Crystal structure of a flexible self-assembled two-dimensional square network complex $[Cu_2(C_3H_2O_4)_2(H_2O)_2(4,4'\text{-bpy})]\cdot H_2O$

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The structure of a self-assembled two-dimensional square network complex, $[Cu_2(C_3H_2O_4)_2(H_2O)_2(4,4'\text{-bpy})]\cdot H_2O$, comprising both flexible and rigid ligands and having a large inner cavity of 15.776(3) × 15.786(2) Å, is reported.

Since the first self-assembly of square supramolecules was reported in 1990,[1a] novel, tetranuclear, cationic macrocycles, with bond angles of *ca.* 90°, have emerged as the newest members of the family of supramolecular assemblies.[1–3] Much less is known about extended two-dimensional systems[4] based on molecular squares, on account of the lack of methods for linking monomer or molecular units. In all these cases, only rigid ligands such as 4,4′-bipyridine are chosen as the bridging ligands, although Fujita *et al.*[1d] and Slone *et al.*[3c] tried to utilize more flexible ligands to link the transition metals, they could not isolate molecular squares but only macrocyclic dinuclear complexes. Flexible organic macrocycles such as crown ethers, cyclophanes, cyclodextrins, calixarenes, clathrates are ubiquitous,[5] and this prompted us to investigate whether it is possible to combine flexible ligands with rigid ligands within a single crystal. Here we report the first X-ray crystal structure of a flexible self-assembled two-dimensional square network $[Cu_2(C_3H_2O_4)_2(H_2O)_2(4,4'\text{-bpy})]\cdot H_2O$ **1** comprising both flexible and rigid bridging ligands and having an inner cavity of 15.776(3) × 15.786(2) Å surrounded by 4,4′-bpy and malonate groups. We thus have introduced a new concept of flexible self-assembly of supramolecules.

When $Cu(C_3H_2O_4)\cdot 2H_2O$† was treated with 4.4′-bipyridine in H_2O–EtOH at ambient temperature [eqn. (1)], deep-blue crystals grew within several days.‡ Yields in excess of 90% were obtained and the structure of **1** was solved by single-crystal X-ray diffraction.§

$$2n\,Cu^{2+} + 2n\,C_3H_2O_4^{2-} + n\,4,4'\text{-bpy} + 2n\,H_2O \xrightarrow{H_2O\text{–EtOH}} \mathbf{1} \quad (1)$$

The crystal structure of **1** is shown in Fig. 1 and can be characterized by the following features. (*i*) It consists of two-dimensional networks which are stacked parallel but in a staggered manner on each other along the *z*-axis, with an interplanar separation of 3.785 Å and angle of 45.0°. The packing of the two-dimensional polymers reveals that the small malonate rings in one layer fit exactly into the large 4,4′-bpy rings in the next, it is almost as if the two rings are acting as templates for each other. This feature is very exciting, and this complementarity of the two rings probably explains the unusually high yield of the complex (Fig. 2). (*ii*) Each network involves a small planar square with Cu^{II} ions and malonate ions at each corner and side, respectively; each Cu^{II} is also bridged by one 4,4′-bpy, thus forming a large square with each edge shared by one malonate group and one 4,4′-bpy ligand. The coordination geometry about each Cu^{II} is a slightly distorted square pyramid (the geometric τ value is 0.15[6]). (*iii*) All the planar squares are distorted only to a small extent. The square-planar angles are 89.89(1) and 89.99(1)° in the large square and 89.25(3) and 89.35(3)° in the small one, very close to the ideal square-planar angle of 90°. The inner cavities have dimensions of 15.776(3) × 15.786(2) Å and 4.644(2) × 4.649(2) Å, respectively and no solvent molecules are clathrated in the cavities. Uncoordinated water molecules are distributed statistically. (*iv*) A malonate ion adopts a bridging position which enhances the stability of the two-dimensional network, the third coordinates to the neighbouring Cu atom. (*v*) All coordinated water molecules are nearly perpendicular to the CuNOOO base plane and two adjacent water molecules are arranged in *trans*-coordination, with two water molecules of two opposite corners being on the same side relative to the Cu_4 plane.

It is particularly interesting that four Cu^{II} ions and four flexible malonate groups form a small planar square and four six-membered chelate rings *via* self-assembly. We define this phenomenon as flexible self-assembly of supramolecules. Recently, Tosik *et al.*[7] pointed out the conformational flexibility of chelated malonate rings through analyses of the large difference of the typical puckering of the five known Cu^{II}-chelated malonate rings. The conclusion can be further confirmed by the variation of bond lengths and angles belonging to the six-membered chelate ring relative to known

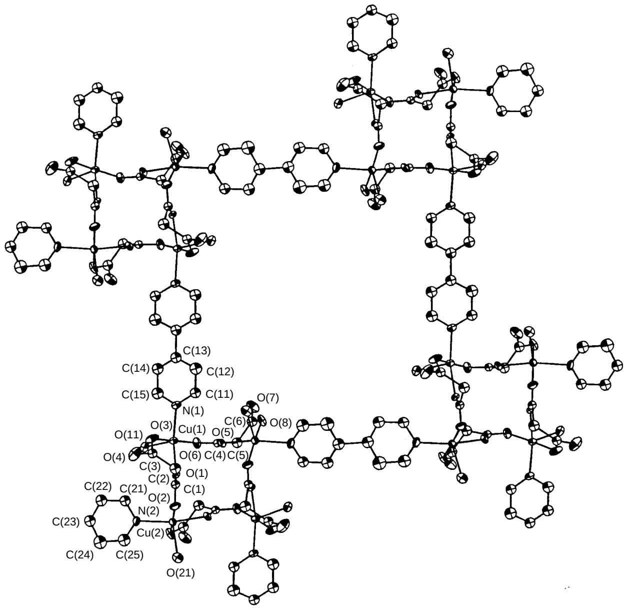

Fig. 1 ORTEP diagram of **1** with labelling scheme. Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.996(7), Cu(1)–O(3) 1.93(1), Cu(1)–O(6) 1.98(1), Cu(1)–O(11) 2.20(1), Cu(1)–N(1) 2.06(1), Cu(2)–O(2) 1.97(1), Cu(2)–O(5^{i}) 1.972(7), Cu(2)–O(8^{i}) 1.93(1), Cu(2)–O(21) 2.191(9), Cu(2)–N(2) 2.06(1), O(1)–Cu(1)–O(3) 89.6(4), O(1)–Cu(1)–O(6) 89.3(4), O(1)–Cu(1)–O(11) 91.4(3), O(1)–Cu(1)–N(1) 166.2(4), O(3)–Cu(1)–O(6) 174.9(4), O(3)–Cu(1)–O(11) 93.2(4), O(3)–Cu(1)–N(1) 87.1(4), O(6)–Cu(1)–O(11) 91.7(4), O(6)–Cu(1)–N(1) 92.8(4), O(11)–Cu(1)–N(1) 102.1(4), O(2)–Cu(2)–O(5^{i}) 89.5(4), O(2)–Cu(2)–O(8^{i}) 174.1(4), O(2)–Cu(2)–O(21) 92.5(4), O(2)–Cu(2)–N(2) 91.5(4), O(5^{i})–Cu(2)–O(8^{i}) 89.8(4), O(5^{i})–Cu(2)–O(21) 92.4(3), O(5^{i})–Cu(2)–N(2) 167.1(5), O(8^{i})–Cu(2)–O(21) 93.3(4), O(8^{i})–Cu(2)–N(2) 87.8(4), O(21)–Cu(2)–N(2) 100.4(4). i: 1 − *x*, −*y*, *z*.

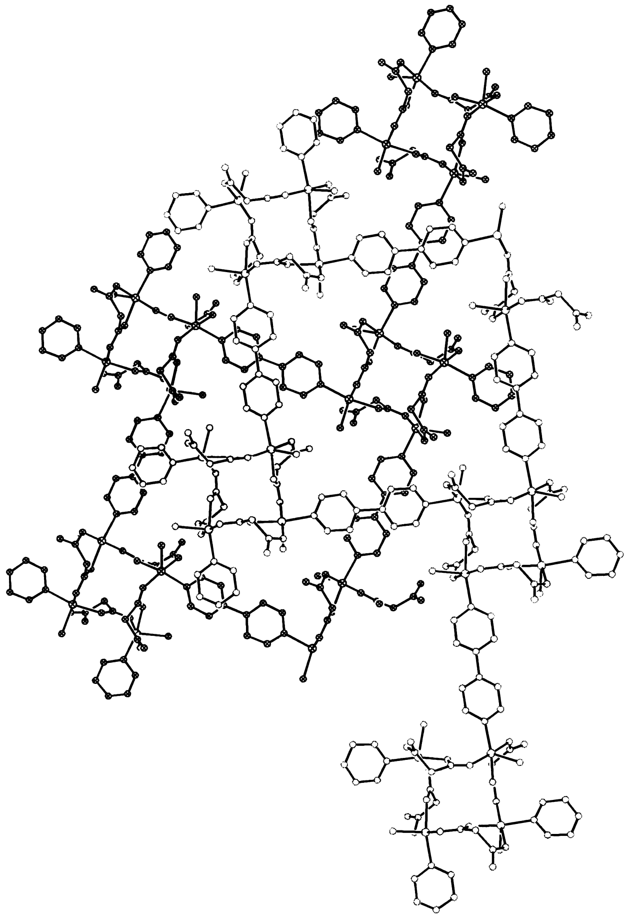

Fig. 2 Packing diagram for **1** along the *z*-axis

compounds. Including our compound, reported Cu–O, C–O and C–C distances[7–9] are in the ranges 1.909–1.996, 1.22–1.272, and 1.48–1.530 Å, respectively, and the O–M–O angles[7–10] range from 85.0 to 94.82° in the metal-chelated malonate rings.

In summary, a novel, self-assembled two-dimensional square network complex, $[Cu_2(C_3H_2O_4)_2(H_2O)_2(4,4'\text{-bpy})]\cdot H_2O$, constitutes the first example that comprises both flexible and rigid ligands within one single crystal structure.

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Footnotes

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† *Preparation of* $Cu(C_3H_2O_4)\cdot 2H_2O$: to a mixture of copper(II) carbonate (2.0 mmol) and hot water (20 ml), malonic acid (1.9 mmol) was added and a dark blue solution was obtained. This was filtered and condensed to 5 ml and a large amount of crystals were obtained. Anal. calc. for $Cu(C_3H_2O_4)\cdot 2H_2O$: C, 17.70; H, 3.47. Found: C, 17.14; H, 3.59%.

‡ *Preparation of* **1**: to an aqueous solution (30 ml) of $Cu(C_3H_2O_4)\cdot 2H_2O$ (1.0 mmol) an ethanol solution (10 ml) of 4,4′-bpy (0.5 mmol) was added. The initially formed very small amount of fine precipitate was filtered off, and the clear filtrate was allowed to stand for several days at ambient temperature to give deep-blue crystals. Yields in excess of 90% were obtained. Anal. calc. for **1**: C, 36.43; H, 3.44, N, 5.31. Found: C, 36.50; H, 3.21; N, 5.09%.

§ *Crystal data* for **1**: M = 2190.68, orthorhombic, space group $P2_12_12_1$ (no. 18), a = 16.348(3), b = 16.364(5), c = 7.570(1) Å, V = 2025.2(8) Å^3, $F(000)$ = 1104, Z = 4, D_c = 1.78 g cm^{-3}, T = 296 K, μ(Mo-Kα) = 21.7 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å. A crystal of approximate dimensions 0.40 × 0.40 × 0.25 mm was mounted on a Rigaku AFC5R diffractometer, using graphite-monochromated Mo-Kα radiation. Cell constants and orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 20 reflections in the range $8 < \theta < 27.5°$, measured by the computer controlled diagonal slit method of centring. Scattering factors were taken from Cromer and Waber.[11] The ω–2θ scan mode with a maximum 2θ value being 50.0° were used to collect intensity data. A total of 2075 reflections were collected, of which 2075 were unique, and 1579 had $I > 3\sigma(I)$ with 199 parameters. The data were corrected for Lorentz-polarization effects, and empirical absorption (from 0.70 to 1.00 in I). The structure was solved by direct methods and refined by full-matrix least-squares calculation. Cu atoms were located in the E map, the remaining atoms were located in succeeding difference Fourier syntheses. H atoms of the disordered water were not included, H atoms of the coordinated water were added by difference Fourier synthesis and the other H atoms were placed at calculated positions. All H atoms were unrefined. All calculations were performed on a COMPAQ computer using Mo1EN/PC.[12] Final R = 0.055, R_w = 0.079 (unit weights), goodness of fit = 1.69, max. shift/e.s.d. = 0.02. The minimum and maximum peaks in the final difference Fourier map are at −0.33 and 0.87 e Å^{-3}, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/464.

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