Supporting Information

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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‡ To a pale-yellow solution of Ni(OAc)$_2$·4H$_2$O (0.240 g, 1.0 mmol), a mixture of di-2-pyridyl ketone (dpk) (0.092 g, 0.5 mmol), sodium azido (0.065 g, 1.0 mmol) and KOTBu (0.224 g, 2.0 mmol) in acetonitrile (20 ml) was slowly added at room temperature for 4 hrs with magnetic stirring, and then maintained undisturbed at ambient temperature. After 3 d, deep-green crystals were collected by filtration, washed with cold Et$_2$O (yield ca. 72%). The same product was prepared under the same reaction conditions except for the use of anhydrous Ni(OAc)$_2$ instead of Ni(OAc)$_2$·4H$_2$O. A tetranuclear cluster$^5$ was obtained if such reaction was carried out without potassium tert-butylate or using NaOH in place of potassium tert-butylate. Elemental analysis for 1·3MeCN·7H$_2$O C$_{98}$H$_{105}$K$_4$N$_{57}$Ni$_{12}$O$_{33}$, calcd: C, 33.92; H, 3.05; N, 23.01. Found: C, 33.79; H, 2.78; N, 22.95. IR data (KBr, cm$^{-1}$): $\nu = 3554$ m, $3398$ m, $3075$ w, $2251$ m, $2073$ vs, $1584$ vs, $1569$ vs, $1472$ s, $1426$ vs, $1351$ m, $1307$ m, $1270$ w, $1246$ w, $1209$ w, $1162$ w, $1130$ w, $1088$ s, $1059$ w, $1032$ m, $985$ w, $920$ w, $880$ w, $846$ w, $792$ w, $766$ w, $740$ w, $685$ w, $649$ w, $637$ w, $561$ w, $525$ w, $490$ w, $453$ w.

§ Crystal and structure refinement parameters. Compound 1·3MeCN·7H$_2$O: C$_{98}$H$_{105}$K$_4$N$_{57}$Ni$_{12}$O$_{33}$, $M = 3470.31$, triclinic, space group $P$-1 (No. 2), $a = 15.634(3)$, $b = 16.604(3)$, $c = 18.257(4)$ Å, $\alpha = 70.34(3)$, $\beta = 85.79(3)$, $\gamma = 69.34(3)$°, $V = 4170.6(14)$ Å$^3$, $Z = 1$, $T = 293(2)$ K, F(000) = 1768, $D_C = 1.382$ g cm$^{-3}$, $\mu$(MoK$\alpha$) = 1.497 mm$^{-1}$; $R_1 = 0.0863$, $wR_2 = 0.2729$ and GOF = 1.084 for 991 parameters, 8232 reflections with $|F_o| \geq 4\sigma(F_o)$. Data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Because the compound contains rich solvated water and acetonitrile molecules, which are easily escaped from the crystals, therefore only 77% of the calculated reflections could be collected for complex 1. The structure was solved with direct methods and refined with full-matrix least-squares (SHELX-97). CCDC reference number
238449. See http://www.rsc.org/suppdata/cc/b4/b415431b for crystallographic data in .cif or other electronic format..
Scheme S1 (a) The formation of a hydrate (R’ = H) or a hemiacetal (R’ = alkyl or aryl) in the reaction of a ketone with water or an alcohol. (b) The attack of nucleophiles upon a coordinated nitrile. (c) The mechanism proposed for the base-catalyzed cyanomethylation of ketone.
**Fig. S1.** Top- and side-views of the Ni$_6$ cycle bridged by the azides, acetates and oxygen atoms of the dpkMeCN-H ligands in sandwich-type heterometallic Ni$_{12}$K$_4$ Cluster of 1. Ni atoms are shown in green, oxygen red, carbon brown, nitrogen blue, and potassium purple. Hydrogen atoms are omitted for clarity.
**Fig. S2.** Plot of the reduced magnetization for 1 ($M/N\beta$) vs $H$ at 2K.

**Fig. S3.** Plot of temperature dependance of the in-phase, $\chi'_M$ and out-of-phase $\chi''_M$ ac magnetic susceptibilities.