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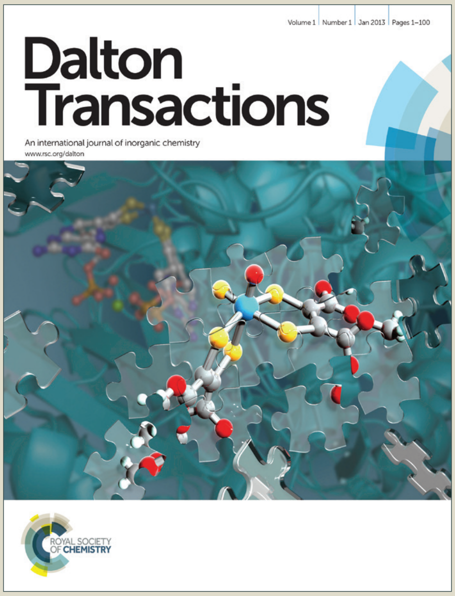

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A (3,6)-connected layer with unprecedented adeninate nucleobase-derived heptanuclear disc

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A (3,6)-connected layer with adeninate nucleobase-derived Cu^{II}_7 disc was reported, in which six spin-paralleled Cu^{II} ions in the exterior of the disc are antiferromagnetically coupled with the central one to give an $S = 5/2$ ground-state.

Heterocyclic nucleobase-based bio-metal-organic frameworks (bio-MOFs) have always received a great interest due to their aesthetically beautiful structures[1-3] and intriguingly promising applications in magnetism,[4-5] absorption,[6-9] catalysis[10] and fluorescence.[11-12] Purines and its diverse derivatives with at least four separate N donors and rigid coplanar backbone have exhibited various binding modes to aggregate metal ions into discrete and/or polymeric species with paddle wheel-, windmill-, cyclic metallaquartet- and bent/helical chain-like motifs.[13-16] However, the nucleobase-involved polynuclear metal clusters with the nuclearity number over four have been scarcely observed up to date,[15] although the family ligands have short bridging modes and sterically unencumbered backbone favorable for the aggregation of the metal ions. Very recently, two important samples with cluster motifs, a decanuclear entity consisting of two $\{Cu_4(\mu_4\text{-}O)\}^{6+}$ cores and two single copper centers as well as an extended aggregate with hexagonal prism-shaped Cu_6I_6 subunit, were successively obtained by varying the modified adenine analogues with different functional sidearms,[17] which have initiated the significant progress on the polymetallic cluster-based bio-MOFs. However, the syntheses and functions of the polynuclear metal clusters generated by the direct binding of nucleobases and metal ions are still challenging and significant. Herein, to continue the fabrications and magnetic investigations along this line, we report a novel (3,6)-connected layered complex with unprecedented adeninate-derived Cu^{II}_7 disc, $\{[Cu_7(H_2O)_4(\mu_3\text{-}OH)_6(ade)_2(sip)_2]\cdot 2.5H_2O\}_n$ (**1**, ade = adeninate and sip = 5-sulfoisophthalate), which exhibits an apparent ferromagnetic coupling to an S =5/2 spin ground-state at low temperature. To the best our knowledge, the local Cu^{II}_7 disc in **1** has been the largest core among all the reported nucleobase-participated clusters up to date, which greatly encourage the systematic investigations on the nucleobase-containing high nuclearity clusters.

Complex **1** was solvothermally obtained as blue block-shaped crystals by self-assembly reaction of inorganic Cu^{II} salt, adenine nucleobase and 3,5-dicarboxybenzene sulfonic acid monosodium salt (NaH_2sip) in slightly weak acidic medium adjusted by triethylamine.[18] The well matched experimental and computer-simulated PXRD patterns evidenced the structural consistency and the phase purity of as-synthesized products of **1** (Fig. S1, ESI†). In the IR spectrum of **1**, a broad absorption centered at 3370 cm^{-1} was resulting from the stretching vibrations of O–H and/or N–H, suggesting the presence of exocyclic amino group of adenine, water molecule and/or hydroxyl group. The asymmetric and symmetric stretching vibrations of the carboxylate group were observed at 1644, 1600, 1544 and 1399, 1369, 1346 cm^{-1}, and a medium band at 1196 cm^{-1} confirmed the presence of the sulfonato groups in **1**.[19] The initial weight-loss process of **1** between 120 and 290 °C was ascribed to the loss of four coordinated water molecules (obsd. 5.6%, calcd. 5.1%), revealing that disordered lattice water molecules were released at room temperature. The polymeric framework of **1** was gradually collapsed, leaving CuO as the final product (obsd. 38.0%, calcd. 39.3%, Fig. S2, ESI†).

Complex **1** crystallizes in the triclinic $P\bar{1}$ space group‡, exhibiting an infinite (3,6)-connected sheet with centrosymmetric Cu^{II}_7 clusters periodically extended by three-connected sip^{3-} linkers. The fundamentally structural unit of **1** contains a centrosymmetric $\{Cu_7(\mu\text{-}H_2O)_4(\mu_3\text{-}OH)_6(\mu\text{-}N3,\ N9\text{-}ade)_2\}^{6+}$ cluster, two crystallographically equivalent sip^{3-} connectors and some disordered lattice water molecules. The Cu^{II}_7 core consists of seven Cu^{II} octahedra with Cu1 located at an inversion center, four bridging water molecules, six μ_3-OH^- groups and two μ-N3, N9-ade^- anions. The Cu1 ion in **1** is hexa-

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coordinated by an O_6 donor set from six μ_3-OH^- groups (Fig. 1a), adopting elongated octahedral coordination geometry with axial Cu–O bond lengths longer by 0.3 Å than those in the equatorial plane. Suited at general positions, the remaining three Cu^{II} ions are in the distorted octahedral coordination surroundings fulfilled respectively by O_6 (for Cu2) and O_5N (for Cu3 and Cu4) donor sets (Table S1, ESI†). Notably, the $Cu–O_{aqua}$ and $Cu–O_{sulfonate}$ bond lengths are generally longer than 2.4 Å due to Jahn-Teller effect, which are commonly observed Cu(II)-containing complexes with sulfonate and bridging water molecule.[20,21]

The central Cu1 site aggregates six peripheral Cu^{II} ions by three pairs of μ_3-OH^- groups, generating a centrosymmetric, disc-like $\{Cu_7(\mu_3\text{-}OH)_6\}^{8+}$ core with the average $Cu^{II}\cdots Cu^{II}$ separations of 3.0199(4)–3.1701(4) Å (Table S2, ESI†). Each Cu^{II} ion-pair in the exterior are bridged by three-fold heterobridges (μ_3-OH^-, μ-N3, N9-ade^- and single-atom bridging sulfonate from sip^{3-} anion for Cu3 and Cu4, μ_3-OH^-, bridging water molecule and μ-*syn*, *syn*-COO^- of sip^{3-} for both Cu2 and Cu3 as well as Cu2 and Cu4A) with the $Cu^{II}\cdots Cu^{II}$ separations of 3.0141(4)–3.2306(3) Å (Table S2, ESI†). Apparently, the generation of the unique Cu^{II}_7 cluster in **1** benefits greatly from the synergistic co-coordination of water molecule, μ_3-OH^- group, carboxylate and sulfonate moieties of sip^{3-} as well as ade^- anion. Moreover, the coexistence of various chelating four-, five- and six-membered metallocycles with less steric hindrance, such as Cu_2O_2, Cu_2OCN_2 and Cu_2CO_3, can also stabilize effectively the unique Cu^{II}_7 disc. To the best of knowledge, the local Cu^{II}_7 cluster in **1** has been the largest nucleobase-based core among all the reported bio-MOFs up to date, which suggests that purines can be hopefully used as core-formation ligand to construct high nuclearity metal clusters with the help of suitable second ligands.

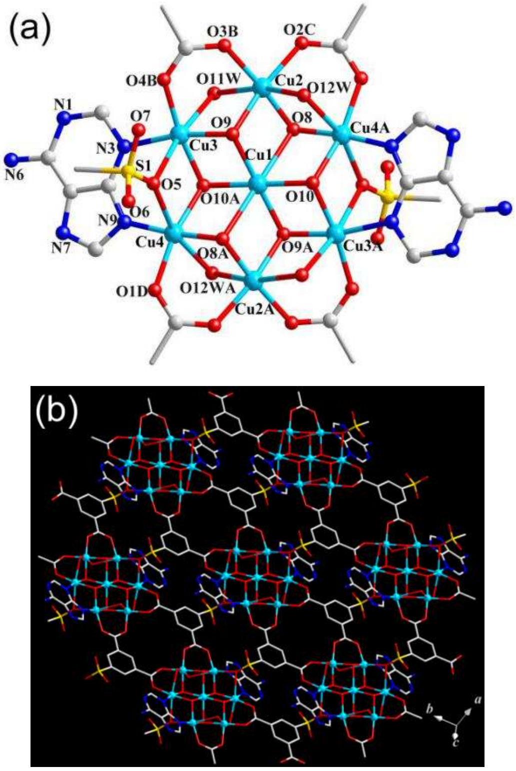

Fig. 1(a) Centrosymmetric heptanuclear subunit of **1** (H atoms and part of phenyl moiety of sip^{3-} were omitted for clarity, symmetry codes: A = 1 – *x*, 1 – *y*, 2 – *z*; B = 2 – *x*, – *y*, 2 – *z*; C = *x* – 1, *y*, *z* + 1; D = 2 – *x*,1 – *y*, 1 – *z*). (b) Linkages of the Cu^{II}_7 cluster and sip^{3-} ligand.

Each centrosymmetric Cu^{II}_7 cluster in **1** is periodically surrounded by six sip^{3-} ligands and can be topologically served as a 6-connected node. By contrast, each sip^{3-} connector holds three separate Cu^{II}_7 clusters through one single-atom bridging sulfonate and two bidentate bridging carboxylate groups, and acts as a 3-connected node. The 3- and 6-connected nodes in **1** are repeatedly arranged into a (3, 6)-connected two-dimensional (2D) layer of **1** with the nearest intercore $Cu^{II}\cdots Cu^{II}$ separation of ca. 7.5518 Å (Fig. 1b), which is almost double of the intracluster distances. Additionally, adjacent 2D layers of **1** are further assembled into a 3D supramolecular network by O–H···O, O–H···N and N–H···O hydrogen-bonding interactions between the hydroxyl group, coordinated water molecules, amino group of μ-ade^- and sulfonate moiety of the sip^{3-} anion (Table S3 and Fig. S3, ESI†). The interlayer distance is 7.7233(11) Å, considerable longer than those intracluster separations. Thus, **1** can be approximately considered as a magnetically isolated cluster with obviously intracluster exchange couplings.

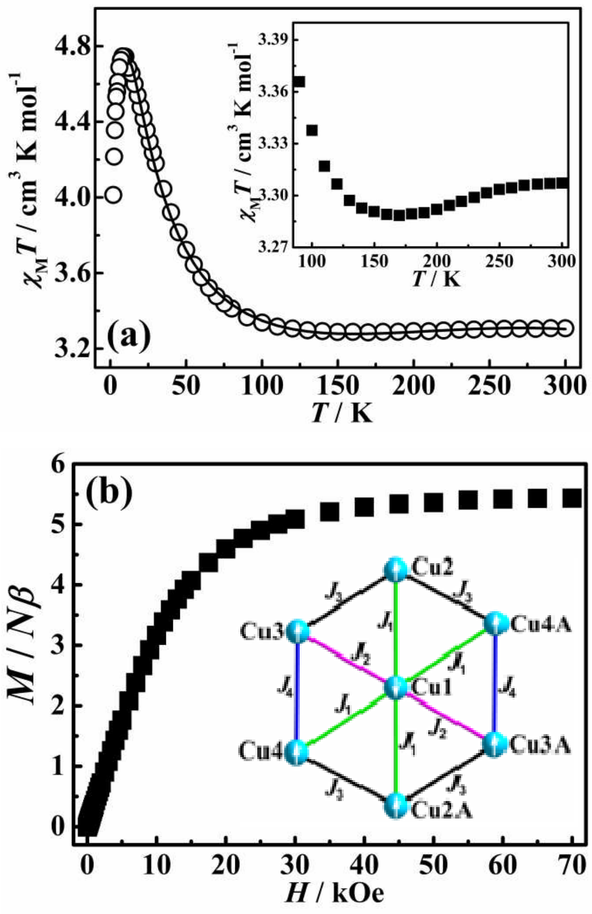

Fig. 2(a) Temperature dependence of $\chi_M T$ for **1**. The solid line corresponds to the best fit indicated in the text. (b) Isothermal magnetization for **1** measured at 2.0 K (Inset: magnetic topology and the 4*J* coupling scheme for the local Cu^{II}_7 cluster).

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The variable-temperature (2–300 K) magnetic susceptibilities were measured on the polycrystalline samples of **1** under a direct-current field of 1 kOe. As shown in Fig. 2a, the $\chi_M T$ product for per Cu^{II}_7 subunit of **1** is 3.31 cm^3 K mol^{-1} at 300 K, which is moderate larger than the spin-only value (2.63 cm^3 K mol^{-1}) expected for seven magnetically non-interacting Cu^{II} ions with S = 1/2 and g = 2.0. Upon cooling, the $\chi_M T$ product decreases slightly and reaches a local minimum of 3.29 cm^3 K mol^{-1} at 170 K. Then it rises moderately to a maximum of 4.74 cm^3 K mol^{-1} at 9.0 K, and finally drops to 4.01 cm^3 K mol^{-1} at 2.0 K. Such $\chi_M T$ $-T$ curve suggests the coexistence of typically antiferromagnetic and ferromagnetic couplings as well as the non-zero spin ground-state of **1** at low temperature. From the viewpoint of the magneto-structural correlations, the superexchange couplings of **1** significantly dominate in the local Cu^{II}_7 cluster mediated by the multiple short heterobridges (μ_3-OH^-, μ-H_2O, μ-COO^-, μ-SO_3^- as well as μ-N3, N9-ade$^-$), because the nearest intercluster $Cu^{II}\cdots Cu^{II}$ separation across the sip^{3-} linker is considerable double distance than those within the Cu^{II}_7 cluster (7.5518 vs 3.1124 Å). To quantitatively evaluate the coupling strength from the different types of pathways, a simplified 4J scheme (Fig. 2b inset) is purposed due to their slight difference of structural parameters and spatial orientations. The experimental magnetic data were thus analyzed on the basis of the Hamiltonian $\boldsymbol{H} = -2J_1(\boldsymbol{S}_{Cu1}\boldsymbol{S}_{Cu2}+\boldsymbol{S}_{Cu1}\boldsymbol{S}_{Cu2A}+\boldsymbol{S}_{Cu1}\boldsymbol{S}_{Cu4}+\boldsymbol{S}_{Cu1}\boldsymbol{S}_{Cu4A})-2J_2(\boldsymbol{S}_{Cu1}\boldsymbol{S}_{Cu3}+\boldsymbol{S}_{Cu1}\boldsymbol{S}_{Cu3A})-2J_3(\boldsymbol{S}_{Cu2}\boldsymbol{S}_{Cu4}+\boldsymbol{S}_{Cu2A}\boldsymbol{S}_{Cu4A}+\boldsymbol{S}_{Cu2}\boldsymbol{S}_{Cu3A}+\boldsymbol{S}_{Cu2A}\boldsymbol{S}_{Cu3})-2J_4(\boldsymbol{S}_{Cu3}\boldsymbol{S}_{Cu4}+\boldsymbol{S}_{Cu3A}\boldsymbol{S}_{Cu4A})$, in which J_1–J_4 describe the superexchange interactions from short and long $Cu^{II}\cdots Cu^{II}$ distances, respectively. The fit of the experimental susceptibilities to the Hamiltonian above 10.0 K, using the MAGPACK program,[22] affords the following parameters: g = 2.17, J_1 = – 27.1 cm^{-1}, J_2 = – 84.2 cm^{-1}, J_3 = 118.2 cm^{-1} and J_4 = 37.4 cm^{-1} with $R = 2.4 \times 10^{-3}$ (R is the agreement factor defined as $R = \Sigma[(\chi_M T)_{obsd} - (\chi_M T)_{calcd}]^2/\Sigma[(\chi_M T)_{obsd}]^2$).

Apparently, weak antiferromagnetic coupling for J_1 should be assigned to the superexchange interactions between the central Cu1 and exterior Cu2 as well as Cu4 ions, because of the good overlap of the magnetic orbits by the double μ_3-OH^- homobridges aligned in the equatorial-axial positions of the two spin carriers. Stronger antiferromagnetic interaction corresponding to J_2 is due to the favorably equatorial-equatorial arrangement of the double μ_3-OH^- groups towards Cu1 and Cu3, as well as the small dihedral angle (5.257°, Table S2, ESI†) between the two coordination planes. In contrast, positive couple constants for J_3 and J_4 reveal that the six cyclic-arranged exterior Cu^{II} ions were ferromagnetically coupled together through 3-fold heterobridges with the coupling strength comparable with those previous reported complexes bearing the analogous heterobridges.[23-25] Thus, the magnetic fitting results clearly indicates that the central Cu^{II} ion is antiferromagnetically coupled with the six peripheral spins, leading to an S = 5/2 spin ground-state of **1** at low temperature.

The isothermal magnetization of **1** measured at 2.0 K shows a rapid increase with the increasing external field lowered than 30 kOe and then slowly reaches the saturated value of 5.43 $N\beta$ at 70 kOe (Fig. 2b). The value is consistent with the saturation value (5.45 $N\beta$) for five isolated Cu^{II} ions with S = 5/2 and g = 2.17, further confirming that six peripheral Cu^{II} ions in the local Cu^{II}_7 disc of **1** are antiferromagnetically coupled with the central one through triple-fold heterobridges to give an S = 5/2 spin ground-state of **1** at low temperature.

In summary, a unique adeninate nucleobase-involved Cu^{II}_7 disc was solvothermally generated, which is extended into a (3,6)-connected two-dimensional layer through 3-connected sip^{3-} connector. Magnetically, the central Cu^{II} ion in the disc-like Cu^{II}_7 core is antiferromagnetically coupled with the six paralleled spins to lead to a S =5/2 spin ground-state at low temperature. These interesting results open up a new window for the novel polynuclear metal cluster-based magnetic bio-MOFs.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Selected bond lengths and angles, geometric parameters of the local Cu^{II}_7 cluster, selected hydrogen-bonding parameters, PXRD pattern, TG curve and picture of 3D supramolecular network of **1**. See DOI:10.1039/b000000x/

‡ *Crystal data*: $C_{26}H_{33}Cu_7N_{10}O_{26.50}S_2$, M_r = 1418.52, triclinic, $P\bar{1}$, a = 7.7233(11), b = 12.3827(17), c = 12.4646(17) Å, α = 68.448(2)°, β = 78.217(3)°, γ = 81.382(3)°, V = 1081.7(3) $Å^3$, Z = 1, D_c = 2.190 g cm^{-3}, μ = 3.579 mm^{-1}, F(000) = 710, GOF = 1.073, a total of 6069 reflections were collected, 3769 of which were unique (R_{int} = 0.0222). $R_1(wR_2)$ = 0.0454 (0.0924) for 348 parameters and 3769 reflections ($I > 2\sigma(I)$). CCDC 1015454. Data were collected on a Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 296 K. The *SADABS* program was used for the absorption correction. All structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the *SHELX97* program package. One ade$^-$ anion and one lattice water molecule (O13) were disordered with the site occupancy of 0.54 and 0.46 assigned to ade and ade', 0.26 and 0.74 assigned to O13 and O13', respectively.

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18 Synthesis of $\{[Cu_7(\mu\text{-}H_2O)_4(\mu_3\text{-}OH)_6(ade)_2(sip)_2]\cdot 2.5H_2O\}_n$ (**1**): A mixture containing $Cu(NO_3)_2\cdot 3H_2O$ (24.2 mg, 0.1 mmol), Hade (6.75 mg, 0.05 mmol), and NaH_2sip (13.4 mg, 0.05 mmol) was dissolved in mixed water–ethanol solution (v : v = 7 : 2, 9.0 mL) and the initial pH value of the mixture was adjusted to *ca.* 6 by triethylamine. Then, the mixture was transferred into a parr Teflon–lined stainless steel vessel (23.0 mL) and heated at 140°C for 72 h under autogenous pressure. After the mixture was cooled to room temperature at a rate of 2.5 °C h^{-1}, blue block-shaped crystals suitable for X–ray diffraction analysis were directly obtained (Yield: 39% based on Cu^{II} salt). Elemental analyses (%) Anal. Calcd for $C_{26}H_{33}Cu_7N_{10}O_{26.5}S_2$: C, 22.01; H, 2.34; N, 9.87. Found: C, 22.10; H, 2.37; N, 9.79. FT-IR (cm^{-1}): 3370(br), 1644(s), 1600(s), 1544(s), 1434(s), 1399(s), 1369(s), 1346(s), 1315(w), 1284(w), 1196(m), 1105(w), 1053(w), 891(w), 777(w), 725(w), 623(m), 583(w), 462(w).

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