Reactivity in polynuclear transition metal chemistry as a means to obtain high-spin molecules: substitution of μ_4-OH$^-$ by η^1,μ_4-N$_3^-$ increases nine times the ground-state S value of a nonanuclear nickel(II) cage

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The reaction of di-2-pyridyl ketone, (2-py)$_2$CO, with Ni(O$_2$CMe)$_2$·4H$_2$O yields the cage [Ni$_9$(OH)$_2$(O$_2$CMe)$_8${(2-py)$_2$CO}$_4$], which reacts further with N$_3^-$ ions to give the structurally similar cluster [Ni$_9$(N$_3$)$_2$(O$_2$CMe)$_8${(2-py)$_2$CO}$_4$] containing extremely rare η^1,μ_4-N$_3^-$ groups; magnetic studies reveal that the spin ground state of the latter is nine times the ground state of the former.

The study of molecules with unusually large numbers of unpaired electrons has taken on added impetus in the last five years,[1–3] since it has been realised that a fairly large ground-state S value is one of the necessary requirements for molecules to be able to function as magnetizable magnets (single-molecule magnets, SMMs) below a critical temperature.[4] In most polynuclear clusters, magnetic exchange interactions are mainly propagated by bridging OH$^-$, O^{2-}, RO$^-$ or RCO$_2^-$ ligands, or a combination of two or more of these groups.[4] These ligands often cause antiferromagnetic interactions and, thus, it is necessary to arrange the metal ions and the bridging groups in an appropriate manner so that they can give a high-spin ground state for the system.[4] No systematic attempts have been made to replace the above mentioned bridging ligands in a known cluster with other groups that are more prone to ferromagnetic coupling, for example end-on N$_3^-$, and, in general, the reactivity chemistry of polynuclear 3d-metal complexes is practically unexplored. We herein describe a novel OH$^-$-bridged, nonanuclear nickel(II) cluster with an $S = 1$ ground state and its reaction with azide ions, which leads to substitution of the μ_4-OH$^-$ ligands and yields a structurally similar cluster with an $S = 9$ ground state.

Reaction of di-2-pyridyl ketone, (2-py)$_2$CO, with 2 equivalents of Ni(O$_2$CMe)$_2$·4H$_2$O in DMF under reflux resulted in a green solution from which [Ni$_9$(OH)$_2$(O$_2$CMe)$_8${(2-py)$_2$CO$_2$}$_4$]·19H$_2$O **1**† precipitated within 4 days in *ca.* 60% yield. The double deprotonation of the *gem*-diol form of di-2-pyridyl ketone (formed *in situ* in the *presence* of the metal ions) is a consequence of the high MeCO$_2^-$ to (2-py)$_2$C(OH)$_2$ ratio (4:1) used in the reaction. The RCO$_2^-$/(2-py)$_2$CO$_2^{2-}$ ligand 'blend' has resulted in a variety of high-nuclearity species in cobalt(II)[5] and copper(II)[6] chemistry.

Complex **1**‡ (Fig. 1) has a fourfold axis passing through Ni(1). The nine Ni^{II} atoms adopt the topology of two square pyramids sharing a common apex at Ni(1) and are held together by four η^1:η^3:η^3:η^1:μ_5 (**A**) (2-py)$_2$CO$_2^{2-}$ ligands. Each Ni···Ni edge of the bases of the pyramids is further bridged by one *syn, syn* η^1:η^1:μ_2 acetate. The four acetate ligands create a concave cavity in each pyramid's base, into which a very rare μ_4-OH$^-$ is effectively trapped capping the square base. A
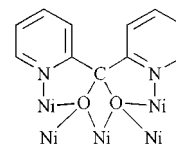
A

salient feature of the structure is the coordination number eight (square antiprismatic geometry) around Ni(1).

The dc $\chi_M T$ product of **1** shows a continuous decrease from the room temperature value of 11.47 cm^3 K mol^{-1} down to 0.40 cm^3 K mol^{-1} at 2 K (Fig. 2), indicating a dominant antiferromagnetic superexchange pattern. A first approach to quantify the magnetic exchange interactions in **1** has been performed by means of the full-matrix diagonalisation program CLUMAG,[7] applying the Hamiltonian (1):

$$H = -J_1(S_1S_2 + S_1S_3 + S_1S_4 + S_1S_5 + S_1S_6 + S_1S_7 + S_1S_8 + S_1S_9)$$
$$- J_2(S_2S_3 + S_3S_4 + S_4S_5 + S_5S_2 + S_6S_7 + S_7S_8 + S_8S_9 + S_9S_6) -$$
$$J_3(S_2S_4 + S_3S_5 + S_6S_8 + S_7S_9) \qquad (1)$$

in which S_1 corresponds to the central metal site [Ni(1)], and S_2, S_3, S_4, S_5 and S_6, S_7, S_8, S_9 correspond to the Ni^{II} atoms placed at the two square bases [Ni(2), Ni(2b), Ni(2c), Ni(2d) and Ni(3), Ni(3b), Ni(3c), Ni(3d), respectively]. In this scheme (**B**), J_1
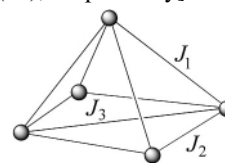
B

relates the central with the peripheral spins, whereas J_2 and J_3 relate the neighboring and the opposite spins, respectively, in each base. To reduce the deviation of the data due to the zero field splitting effect, the fit was performed in the 300–12 K temperature range. The best fit parameters obtained are $J_1 = 6.0$ cm^{-1}, $J_2 = 18.0$ cm^{-1} and $J_3 = -57.0$ cm^{-1} for a g value of 2.30. The strong antiferromagnetic interaction J_3 is consistent with the large Ni–O–Ni angles of *ca.* 140°, whereas the weak to moderate ferromagnetic interactions J_1 and J_2 were expected for the observed Ni–O–Ni angles that are slightly larger than 90°.[8] The ground state of **1**, obtained from the low temperature data and magnetization measurements ($M/N\beta$ value of 1.05 under an external field of 5 T at 2 K) is $S = 1$.

We have wondered whether the end-on azido ligand, a well known ferromagnetic coupler, would be incorporated into the
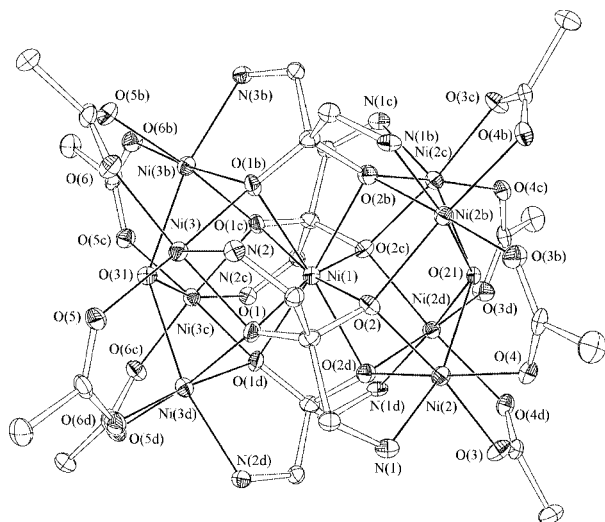
Fig. 1 ORTEP representation of complex **1** at the 20% probability level. Letters b, c and d refer to equivalent positions. b: $x, -y + 1/2, z$. c: $-x + 1/2, -y + 1/2, z$. d: $-x + 1/2, y, z$.
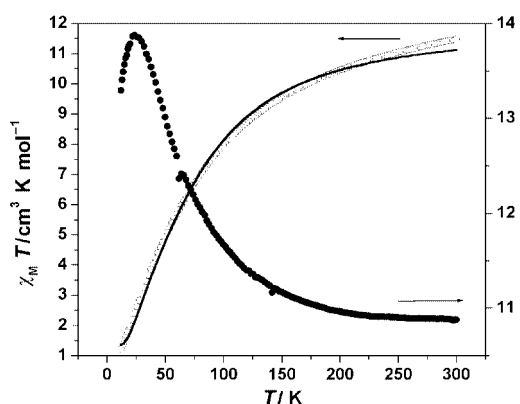

Fig. 2 Plots of $\chi_M T$ *vs. T* for complexes **1** (left *y* axis, open circles) and **2** (right *y* axis, solid circles). The solid line is a fit of the data to the appropriate theoretical expression; see text for fitting parameters.
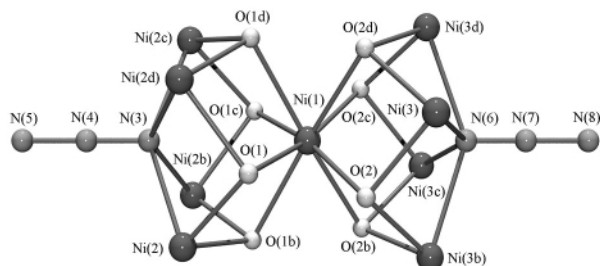

Fig. 3 The molecular structure of complex **2**. For clarity, only the Ni^{II} atoms, nitrogen atoms of the azido ligands and triply bridging oxygen atoms of (2-py)$_2$CO$_2^{2-}$ are shown. Symmetry transformations used to generate equivalent atoms are: b: $x, -y + 1/2, z$. c: $-x + 1/2, -y + 1/2, z$. d: $-x + 1/2, y, z$.

Ni$_9$ cage skeleton replacing the hydroxo ligands, which cause the strong antiferromagnetic interaction J_3 (see **B**). This has, indeed, turned out to be the case. Reaction of **1** with 2–3 equivalents of NaN$_3$ in DMF–MeOH (2:1 v/v) gave green crystals of [Ni$_9$(N$_3$)$_2$(O$_2$CMe)$_8$\{(2-py)$_2$CO$_2$\}$_4$]·4DMF·4.5H$_2$O **2**† in 80% yield.

Complex **2**‡ (Fig. 3), which also has a fourfold axis passing through Ni(1), bears striking structural similarity to **1**, the main difference being the replacement of the μ$_4$-OH$^-$ ligands of the latter by the η^1,μ$_4$-N$_3^-$ ligands in the former. Such η^1,μ$_4$ azido ligands had been totally unknown and were first observed in the recently reported[9] nonanuclear cage [Co$_9$(N$_3$)$_2$(O$_2$CMe)$_8$\{(2-py)$_2$CO$_2$\}$_4$] **3**.

Complexes **1** and **2** join a handful of structurally characterized discrete, non-organometallic nonanuclear Ni^{II} complexes with O,N-ligation.[10–13]

The dc $\chi_M T$ product of **2** increases from the room temperature value of 10.87 cm^3 K mol^{-1} to a maximum of 13.88 cm^3 K mol^{-1} at 24 K, and then decreases continuously down to 2 K (Fig. 2). This behaviour is compatible with a moderate ferromagnetic coupling; the low-temperature decrease of the magnetic moment is associated with the anisotropy of the Ni^{II} ions. Magnetization data collected for **2** show a rapid increase of $M/N\beta$ upon increasing the external field, reaching a value of 9.59 at 5 T. Thus, the magnetic data for **2** should be associated with ferromagnetic coupling mediated by the η^1, μ$_4$-N$_3^-$ ligand (giving a total S value of nine times the local spin), assuming ferromagnetic coupling between the central and the peripheral Ni^{II} ions (as in **1**); this assumption is reasonable because the structural parameters of complexes **1** and **2** do not differ much. The low temperature fall in $\chi_M T$ might be very exciting and the study of the relaxation behaviour of **2** is in progress.

In conclusion, the structures of both **1** and **2** feature very rare characteristics, such as the coordination number 8 for the central Ni^{II} ion, the μ$_5$ coordination mode of (py)$_2$CO$_2^{2-}$, and the η^1,μ$_4$ coordination mode of both the hydroxo and azido ligands. However, the most remarkable result of this work is the fact that rational reactivity chemistry of a polynuclear complex results in a new cluster of the same nuclearity, which retains the structural identity of and has much more attractive magnetic properties than the starting material. The described N$_3^-$ for OH$^-$ substitution has the potential for general application in the area of high-spin molecules.

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