A novel high-spin heterometallic Ni$_{12}$K$_4$ cluster incorporating large Ni–azide circles and an *in situ* cyanomethylated di-2-pyridyl ketone†

Ming-Liang Tong,[*a] **Montserrat Monfort,**[b] **Juan Modesto Clemente Juan,**[c] **Xiao-Ming Chen,**[a] **Xian-He Bu,**[d] **Masaaki Ohba**[d] **and Susumu Kitagawa**[*d]

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($\mu_{1,1}$-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*-Cu^{II}(μ-OH)(μ-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–($\mu_{1,1}$-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⊂[Ni$_6$(μ_6-CO$_3$)($\mu_{1,1}$-N$_3$)$_6$(μ-OAc)$_3$-(dpkMeCN–H)$_3$]}$_2$[K$_2$(H$_2$O)$_2$]·3MeCN·7H$_2$O (**1**·3MeCN·7H$_2$O), which is composed of two large [Ni($\mu_{1,1}$-N$_3$)]$_6$ circles joined by a K$_2$(H$_2$O)$_2$ unit forming a new sandwich-type hetero-metallic 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 **1**·3MeCN·7H$_2$O 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–H)$_4$(N$_3$)$_2$(OAc)$_2$]·2MeCN (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)$_2$·4H$_2$O. 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
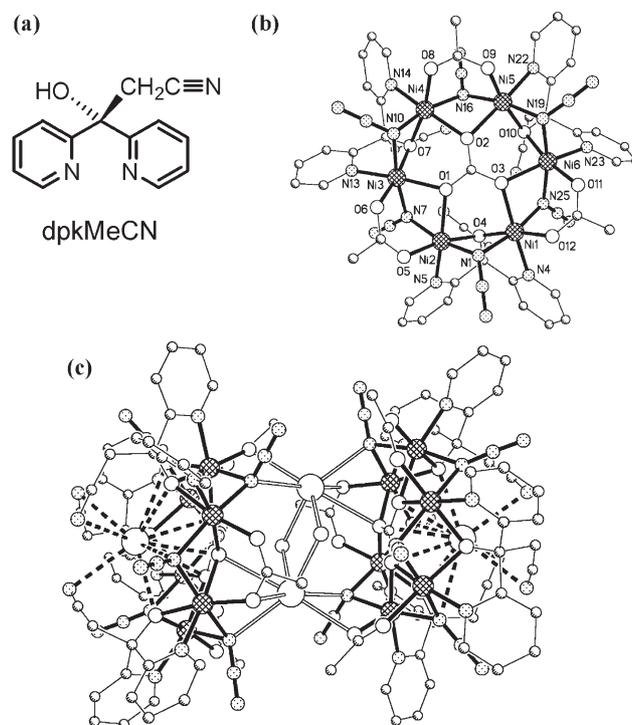

Fig. 1 Schematic presentation of the dpkMeCN ligand generated *in situ* (a), and perspective views of the local coordination geometries (b) and sandwich-type heterometallic Ni$_{12}$K$_4$ cluster (c) in the structure of **1**.

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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$\cdots$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 μ_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 $[Ni(\mu_{1,1}-N_3)]_6$ 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 $[Ni(\mu_{1,1}-N_3)]_4$ circle found in $[Ni_4(2\text{-oxo-}1,3\text{-diaminopropane})_2(2\text{-hydroxo-}2,3\text{-diaminopropane})_2(\mu_{1,1}\text{-}N_3)_4](ClO_4)_2$.[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 $[Ni(\mu_{1,1}-N_3)]_6$ 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.

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 (χ'_M) and out-of-phase magnetic susceptibility (χ''_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$\cdots$Ni ferromagnetic exchange pathways to be dominant (90 $\pm$ 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$\cdots$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.
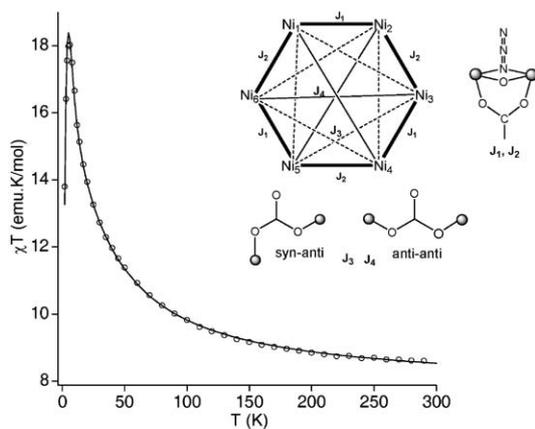
Fig. 2 Plot of $\chi_M T$ *vs.* T. Solid line represents the best fit with the parameters given in the text (inset: the exchange pathway connecting the Ni(II) ions).

Ming-Liang Tong,*[a] **Montserrat Monfort,**[b]
Juan Modesto Clemente Juan,[c] **Xiao-Ming Chen,**[a] **Xian-He Bu,**[d]
Masaaki Ohba[d] **and Susumu Kitagawa***[d]

[a]*School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China. E-mail: cestml@zsu.edu.cn; Fax: +86 20 8411-2245*
[b]*Departament de Química Inorgànica, Universitat de Barcelona, Martíi Franquès 1–11, 08028-Barcelona, Spain*
[c]*Instituto de Ciencia Molecular, Universidad de Valencia, C/ Dr. Moliner 50, E-46100 Burjassot, Spain*
[d]*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: kitagawa@sbchem.kyoto-u.ac.jp*

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‡ CCDC 238449. See http://www.rsc.org/suppdata/cc/b4/b415431b/ for crystallographic data in .cif or other electronic format.

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