# A novel high-spin heterometallic $Ni_{12}K_4$ cluster incorporating large Ni–azide circles and an *in situ* cyanomethylated di-2-pyridyl ketone†

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**Reaction of di-2-pyridyl ketone (dpk) with nickel acetate and azide in the presence of potassium *tert*-butylate as a catalytic base generates the title compound, which contains the largest $[Ni(\mu_{1,1}\text{-}N_3)]_6$ circles in the discrete ferromagnetically-coupled $M^{II}$–azide cluster family, and shows an unprecedented *in situ* cyanomethylation of ketone.**

The synthesis of new magnetic metal circles with high-spin topologies is one of the central topics in the field of molecular magnetism. Several transition metals and bridging ligands have been employed in the synthesis of a variety of metallacyclic rings, such as the intriguing decanuclear "ferric wheels" of formula $[\{Fe(OMe)_2(L)\}_{10}]$[1a] pioneered by Lippard and co-workers and $[\{cis\text{-}Cu^{II}(\mu\text{-}OH)(\mu\text{-}pz)\}_n]$ rings ($n$ = 6, 8, 9, 12, and 14).[1b] Of strongly ferromagnetic superexchange bridges, the azide ligand is the most versatile at bridging metal ions. A number of polynuclear and polymeric magnetic complexes with azido bridging ligands have been reported to date.[2,3] It is clear that the $N_3^-$ anion acts as a bridging ligand in two typical coordination modes, end-on (EO or 1,1) and end-to-end (EE or 1,3). The end-to-end (EE) coordination mode usually exhibits antiferromagnetic coupling, the end-on (EO) exhibits ferromagnetic coupling, and the magnetic coupling may be reversed for very large M–$(\mu_{1,1}\text{-}N_3)$–M bond angles.[4] However, it is still a challenge for the discrete $M^{II}$–azido magnetic cluster system to assemble large metal circles bridged by the ferromagnetically-coupled $\mu_{1,1}$-azido ligands. To our knowledge, such systems remain extremely rare thus far. Working towards this goal, we did successfully furnish such an interesting magnetic cluster system, $\{K{\subset}[Ni_6(\mu_6\text{-}CO_3)(\mu_{1,1}\text{-}N_3)_6(\mu\text{-}OAc)_3(dpkMeCN\text{–}H)_3]\}_2[K_2(H_2O)_2]\cdot3MeCN\cdot7H_2O$ ($\mathbf{1}\cdot3MeCN\cdot7H_2O$), which is composed of two large $[Ni(\mu_{1,1}\text{-}N_3)]_6$ circles joined by a $K_2(H_2O)_2$ unit forming a new sandwich-type high-spin heterometallic $Ni_{12}K_4$ cluster, and an unprecedented polydentate ligand generated *in situ* (Fig. 1a) as a result of the cyanomethylation of ketone was also obtained.

Reaction of $Ni(OAc)_2$ with di-2-pyridyl ketone (dpk), sodium azide, and potassium *tert*-butylate (*t*-BuOK) (1 : 0.5 : 1 : 2 molar ratio) in acetonitrile at room temperature led to a pale green solution from which the block deep green crystals of $\mathbf{1}\cdot3MeCN\cdot7H_2O$ were isolated.‡

One of the most intriguing features regarding the synthesis is the direct structural observation of the C–H bond activation of the acetonitrile; a product of the α-alkylation of acetonitrile, dpkMeCN, was generated *in situ* by the reaction of acetonitrile and di-2-pyridyl ketone under the mild conditions of ambient temperature and the presence of air. It should be noted that another tetranuclear cluster, $[Ni_4(dpd\text{–}H)_4(N_3)_2(OAc)_2]\cdot2MeCN$ (dpd–H = (2-py)C(OH)(O)–),[5] was obtained if such a reaction was carried out without potassium *tert*-butylate, suggesting that the presence of potassium *tert*-butylate is the key to performing such a ligand reaction. The same product as **1** was prepared under the same reaction conditions except for the use of anhydrous $Ni(OAc)_2$ instead of $Ni(OAc)_2\cdot4H_2O$. The acetonitrile and dpk in the synthesis of **1** prefer undergoing an unprecedented reaction (Scheme S1†), different from previously reported phenomena.[6–8] Moreover, our synthetic route to β-hydroxy nitriles suggests that it may be potentially useful for the addition of nitrile anions to

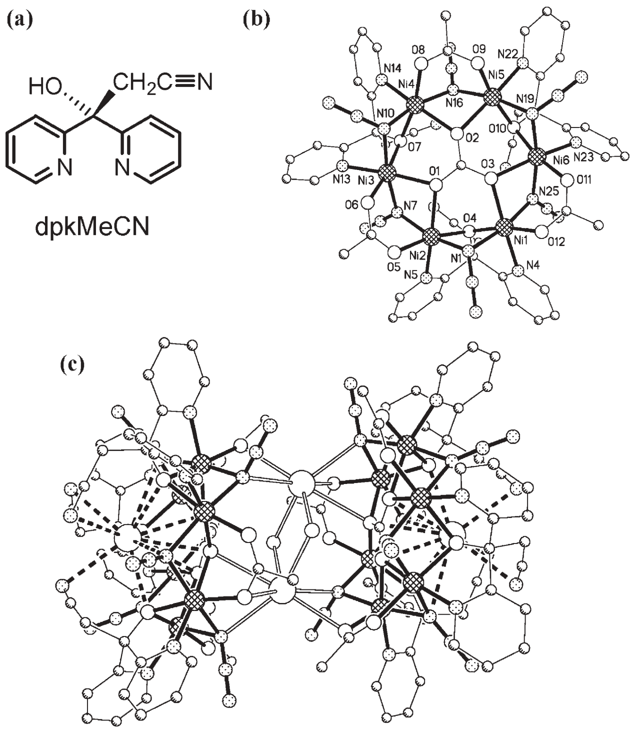

**Fig. 1** Schematic presentation of the dpkMeCN ligand generated *in situ* (a), and perspective views of the local coordination geometries (b) and sandwich-type heterometallic $Ni_{12}K_4$ cluster (c) in the structure of **1**.

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† Electronic supplementary information (ESI) available: synthesis and X-ray crystallography, figures, ac magnetic susceptibilities and field dependence of **1**. See http://www.rsc.org/suppdata/cc/b4/b415431b/
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aldehydes (or ketones), which yield an important group of synthetic organic intermediates.

The crystal structure of **1** comprises $Ni_{12}K_4$ clusters and disordered solvated water and acetonitrile molecules. The $Ni_{12}K_4$ cluster is located on a crystallographic inversion centre. There are six crystallographically unique (but chemically similar) Ni atoms, two unique K atoms, one carbonato, three unique dpkMeCN–H ligands, six unique $N_3^-$ ions, three unique acetates and one aqua ligand in the structure of **1** (Fig. 1b,c). The six Ni atoms are bridged by six $\mu_{1,1}$-$N_3$ groups (three up and three down the circle plane) to form a $[Ni(N_3)]_6$ circle (Ni···Ni = 2.960–3.145 Å), and the three mono-oxygen bridges from three dpkMeCN–H ligands and three μ-acetate bridges are alternately mounted between the six Ni atoms. The six pyridyl N atoms from three dpkMeCN–H ligands coordinate to the six Ni atoms from the outside of the $[Ni(N_3)]_6$ circle. The three acetate groups are oriented downwards from the circle and the three cyanomethyl groups of the three dpkMeCN–H ligands are oriented upwards, resulting in a cage. The K atom is located in this cage and interacts with the surrounding O atoms from the dpkMeCN–H ligands (2.836(6)–3.141(7) Å), the N atoms from the azide groups and cyano groups (2.964(13)–3.149(13) Å) and the C atoms from the cyano groups (3.135(13)–3.155(12) Å). It is interesting to note that one carbonate is located at the center of the $[Ni(N_3)]_6$ circle coordinated to the six Ni atoms in a less common $\mu_6$ hexadentate fashion.[9] Therefore, each Ni is coordinated to three N atoms (two from two *trans*-azides with Ni–N = 2.070(8)–2.122(8) Å and one from a pyridyl with Ni–N = 2.042(8)–2.072(9) Å) and three O atoms separately from one acetate (Ni–O = 2.006(7)–2.058(7) Å), one dpkMeCN–H (Ni–O = 2.048(7)–2.065(7) Å) and one carbonate (Ni–O = 2.086(6)–2.181(6) Å). It is noteworthy that the six-membered $[Ni(\mu_{1,1}\text{-}N_3)]_6$ circle in **1** is the largest metal circle bridged by ferromagnetically-coupled $\mu_{1,1}$-azide ligands present in M–azide magnetic cluster systems to date. Another example is the $[Ni(\mu_{1,1}\text{-}N_3)]_4$ circle found in $[Ni_4(2\text{-oxo-1,3-diaminopropane})_2(2\text{-hydroxo-2,3-diaminopropane})_2(\mu_{1,1}\text{-}N_3)_4](ClO_4)_2$.[10] The whole structure of **1** is a heterometallic $Ni_{12}K_4$ cluster. The centrosymmetrically related $K_2(H_2O)_2$ unit is situated between two $[Ni(\mu_{1,1}\text{-}N_3)]_6$ circles and makes close contact with the acetate and azide groups (K–O = 2.748(9)–3.164(9); K–N = 2.837(9)–3.004(9) Å), resulting in a sandwich-type cluster.

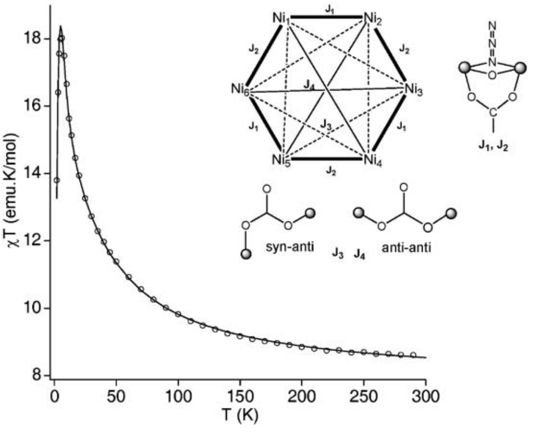

**Fig. 2** Plot of $\chi_M T$ *vs.* $T$. Solid line represents the best fit with the parameters given in the text (inset: the exchange pathway connecting the Ni(II) ions).

The magnetic behaviour between 2 and 300 K was investigated (Fig. 2). The $\chi_M T$ curve increases continuously upon cooling from 300 K to 4.5 K, after which $\chi_M T$ rapidly decreases. This pattern is compatible with moderate ferromagnetic coupling; the sudden decrease in $\chi_M T$ is associated with the anisotropy of the Ni(II) ions. The field magnetization data in the range 0–5 T were checked at 2 K (Fig. S2†). The value of the magnetization at 5 T (12.4 $N\beta$) is smaller than expected for an $S = 6$ state (13.6 for $g = 2.28$). The in-phase ($\chi'_M$) and out-of-phase magnetic susceptibility ($\chi''_M$) signals (Fig. S3†) were checked. No out-of-phase ac signal and no hysteresis loop indicate that **1** does not behave as a SMM.

A full analysis of the magnetic exchange interactions has been performed by means of the full-matrix diagonalization program MAGPACK,[11] applying the Hamiltonian, $H = -\Sigma J_{i,j}S_iS_j + \Sigma D_iS_i^2$, the exchange pathway connecting the Ni(II) ions can be schematized as shown in Fig. 2. The best-fit parameters obtained with this computing model are: $J_1 = 2.88\ cm^{-1}$, $J_2 = 25.4\ cm^{-1}$, $D = 10.3\ cm^{-1}$ and $g = 2.28$ ($J_3$ and $J_4$ were fixed to 0).

All values of the $J$ and $D$ parameters seem to be consistent, taking into account the symmetry and the geometry of Ni(II) ions. $J_1$ and $J_2$ relate the peripheral neighboring spins in alternate form. The net superexchange coupling value found corresponds to the combined interactions due to the end-on azido bridges for both $J_1$ and $J_2$, an oxo group supplied from the ligand in $J_1$ and from carbonate in $J_2$ and a carboxylate group in *syn–syn* mode (carbonate in $J_1$ and acetate in $J_2$). For the EO azido bridge in Ni(II) complexes, the interaction is predicted to be ferromagnetic, with $J$ increasing upon increasing the angle, yielding a maximum at 104°.[4] In the present compound, the Ni–$N_{azido}$–Ni angle between the Ni(II) ions related by $J_1$ is smaller than that related by $J_2$,. The Ni–O–Ni angles are in the range for Ni···Ni ferromagnetic exchange pathways to be dominant (90 ± 14°).[12] Weak antiferromagnetic interactions are observed in the carboxylato-bridged nickel(II) in *syn–syn* mode.[13] This contribution diminishes the ferromagnetic exchange in both $J_1$ and $J_2$. It is well demonstrated that in the compounds where azido and acetato bridges simultaneously coexist, the effect of the countercomplementarity is found and enhances the ferromagnetic interaction.[14] Then the large value for the Ni–$N_{azido}$–Ni angle present in the Ni···Ni pathway related by $J_2$ and the effect of the counter-complementarity mentioned just about justifies the greater value for $J_2$ than for $J_1$.

*Syn–anti* and *anti–anti* coordination modes for carbonate magnetically allow weak ferro or antiferromagnetic coupling. Due to very small values found (less than $\pm 0.1\ cm^{-1}$) for $J_3$ and $J_4$ and the over-parametrization, it is impossible to determine properly their values and they were fixed to zero in the best fit.

The sign of the $D$ parameter in the best fit is positive and attempts to fit the susceptibility data with negatives values of $D$ failed. A value of $D > 0$ is in agreement with the absence of SMM properties.

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## Notes and references

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