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A Tetranuclear Cu^{II}-Based 2D Aggregate with an Unprecedented Tetradentate μ_4-N1,N3,N7,N9-Adeninate Nucleobase

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A unique tetranuclear Cu^{II}-based 2D aggregate containing 26-membered Cu^{II}ade macrocycles, $[Cu_4(DMF)_6(\mu_4\text{-ade})_2(\mu_2\text{-Cl})_2Cl_4]_n$ (**1**; Hade = adenine, DMF = *N*,*N*-dimethylformamide), was isolated by the reaction of $CuCl_2$ and Hade in a mixed DMF−methanol medium and structurally characterized by X-ray crystallography, elemental analysis, Fourier transform infrared, fluorescence spectroscopy, and thermogravimetry−differential thermal analysis techniques. Unexpectedly, the adeninate in **1** represents an unprecedented tetradentate μ_4-N1,N3,N7,N9-bridging mode, which significantly contributes to both the aggregate of four Cu^{II} cores within the subunit and the extension of the 2D covalent framework. Additionally, **1** displays the intense Hade-based fluorescence emission in solution at room temperature.

The interactions of nucleic acids or their constituents with metal ions have currently received intense interest owing not only to the biological importance of the metal−nucleobase bonds, the functions of nucleic acids, and genetic information transfer but also to their structural diversity, molecular recognition behaviors, and potential applications as advanced functional materials.[1−3] Native adenine (Hade) nucleobase with considerable water solubility and five possible donor sites (the endocyclic N1, N3, N7, and N9 and exocyclic N6 atoms) has already exhibited the widest range of binding possibilities including monodentate N9,[4−12] N7,[3,13,14] and N3[13,15,16] bidentate bridging and/or chelating μ_2-N7,N9,[17−20] μ_2-N3,N9,[21] μ_2-N3,N7,[13] μ_2-N1,N9,[22] and μ_2-N6,N7[23] as well as tridentate μ_3-N3,N7,N9[18,24,25] modes, which depend essentially on the properties of the metal ion (main group or transition metal, charge, d-electron configuration, and hard- or softness), the nature of the Hade nucleobase (the basicity of the N-donor site, the degree of protonation, as well as the different tautomeric forms), and, sometimes, the auxiliary ligands that complete the metal coordination sphere.[1,13] However, the polymeric structures bridged by Hade are relatively uncommon.[1−3,22,24,25] Especially, the discrete/polymeric Hade-based metal complex, in which the unsubstituted Hade ligand binds the metal ion either by its individual N1 site or by combinations of N1 with more other two N donors, has never been observed by far, although it is reasonable in principle.[2] On the other hand, in addition to the classical coordination bonds, the presence of a primary 6-amino group in Hade also offers interesting possibilities for acting as an H donor in interligand hydrogen-bonding interactions, which cooperates with the coordination bonds to stabilize and/or extend the resulting complexes into higher dimensional architectures.[2] Thus, as a continuation of the significant research field, herein, a unique two-dimensional (2D) aggregate with an ade nucleobase, $[Cu_4(DMF)_6(\mu_4\text{-ade})_2(\mu_2\text{-Cl})_2Cl_4]_n$ (**1**; Hade = adenine, DMF = *N*,*N*-dimethylformamide), was isolated and structurally characterized by X-ray crystallography, elemental analysis, Fourier transform infrared (FT-IR), thermogravimetry−differential thermal analysis (TG−DTA), and fluorescence spectroscopy. To the best of our knowledge, this interesting tetranuclear Cu^{II}-based polymer is the first example in which the adeninate ion coordinates to the metal ion by a tetradentate

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μ_4-N1,N3,N7,N9-coordination mode and simultaneously presents its exocyclic amino group to consolidate the metal−nucleobase bonds by 4-fold intraligand hydrogen-bonding interactions. More importantly, the unprecedented tetradentate adeninate is significantly responsible for both the aggregate of four Cu^{II} cores within the subunit and the extension of the overall framework structure.

In the presence of octanedioic acid, the one-step reaction of $CuCl_2$ and Hade with a molar ratio of 4:1 in a mixed DMF−methanol medium affords blue block-shaped crystals, complex **1**.[26] The nucleobase ligand in **1** is a monodeprotonated adeninate ion (ade), not a neutral molecule (Hade) or adeninium cations (H_2ade and H_3ade). Notably, the presence of octanedioic acid is to increase the solubility of the mother liquor that produces well-shaped crystals of the target polymer even though this octanedioic acid itself is potentially able to produce a mixed-ligand complex.[24] Such a specific role of octanedioic acid is somewhat similar to that of thymine in $[Cu_2(NBzIDA)_2(H_2O)_2(\mu\text{-N7,N9-Ade-(N3)H})]\cdot 3H_2O$ (NBzIDA = *N*-benzyliminodiacetate).[17]

The X-ray crystal structural analysis[27] revealed that **1** is an unusual tetranuclear Cu^{II}-based 2D covalent layer containing 26-membered Cu^{II}ade macrocycles. As shown in Figure 1, the fundamental subunit of **1** is a dimer of two crystallographically asymmetric units with an inversion center and is composed of four Cu^{II} cores, two ade anions, six terminal DMF molecules, and six chloride anions. Locating at a distorted octahedral geometry, six-coordinated Cu1 is surrounded by two N atoms (imidazole N7 and pyrimidinic N1) from two different ade anions, three O atoms from terminal DMF molecules, and one terminal chloride anion. In contrast, Cu2 is in a flattened trigonal-bipyramidal geometry (Addison parameter $T = 0.93$) with three chloride ions (two Cl anions are bridge and the third one is terminal) locating at the basal plane and two N atoms (imidazole N9 and pyrimidinic N3) from a pair of head-to-tail arranged ade ligands occupying the apical positions. The bond lengths of Cu−N are in the range of 1.892(5)−2.062(8) Å and are comparable to previously reported values (see Table S1 in the Supporting Information).[2,12,17,18,25] Moreover, the Cu−N bonds are further reinforced by interligand hydrogen-bonding interactions between ade and DMF−Cl (see Figure 1 and Table S2 in the Supporting Information). Two pairs of different linkers (Cl and ade anions) quadruply bridge the Cu2 and Cu2A to generate a tetranuclear Cu^{II} subunit, with the four Cu^{II} cores locating at the same plane, along with the two ade anions, further linking Cu1 and Cu1A (Figure 1). Thus, the ade anion within the subunit acts as a bridge to hold three Cu^{II} atoms together (Cu1, Cu2, and Cu2A) by a μ_3-N3,N7,N9 binding mode. The Cu···Cu separations across the same ade are 5.8607(6) Å for Cu1 and Cu2 and 2.9206(16) Å for Cu2 and Cu2A.

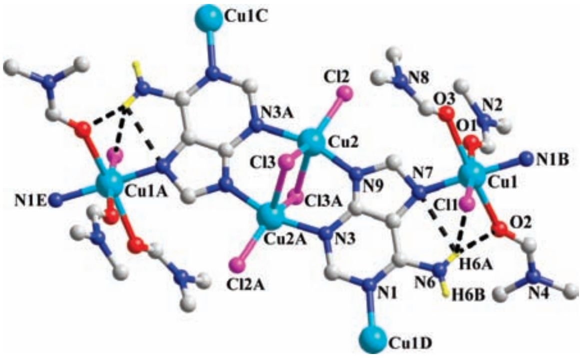

Figure 1. Tetranuclear subunit of **1** with atomic labels in the asymmetric unit and the binding mode of ade (H atoms are omitted for clarity, and the hydrogen-bonding interactions within the subunit are shown as black broken lines). Symmetry codes: (A) $-x, -y, 2 - z$; (B) $0.5 - x, 0.5 + y, 1.5 - z$; (C) $-0.5 + x, 0.5 - y, 0.5 + z$; (D) $0.5 - x, -0.5 + y, 1.5 - z$; (E) $-0.5 + x, -0.5 - y, 0.5 + z$.

Unexpectedly, in addition to affording N3, N7, and N9 as donor atoms, the adeninate anion also presents its N1 site to covalently coordinate with the Cu1 atoms from the adjacent subunits, extending the tetranuclear Cu^{II} subunits into an

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(26) Synthesis of **1**: To a DMF solution (6 mL, pH = 6.5) containing Hade (6.75 mg, 0.05 mmol), octanedioic acid (8.7 mg, 0.05 mmol), and appropriate NaOH (0.1 M) was slowly added a methanol solution (4 mL) of $CuCl_2\cdot 2H_2O$ (34.1 mg, 0.2 mmol) with constant stirring. The resulting mixture was allowed to stir for about 1 h and filtered. Blue block-shaped crystals suitable for X-ray analysis were obtained within 5 days by slow evaporation of the filtrate under an ambient environment. Yield: 60% (based on Hade). Anal. Calcd for $C_{14}H_{25}Cl_3Cu_2N_8O_3$: C, 28.65; H, 4.29; N, 19.09. Found: C, 28.58; H, 4.32; N, 19.22. FT-IR (KBr pellets, cm^{-1}): 3329(w), 3176 (w), 1655(vs), 1609(w), 1562(w), 1465(w), 1407(s), 1318(w), 1207(m), 1148(m), 791(w), 736(w), 667(w), 649(w), 573(w).

(27) Crystal data for **1**: $C_{14}H_{25}Cl_3Cu_2N_8O_3$, $M = 586.85$ g mol^{-1}, crystal dimensions 0.28 × 0.22 × 0.20 mm, monoclinic system, space group $P2_1/n$, $a = 13.228(2)$ Å, $b = 13.360(2)$ Å, $c = 13.967(2)$ Å, $\beta = 108.437(3)°$, $Z = 4$, $V = 2341.8(7)$ Å^3 $\mu = 2.191$ mm^{-1}, $D_c = 1.665$ g cm^{-3}, $F(000) = 1192$, $T = 296(2)$ K, λ(Mo Kα) = 0.710 73 Å. Semiempirical absorption corrections were applied (*SADABS*), and the program *SAINT* was used for integration of the diffraction profiles.[28] A total of 11 503 reflections up to $\theta = 25.03°$ were collected, of which 4044 unique reflections were used. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the *SHELXS-97* and *SHELXL-97* programs.[28] R1 = 0.0644, wR2 = 0.1482 [$I > 2\sigma(I)$], R1 = 0.0831, wR2 = 0.1610 (all data), GOF = 1.038, maximum residual electron density and hole +1.891 and −1.193 e Å^{-3}, respectively. Anisotropic thermal parameters were assigned to all non-H atoms. The organic H atoms were generated geometrically.

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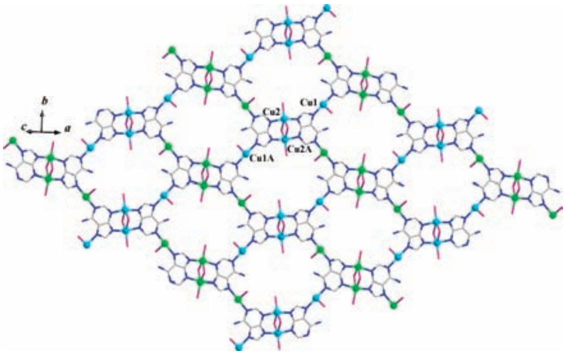

Figure 2. 2D covalent layer of **1** with 26-membered Cu-ade macrocycles (the tetranuclear Cu^{II} cores with Λ and Δ arrangement are differentiated by blue and green balls, respectively; the terminal DMF molecules are omitted for clarity).

infinite 2D layer (Figure 2). As a consequence, the versatile ade finally displays an unprecedented tetradentate μ_4-N1,N3,N7,N9-bridging mode and thus plays a dual role for both the aggregation of four Cu^{II} cores within the subunit and the extension of an infinite 2D covalent layer. On the other hand, the self-assembly pattern directed by the Cu^{II}ade linkages creates scarce 26-membered Cu^{II}ade macrocycles. Furthermore, the adjacent tetranuclear Cu^{II} subunits within the 2D plane are interestingly arranged in a chiral Λ and Δ way (Figure 2) to generate a common 4,4 topology, which is somewhat similar to the linear trinuclear Cd^{II}-based complex with the ade nucleobase.[24] Additionally, the exocyclic N6 amino group in **1** remains uncoordinated and acts as a H donor to produce 4-fold hydrogen-bonding interactions with N7, O2, O3, and Cl1 atoms (see Table S2 in the Supporting Information) to consolidate the metal coordination sphere as well as the 2D covalent layer (see Figures 1and S1 in the Supporting Information). Thus, **1** is the first crystal structure to support the theory the ade anion binds a metal ion on N1 and uses the N6−H bond to reinforce this coordination with suitable hydrogne-bonding interactions.[2]

Surprisingly, probably owing to the presence of long and flexible DMF, extensive interlayer C−H···π weak interactions can be observed (see Table S3 in the Supporting Information) but no popular π−π-stacking interactions (the distance between the adjacent layers is ca. 7.874 Å), which finally leads to the formation of the overall three-dimensional supramolecular architecture of **1** (see Figure S2 in the Supporting Information).

The FT-IR spectrum of **1** shows characteristic bands at 3329 and 3176 cm^{-1} for the asymmetric and symmetric stretching vibrations of the exocyclic amino chromophore of ade, respectively. TG experiments (see Figure S3 in the Supporting Information) of **1** reveal that the first weight-loss process with two continuously endothermic DTA peaks was observed from room temperature to 260 °C, corresponding to the removal of terminal DMF molecules and terminal/bridged chloride anions (expt, 56.3%; calcd, 55.5%). Also, the adeninate ion is decomposed between 396 and 462 °C (expt, 24.0%; calcd, 22.9%), accompanying a strong and sharp exothermic effect.

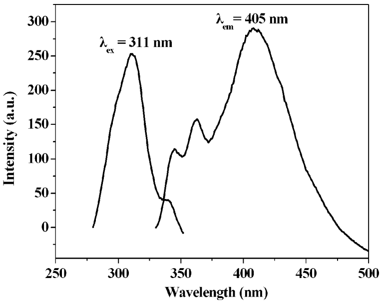

Figure 3. Fluorescence spectra of **1** in a DMF−methanol solution at room temperature.

At room temperature, **1** in a DMF−methanol solution exhibits a strong emission peak at 405 nm upon excitation at 311 nm (Figure 3). The strong emission behavior can be assigned to an intraligand charge transfer because a similar emission can be observed for the free Hade ligand.

In conclusion, the first 2D photoluminescent Cu^{II}-based complex with tetradentate μ_4-N1,N3,N7,N9-adeninate nucleobases was constructed and fully characterized. Undoubtedly, the new metal−nucleobase binding pattern is of significance for the investigations of the DNA−metal binding processes in the development of new biologically active metallodrugs as well as the stability and functions of nucleic acids.[29]

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Supporting Information Available: X-ray crystallographic file in CIF format, Tables S1−S3, and Figures S1−S3 of **1**. This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates for **1** have been deposited with the Cambridge Crystallographic Data Centre as CCDC No. 715529. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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