A novel three-dimensional heterometallic compound: templated assembly of the unprecedented planar "Na⊂[Cu_4]" metalloporphyrin-like subunits†

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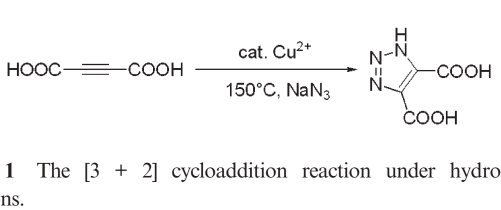
A 3D heterometallic compound, [$Cu_4Na_4(TzDC)_4(H_2O)_7$]$_n$ (H_3TzDC = 1,2,3-triazole-4,5-dicarboxylic acid), which contains unprecedented planar "Na⊂[Cu_4]" metalloporphyrin-like subunits, was synthesized by hydrothermal reactions involving *in situ* formation of the ligand and templated assembly of the metalloporphyrin-like subunits.

Recently, a great number of new coordination compounds with interesting architectures and novel properties have been studied involving *in situ* formation of organic ligands.[1] The characterization of these *in situ* reactions has activated great interest in the research of environmental friendly and relatively simple synthetic approaches in coordination chemistry and organic chemistry. An interesting example is the hydrothermal synthesis of coordination compounds with 5-substituted 1*H*-tetrazole ligands formed *in situ* through an environmental friendly route of [3 + 2] cycloaddition of sodium azide to nitriles in water with zinc salts as catalyst.[2] With the tetrazole ligand formed *in situ* under hydrothermal conditions, many interesting coordination compounds have been reported.[3] Similarly, the "click" chemistry of azide–alkyne [3 + 2] cycloaddition[4] is useful to synthesize coordination compounds with the resultant 1,2,3-triazoles as ligands.[5] Here, we report a novel three-dimensional (3D) heterometallic Cu(II)–Na(I) coordination polymer of 1,2,3-triazole-4,5-dicarboxylic acid (H_3TzDC), which is generated *in situ* from but-2-ynedioic acid with sodium azide under hydrothermal conditions (Scheme 1). The resultant compound [$Cu_4Na_4(TzDC)_4(H_2O)_7$]$_n$ **1** exhibits an interesting 3D network built of unprecedented metalloporphyrin-like Na⊂[Cu_4] motifs, which are templated by sodium ions. Quantum chemistry calculations using density functional theory (DFT) are also performed for better understanding the template effect of sodium ion and the magnetic coupling interaction mechanism between the paramagnetic Cu(II) ions.



Scheme 1 The [3 + 2] cycloaddition reaction under hydrothermal conditions.

The deep-blue rhombic crystals of **1** obtained through the hydrothermal reaction of $Cu(NO_3)_2{\cdot}6H_2O$, NaN_3 and but-2-ynedioic acid are stable in air and insoluble in water and common organic solvents. Single-crystal structural determination‡ and elemental analysis reveals that **1** is a compound of copper coordinated with *in situ* formed $TzDC^{3-}$. The compound crystallizes in the *C*2/*c* space group and has a three-dimensional coordination network constructed by planar "Na⊂[Cu_4]" pentanuclear motifs. As shown in Fig. 1, there are two crystallographically independent but chemically similar Cu(II) centers in the pentanuclear motifs. Each Cu(II) ion is placed in a distorted square pyramidal environment, which is completed by two triazole nitrogens and two carboxylate oxygens from two $TzDC^{3-}$ ligands at the basal positions, and a water molecule (Ow1 or Ow2) at the apical position with the apical Cu–O distance (2.258 or 2.304 Å) being significantly longer than the basal Cu–O and Cu–N distances (av. 1.97 Å). Each $TzDC^{3-}$ ligand assumes a nearly planar geometry (two different coordination modes depicted in Scheme 2). The separation of two Cu(II) ions bridged by the same ligand is 6.0 Å (av.), and the basal [CuN_2O_2] planes containing both Cu(II) ions are nearly coplanar with the bridging ligand. As a consequence of this planarity and the *cis* arrangement of the two N–C–C–O chelate sites in the base of each Cu(II), four Cu(II) ions and four triazole rings form an unusual centrosymmetric

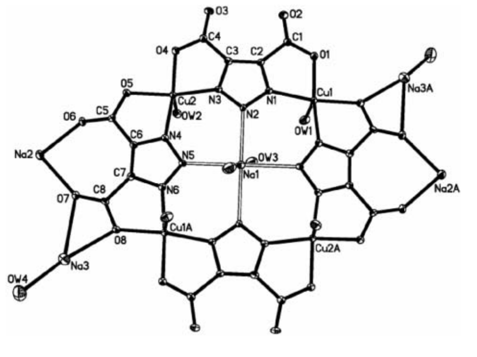


Fig. 1 Planar "Na⊂[Cu_4]" pentanuclear motif in **1**. Selected bond distances (Å) and angles (°): Cu(1)–N(1) 1.968(3), Cu(1)–OW1 2.258(3), Na(1)–N(2) 2.482(3), N(1)–N(2) 1.330(4); Cu(1)–N(6)A 1.978(3), Na(3)–O(3)E 2.513(3), OW2–Na(3)B 2.430(3), O(6)–Na(2)–O(7)C 91.1(1), O(6)D–Na(2)–O(7) 90.9(1), N(3)–N(2)–N(1) 106.5(3). Symmetry codes: A, $-x + 1/2$, $-y + 1/2$, $-z$; B, $-x$, $-y + 1$, $-z$; C, $x + 1/2$, $y - 1/2$, z; D, $-x + 1/2$, $-y + 3/2$, $-z$; E, $-x + 1$, $-y + 1$, $-z$.

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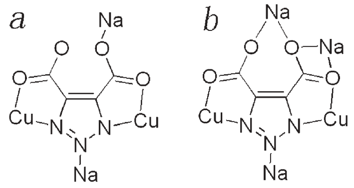

Scheme 2 The coordination modes of $TzDC^{3-}$ in **1**.

tetrametallamacrocyclic moiety in which all the metal atoms and the ligands are nearly coplanar. Such a square $[Cu_4(TzDC)_4]$ moiety differs evidently from the imidazoledicarboxylate ($ImDC^{3-}$) bridged compounds reported recently.[6] In the latter compounds, two $ImDC^{3-}$ ligands binding the same metal ion are perpendicular. However, this feature of pseudo-planar coordination conformation is the same as that in the reported binuclear metal complexes bridged by $TzDC^{3-}$ ligand.[7] The $[Cu_4(TzDC)_4]$ moiety differs from other reported tetranuclear Cu(II) clusters in which the Cu(II) ions are not coplanar with all the bridging atoms.[8] It is interesting to note that the motif resembles porphyrins in the way that four coplanar five-membered rings are linked into a planar macrocycle, except metal ions instead of connecting CH groups and triazole instead of pyrrole. Therefore, the resulting hexadecacyclic moiety is an unprecedented carbon-free $[Cu_4N_{12}]$ macrocycle. Similar to porphyrins, the macrocyclic moiety in **1** has four nitrogen atoms pointing toward the center, with the N···N distances (av. 4.90 Å) significantly larger than those in porphyrins, due to the longer Cu–N distances compared with C–C distances. The size of the planar coordination pocket fits the sodium ion well, and consequently, a sodium ion is encapsulated at the center of the pocket, with the Na–N distances being exactly halves of the above N···N distances, forming a metalloporphyrin-like pentanuclear $NaCu_4$ motif, which is denoted as $Na\subset[Cu_4]$. The Na1 atom, which lies in an inversion centre, is axially bound by two symmetry-related water molecules (Na1–Ow3, 2.50 Å), resulting in an axially elongated octahedral geometry.

The negative $Na\subset[Cu_4]$ motifs with a number of peripheral carboxylato oxygens are interlinked into 3D networks *via* weak interactions involving additional Na ions (Na2 and Na3) and water molecules. Located at an inversion center, Na2 is coordinated by four carboxylato oxygens (O6, O7, O6A and O7A, symmetry code A: $1/2 - x$, $3/2 - y$, $-z$) from two neighboring $NaCu_4$ motifs, and Na3 is coordinated by a chelating carboxylato group from one $NaCu_4$ motif and by a water molecule (Ow4) which lies on a twofold axis and acts as a μ_2 bridge linking two Na2 atoms interacting with different $NaCu_4$ motifs. The above Na–O interactions join the $Na\subset[Cu_4]$ motifs into a 2D sheet along the *ab* plane (Fig. 2). Furthermore, Na3 from one sheet is also coordinated by a carboxylato oxygen from another sheet, and a carboxylato oxygen, and two water molecules (Ow2 and Ow3) from a third sheet. There are also weak interactions between Na2 from one sheet and two triazole nitrogens (N2) from two neighboring sheets (Na2···N2, 3.06 Å).[9] These intersheet Na–O and Na–N interactions lead to offset stacking of the sheets to yield a 3D network (Fig. 3).

A polycrystalline sample was also prepared under hydrothermal conditions from copper(II) salt and pre-synthesized H_3TzDC, which was prepared from oxidation of benzotriazole,[9] in the presence of NaOH . Elemental analysis, IR spectra and powder XRD patterns confirmed the compound obtained was identical with **1** (see ESI†).

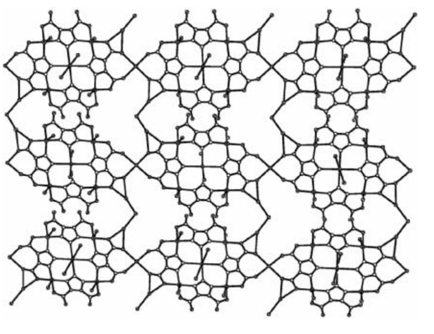

Fig. 2 The 2D sheet along the *ab* plane in **1**.

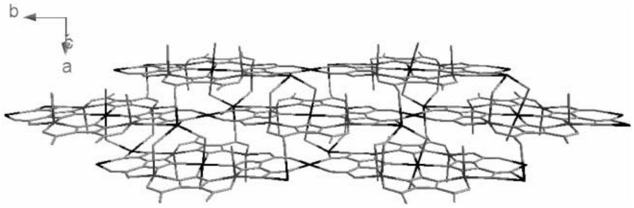

Fig. 3 The 3D network of **1**.

Interestingly, attempts to obtain similar compounds by using KOH or LiOH, instead of NaOH, were unsuccessful. These observations suggest the template effect of the sodium ion in the formation of the porphyrin-like planar $[Cu_4N_{12}]$ macrocyclic motif. As indicated by structural data, while the potassium or lithium ion is too large or too small to fit into the cavity of the macrocyclic motif, the sodium ion has the appropriate size and hence can serve as a template for the assembly of the Cu(II) and $TzDC^{3-}$ ions into the macrocycle. Meanwhile, the template ions simultaneously coordinate four ligands in a rare perfect planar fashion.[10]

DFT calculation was carried out to explain theoretically the sodium template effect in this system. We optimized the distance between A^+ (A is Li, Na or K) ion and 2-N of the triazole using DFT with hybrid B3LYP functional.[11] The calculation model is about a quarter of the whole "$Na\subset[Cu_4]$" pentanuclear motif including one triazole and two coordination Cu(II) ions. The optimized distances of Li^+–N, Na^+–N and K^+–N are 2.16, 2.38 and 2.77 Å, respectively. Comparing with the hole radius of $Na\subset[Cu_4]$ of 2.45 Å, the Na^+ ion fits the pocket best.[12]

The magnetic susceptibility of compound **1** was measured at 2–300 K at 2000 G. The $\chi_M T$ product per pentanuclear subunit (1.25 emu mol^{-1} K, χ_M is the molar magnetic susceptibility) at room temperature is somewhat lower than the spin-only value for four Cu(II) ions (1.5 emu mol^{-1} K with $g = 2.00$). Upon cooling, $\chi_M T$ decreases monotonically to 0.008 emu mol^{-1} K at 2 K, while the χ_M values first increase to a rounded maximum of 0.005 emu mol^{-1} at about 150 K, then decrease rapidly to a minimum of 0.001 emu mol^{-1} at about 25 K, and finally increase rapidly upon further cooling (Fig. 4). These features indicate a dominant antiferromagnetic interaction in compound **1**, and the increase of χ_M below 25 K is attributable to the presence of paramagnetic impurities. The least-squares fits of the experimental data to a Cu^{II}_4 square model[13] led to $J = -139.0$ cm^{-1}, $g = 2.12$

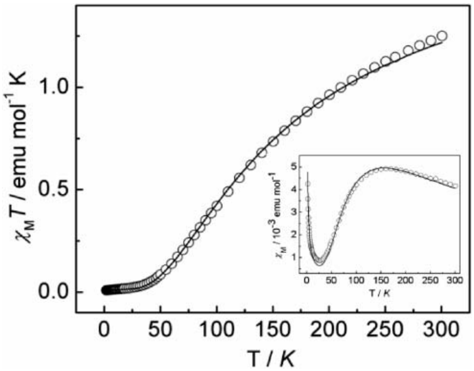

Fig. 4 The $\chi_M T$ *vs.* T plot for **1**. Inset: The χ_M *vs.* T plot for **1**. The solid lines represent the best fit of the experimental data.

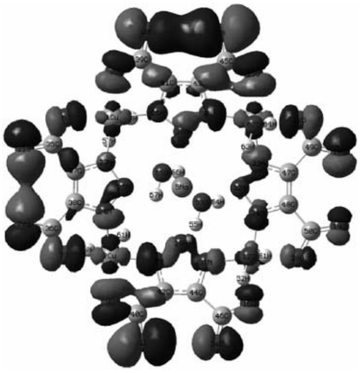

Fig. 5 One of the four magnetic orbitals for the Na⊂[Cu$_4$] motif.

and ρ = 0.0055, where J is the parameter characterizing the magnetic exchange constant mediated through the imidazolato group, and ρ is the molar fraction of the paramagnetic impurities. The Hamiltonian $H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_1)$ is used in the fitting procedure, and it is assumed the exchange coupling constants of adjacent Cu(II) ions are the same and that the interactions between diagonal metal ions in the same Na⊂[Cu$_4$] motif and the inter-unit interactions are negligible.

Based on the Hamiltonian described above, the exchange coupling properties are calculated using the DFT combined broken symmetry approach proposed by Noodleman *et al.*[14] The calculation model included the whole Na⊂[Cu$_4$] motif with the structure obtained from the experimental crystal data. The details of the computation is described in the ESI.† The calculated magnetic coupling constant is -130.5 cm^{-1}, which is well consistent with the experimental value of -139.0 cm^{-1}. Both the theoretical and experimental J values indicate a strong antiferromagnetic coupling between Cu(II) cations occurs through the triazole group. To explore the magnetic coupling pathway of the molecule, the single occupied molecular orbitals (SOMOs) of high spin state are also calculated using DFT with hybrid B3LYP functional. These SOMOs are mainly composed of the $d_{x^2-y^2}$ orbitals of paramagnetic Cu(II) ions and p_x and p_y orbitals of the N atom of triazole group. Fig. 5 shows one of the four magnetic orbitals, which is a σ* type orbital. For the four $d_{x^2-y^2}$ orbitals of the Cu(II) ions with the same symmetry and having direct overlap integrals, the magnetic coupling interaction is antiferromagnetic on the basis of the Goodenough–Kanamori rules.[15] Similarly, the conjugated N_3 moiety of the triazole, which bridges two paramagnetic Cu(II) ions, is analogous to the azide group linked in an end-to-end manner, and could transmit strong antiferromagnetic interactions.[16]

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Notes and references

‡ *Crystal data*: $C_{16}H_{14}Cu_4N_{12}Na_4O_{23}$, M_r = 1088.52, monoclinic, space group *C*2/*c*, a = 8.7558(1), b = 16.6604(3), c = 21.5919(4) Å, β = 95.3476(10)°, V = 3105.11(9) Å^3, T = 293 K, Z = 4, μ(Mo-Kα) = 2.880 mm^{-1}, 29968 reflections measured, 3570 unique (R_{int} = 0.0958), R_1 = 0.0347, wR_2 = 0.1054 (all data). CCDC 618769. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618296h

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