Supplementary Material (ESI) for Chemical Communications

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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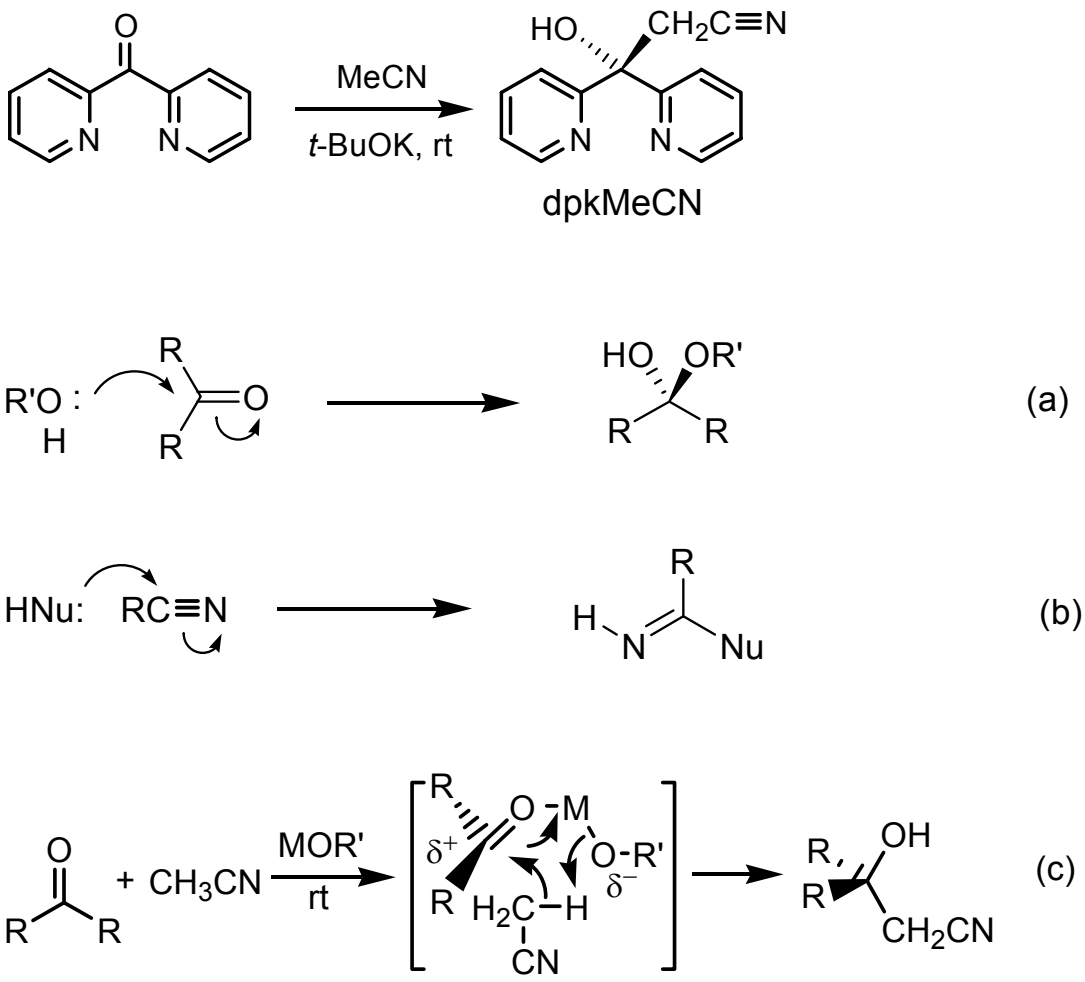
‡ To a pale-yellow solution of $Ni(OAc)_2 \cdot 4H_2O$ (0.240 g, 1.0 mmol), a mixture of di-2-pyridyl ketone (dpk) (0.092 g, 0.5 mmol), sodium azido (0.065 g, 1.0 mmol) and KOtBu (0.224 g, 2.0 mmol) in acetonitrile (20 ml) was slowly added at room temperature for 4 hrs with magnetic stirring, and then maintained undisturbed at ambient temperature. After 3 d, deep-green crystals were collected by filtration, washed with cold Et_2O (yield ca. 72%). The same product was prepared under the same reaction conditions except for the use of anhydrous $Ni(OAc)_2$ instead of $Ni(OAc)_2 \cdot 4H_2O$. 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_2O $C_{98}H_{105}K_4N_{57}Ni_{12}O_{33}$, 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}): ν = 3554m, 3398m, 3075w, 2251m, 2073vs, 1584vs, 1569vs, 1472s, 1426vs, 1351m, 1307m, 1270w, 1246w, 1209w, 1162w, 1130w, 1088s, 1059w, 1032m, 985w, 920w, 880w, 846w, 792w, 766w, 740w, 685w, 649w, 637w, 561w, 525w, 490w, 453w.

§ Crystal and structure refinement parameters. Compound **1**·3MeCN·7H_2O: $C_{98}H_{105}K_4N_{57}Ni_{12}O_{33}$, M = 3470.31, triclinic, space group P-1 (No. 2), a = 15.634(3), b = 16.604(3), c = 18.257(4) Å, α = 70.34(3), β = 85.79(3), γ = 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 $|Fo| \geq 4\sigma(Fo)$. Data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 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.

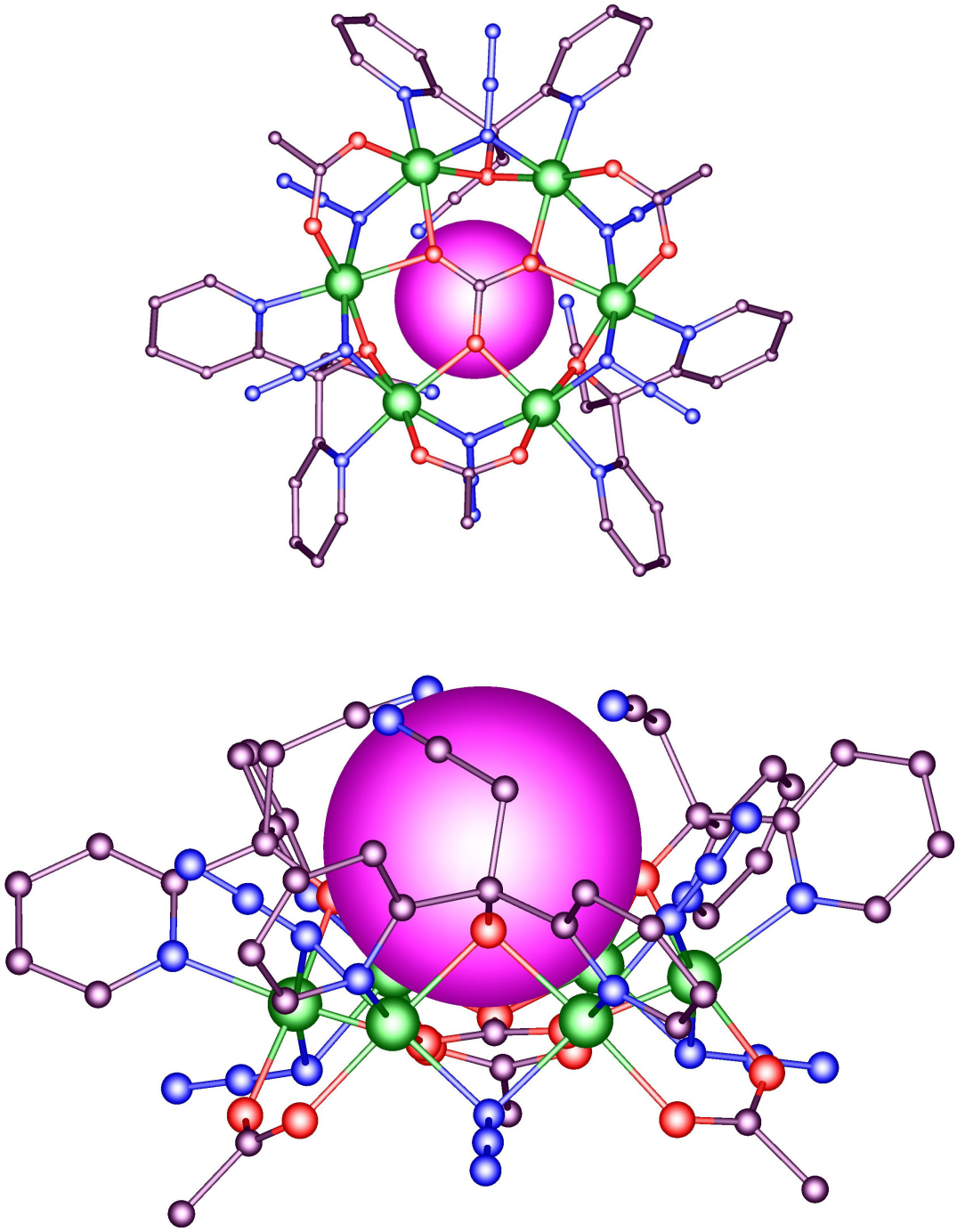


Fig. S1. Top- and side-views of the Ni_6 cycle bridged by the azides, acetates and oxygen atoms of the dpkMeCN-H ligands in sandwich-type heterometallic $Ni_{12}K_4$ Cluster of **1**. Ni atoms are shown in green, oxygen red, carbon brown, nitrogen blue, and potassium purple. Hydrogen atoms are omitted for clarity.

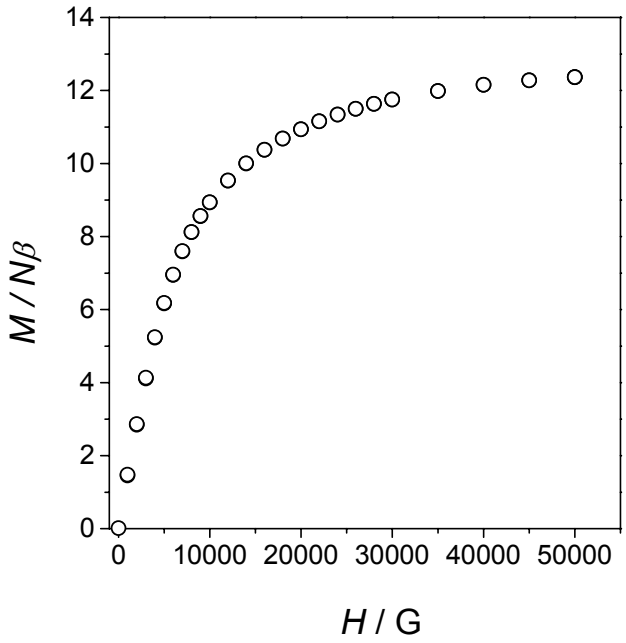


Fig. S2. Plot of the reduced magnetization for **1** (*M*/Nβ) vs *H* at 2K.

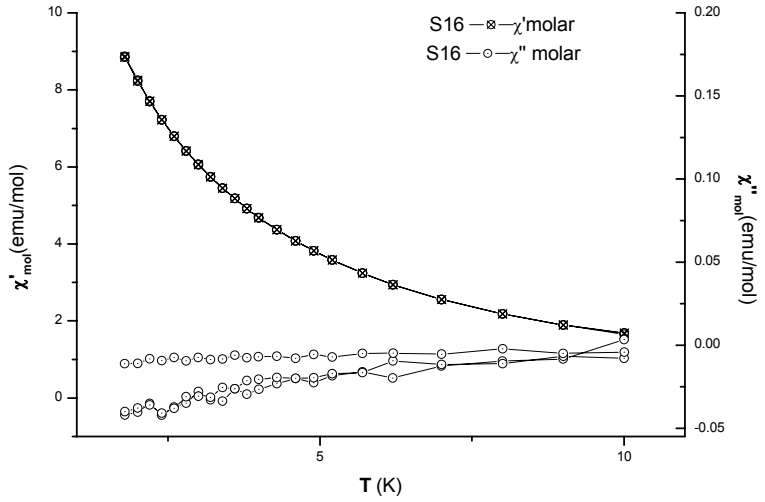


Fig. S3. Plot of temperature dependance of the in-phase, χ'_M and out-of-phase χ''_M ac magnetic susceptibilities.