-1} K) at 10 K; below 10 K there is a sharp drop reaching a value of μ_{eff} = 6.22 μ_B ($\chi_M T$ = 4.834 cm^3 mol^{-1} K) at 2 K. This magnetic behaviour clearly indicates the presence of an overall antiferromagnetic exchange coupling between the Ni(II) centers in **1**. The μ_{eff} value at 2 K indicates a non-diamagnetic low-lying state. The sharp drop at the lower temperatures might be to due to the zero-field splitting (*D*) of the ground state and/or very weak antiferromagnetic interactions.

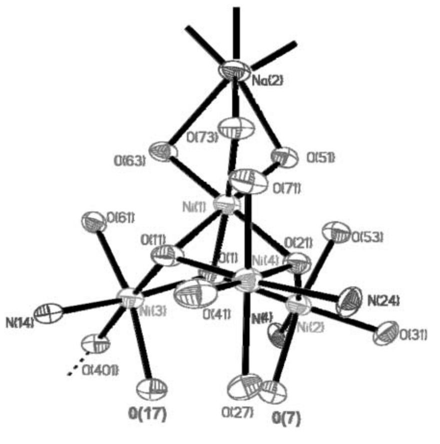

Fig. 2 The core containing the tetranickel(II) unit in $[Na^{I}_2\{Ni^{II}_4(HL)_3(OOCCH_3)_5(HCOO)_{0.5}\}_4]$ (50% ellipsoids).

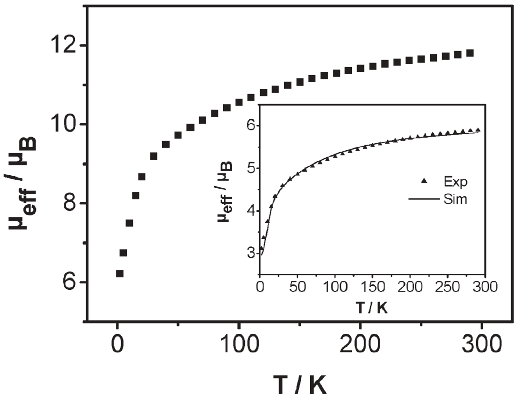

Fig. 3 Temperature-dependence of the magnetic moment μ_{eff}/molecule for complex **1**, $Ni^{II}_{16}Na_2$, at an applied magnetic field of 1 T. Inset: Temperature-dependence of the magnetic moment μ_{eff} for the tetranickel(II) core at an applied magnetic field of 1 T.

The total spin degeneracy of hexadecanuclear Ni(II) is 3^{16} leading to a matrix of $3^{16} \times 3^{16}$ to be diagonalized for simulation of the experimental data. So it is apparent that reduction of the dimension of the matrix is required for simulation. A close examination of the structure indicates that application of the symmetry of the cluster can lead to the desired reduction of the matrix. Thus, the tetranuclear Ni(II) units, each of which does not interact strongly with each other and can be considered as a separate unit, as the Ni···Ni separations of 5.93 and 6.03 Å between the tetranuclear units are too long. These separations correspond to the formate ($HCOO^-$) and Na-bridges, respectively. Thus, we have analyzed the magnetic data by considering the smallest core of **1**, *i.e.* $[Ni^{II}_4(LH)_3(OOCCH_3)_5(HCOO)_{0.5}]Na_{0.5}$. As is evident from the structure of the Ni(II) centers in the tetranuclear unit, at least two types of exchange interactions, J_1 and J_2 have to be considered for simulating the susceptibility data. J_1 represents the exchange interaction between the Ni(II)-center (Ni(1) in Fig. 2) at the apex of the pyramid and the Ni(II) centers (Ni(2), Ni(3) and Ni(4) of Fig. 2), which constitute the triangular base of the pyramid; whereas J_2 the exchange parameter between the three centers Ni(2), Ni(3) and Ni(4) of Fig. 2). Thus, the spin Hamiltonian used is:

$$\hat{H} = -2J_1(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_1\cdot\hat{S}_3 + \hat{S}_1\cdot\hat{S}_4) - 2J_2(\hat{S}_2\cdot\hat{S}_3 + \hat{S}_3\cdot\hat{S}_4 + \hat{S}_4\cdot\hat{S}_2). \tag{1}$$

A satisfactory simulation, shown as a solid line in Fig. 3, inset, using a least-squares fitting computer program with a full-matrix diagonalization, is obtained with the parameters J_1 = +4.3 cm^{-1}, J_2 = −15.1 cm^{-1}, $g_1 = g_2 = g_3 = g_4$ = 2.18. The nature of the evaluated J-values are in accord with the Ni–O(alkoxo)–Ni angles prevailing in the cluster: Ni(1)–O_{alk}–Ni(X) lying between 90 and 93°, whereas Ni–O_{alk}–Ni angles between the Ni(2), Ni(3) and Ni(4) centers are 132–134°. The strength of ferromagnetic coupling J_1 related to the angle 90–93° is relatively weak, presumably due to additional presence of acetate ligand in *syn–syn* mode: acetate bridging contributes in general antiferromagnetic coupling to the overall exchange and thus reduces the magnitude of the ferromagnetic coupling. That the average bridging angle of 133° leads to antiferromagnetic interactions is known in the literature and J_2 is also accordingly antiferromagnetic in nature.[7,8,11] The nature of the exchange coupling constants J_1 and J_2 are thus in full agreement with the Ni–O–Ni/J correlation, supporting the simplest "two-J"-model used. Moreover, that the contributions to the exchange coupling of the bridging formate and sodium ions are negligible are also supported by the good quality of the fit obtained by using a tetranuclear core with a "two-J" model. Additionally, by keeping $J_1 = 0$ (fixed), the good quality of the simulation could not be reproduced, indicating the importance of J_1 for the fitting procedure.

The presence of paramagnetic low-lying states has been verified by the variable-temperature (1.9–5 K), variable-field (4 and 7 T) magnetization (VTVH) measurements (ESI,† Fig. S1). The magnetization increases with the field up to $M/Ng\beta = 4.94$ at 7 T and 1.9 K where it is nearly saturated. Furthermore, the magnetization data for different fields do not superimpose, which reveals the presence of excited states at energies in the order of the Zeeman splitting. The saturated magnetization value of 4.94 measured at 1.9 K and 7 T clearly indicates the participation of $M_S = -4$ or -5 Zeeman components. We conclude that the expected lowest energy state S_t = 4,3,2,1 or zero (as the ground state for the tetranuclear core with the evaluated positive and negative J values is $S_{core} = 1$) is not well isolated and the excited states with S values 4 or higher are within a few wavenumbers from the lowest lying state.

In conclusion, the synthesis, structure and preliminary magnetic studies of an octadecanuclear $Ni^{II}_{16}Na^{I}_{2}$ cluster with a nondiamagnetic spin ground state are reported and the involvement of formate in bridging the core structures suggests that this is a vital component in the formation of this unusual structure. Complex **1** offers the possibility of including formate in other alkali metal templated synthesis of polynuclear complexes and will be reported in due course.

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Notes and references

‡ *Crystal data* for $C_{102}H_{206}N_{12}Na_2Ni_{16}O_{68}\cdot 3CH_3CN\cdot 21H_2O$; **1**·$3CH_3CN\cdot 21H_2O$; M = 4175.6, orthorhombic, space group $P2_12_12_1$, a = 19.3308(6), b = 26.0589(8), c = 36.1281(12) Å, V = 18199(10) Å^3, Z = 4, D_c = 1.524 g cm^{-3}, T = 100(2) K, reflections collected = 136 036, unique = 26843 (R_{int} = 0.1330), R_1 = 0.0798 ($I > 2\sigma(I)$, R_1 = 0.1066 (all data), absolute structure parameter = 0.029(15). The Siemens ShelXTL software package (G. M. Sheldrick, Universität Göttingen) was used for solution, refinement, and drawing of the structure. CCDC 619330. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613782b

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