Three-fold Interpenetrating Diamondoid Frameworks with π–π Stacking of Alternate Coordinated and Uncoordinated Ligands: Crystal Structures of Copper(I) Coordination Compounds, $[Cu(DMTPN)_2]X(DMTPN)(thf)$ (DMTPN = 2,5-Dimethylterephthalonitrile; X = BF_4, ClO_4)

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Two novel coordination polymer compounds, $[Cu(DMTPN)_2]X(DMTPN)(thf)$ (DMTPN = 2, 5-dimethylterephthalonitrile, X = BF_4 (**1**) and ClO_4 (**2**)) are prepared and characterized by single crystal X-ray analysis; both are isostructural and have three-fold interpenetrated diamondoid structure with π–π stacking column of alternate coordinated and uncoordinated DMTPN.

A suitable combination of a tetrahedral metal ion and a rod-like linking ligand can form a diamondoid framework,[1-8] whose conformation and multiplicity of interpenetration are strongly dependent on length and bulkiness of the linking ligand. For example, a copper(I) coordination compound Cu(2,5-dimethylpyrazine)$_2$(PF_6),[6] whose Cu•••Cu distance linked by bridging pyrazine is ca. 7 Å, has a single diamondoid framework, while Cu(DMDCNQI)$_2$[9] (DMDCNQI = 2,5-dimethyl-*N,N'*-dicyanoquinonediimine) with Cu•••Cu linkage of 12.76 Å has seven independent diamondoid frameworks interpenetrating each other.

The latter compound is well known as a metallic conductor down to 1.3 K.[9] This behavior is interpreted by the coexsistence of one-dimensional (1D) and three-dimensional (3D) Fermi surface characters,[10,11] which is correlated to the structural characteristic of this compound having both 1D π–π stacking of ligands and 3D diamondoid frameworks.[4,12] However, so far as we know, no other compounds having such a structural characteristic have been reported than DCNQI derivatives.[13-15] In order to design new compounds having 3D diamondoid structure together with π–π stacking, we chose a copper(I) ion as a central metal and 2,5-dimethylterephthalonitrile (DMTPN) as a linking ligand. Although non-substituted TPN with copper(I) ion forms Cu(TPN)$_2$(BF_4)[5] with 5-fold interpenetrated diamondoid frameworks, it has no π–π stacking of ligands. On the other hand, by using substituted TPN as linking ligand, we could form 3-fold interpenetrated diamondoid structure with significant π–π stacking composed of alternate coordinated and uncoordinated ligands. This is the first example of a diamondoid structure with an intercalated π–π stacking.

Crystals of $[Cu(DMTPN)_2]X(DMTPN)(thf)$ (X = BF_4 (**1**), ClO_4 (**2**)) were obtained by slow diffusion of DMTPN solution into corresponding copper(I) solution.[16] Successful analyses of X-ray diffraction revealed that both compounds have almost the same structure:[17,18] an asymmetric unit contains one copper(I) atom, two DMTPN coordinating to the copper(I) atom, one tetrafluoroborate or perchlorate as a counter anion and one metal-free DMTPN and one thf as guests. As can be seen from Figure 1, the copper(I) ion has a tetrahedral coordination through four nitrogen atoms of four cyano groups of different DMTPN:

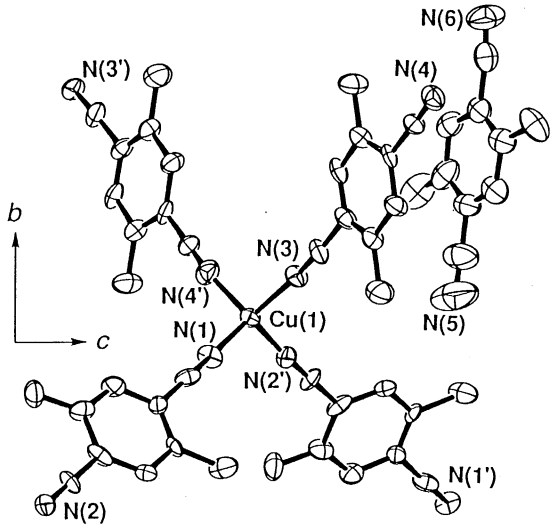

Figure 1. ORTEP drawing of coordinated and uncoordinated DMTPN around a copper(I) ion in $[Cu(DMTPN)_2](ClO_4)(DMTPN)(thf)$ (2) showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. Only important atoms are labeled.

DMTPN(1), DMTPN(1'), DMTPN(2) and DMTPN(2'), where DMTPN(*i*) denotes the DMTPN containing the N(2*i*) atom. DMTPN(1') and DMTPN(2') are related to the DMTPN(1) and DMTPN(2) by symmetry operations of (x, -y, z+1/2) and (x-1/2, -y+1/2, z+1/2), rspectively. All Cu-N bond lengths are normal compared to those of four-coordinated Cu(I) complexes with N-donor ligands.[19] The average N-Cu-N' angle of 109.4° for both compounds **1** and **2** are very close to 109.5° of the internal angle of diamond, indicating that both CuN_4 chromophores are almost a regular tetrahedron. The DMTPN(2) is almost parallel to the DMTPN(2') (3.2°: a dihedral angle in average for **1** and **2**) and to the metal-free DMTPN(3) (2.3°) while the DMTPN(1) is parallel neither to the DMTPN(1') (58.6°) nor to the DMTPN(2) (81.4°).

The cyano group at the other end of each DMTPN also coordinates to another copper atom, resulting in a formation of a 3D diamondoid framework as shown in Figure 2. It should be noted that there are three independent frameworks interpenetrating each other. As noted previously, the interpenetration of 3D frameworks is often found in coordination compounds with diamondoid structure: Ag(4-CN-py)$_2$(BF_4)[7] and Cu(4,4'-bipy)$_2$(PF_6)[8] show 4-fold, Cu(TPN)$_2$(BF_4)[5] shows 5-fold, and $[Cu(NC(CH_2)_4)CN)_2](NO_3)$[1] shows 6-fold interpenetrated diamondoid frameworks, and M•••M distances bridged by linking ligands in these compounds are 9.93 Å, 11.16 Å, 11.9 Å, and 12.9 Å, respectively. Since the Cu•••Cu distance bridged by DMTPN in compounds **1** and **2** is same as that bridged by TPN

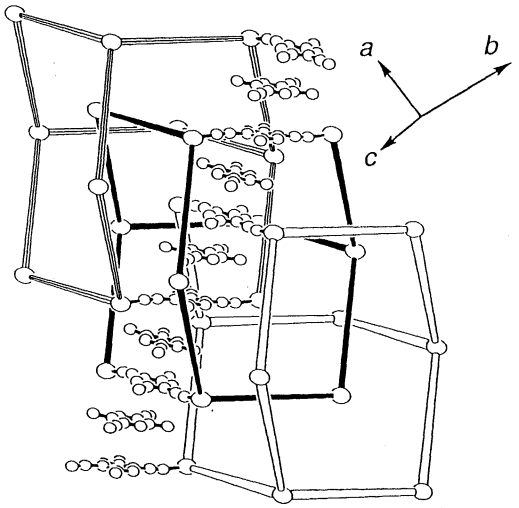

Figure 2. Three independent diamondoid frameworks of copper atoms connected through DMTPN in 2. Large circles and rods represent copper atoms and DMTPN, respectively. Three different types of rods represent independent diamondoid networks interpenetrated each other. Also shown is a part of π–π stacking column composed of alternate coordinated and uncoordinated DMTPN.

in $Cu(TPN)_2(BF_4)$, the fewer interpenetration in **1** and **2** should be caused by the bulkiness of methyl groups in DMTPN. This is also strongly related to the incorporation of guest molecules.

Metal-free DMTPN(3) molecules incorporated in the $Cu(DMTPN)_2$ lattice participate in the formation of π–π stacking column. As can be seen from Figure 3, coordinated and uncoordinated DMTPN stack alternately. There are two types of the nearest carbon distances between two DMTPN's: 3.37(2) Å and 3.51(2) Å which are corresponding to the separation between DMTPN(2) and DMTPN(3') and that between DMTPN(2) and DMTPN(3), respectively. The column is, therefore, composed of sequential stacking of DMTPN's with the order of DMTPN(2) •••DMTPN(3')•••DMTPN(2')•••DMTPN(3)•••DMTPN(2). The

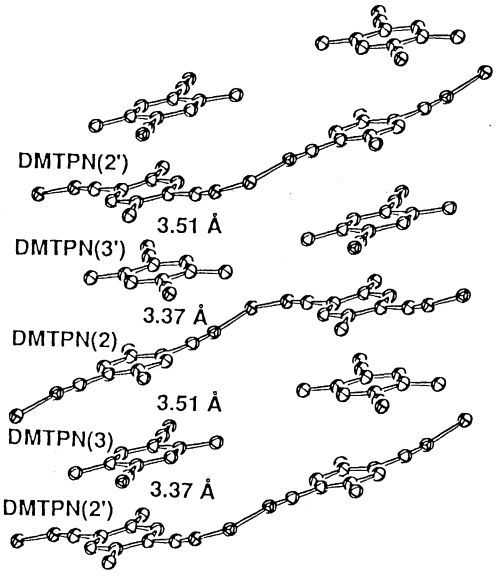

Figure 3. Side view of π–π stacking of DMTPN in 2. Distances indicated are nearest carbon distances between DMTPN's.

stacking columns run through the diamondoid frameworks along the (101) direction. (See Figure 2)

Comparison of **1** and **2** gives significant information about the crystal stability. Compound **1** can be obtained as a pure crystalline form, while the glass tube for **2** contains byproducts with less clarity. Crystals of **1** show no change without mother liquid while those of **2** easily loose clarity when dried, indicating that thf molecules included in **2** is more labile than those in **1**. These facts imply that the size of the BF_4^- anion fits in the space determined by the $Cu(DMTPN)_2$ lattice better than the ClO_4^- anion.

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15 Although $[Ag(4\text{-}CN\text{-}py)_2](BF_4)$[7] seems to have such a structural characteristics, a relatively long interplanar distance of 4.0 Å indicates that there is no significant π–π interaction.
16 Syntheses of **1** and **2**: All operations were carried out under argon or ethylene by using the standard Schlenk technique. A solution of copper(I) tetrafluoroborate or copper(I) perchlorate in thf (30 mM, 1.2 mL) was poured to a bottom of a glass tube. Then thf (0.6 mL) and a solution of 2,5-dimethylterephthalonitrile (DMTPN) in thf (120 mM, 0.6 mL) were added slowly in sequence. The glass tube was sealed under argon and kept at room temperature. After three days, pale yellow, plate crystals were obtained for both anions corresponding to **1** and **2**. Analytical data for **1**: Found: C 58.81, H 4.77, N 12.09 %; Calcd for $C_{34}H_{32}BCuF_4N_6O$: C 59.10, H 4.67, N 12.16 %. A low yield of **2** together with the existence of byproducts with less clarity prevent a precise determination of analytical data for **2**.
17 Crystal data for **1**: $C_{34}H_{32}BCuF_4N_6O$, M = 691.02, monoclinic, Cc, a = 9.599(3), b = 27.298(5), c = 13.367(3) Å, β = 105.45(2)°, U = 3376(1) Å^3, Z = 4, D_{cal} = 1.359 g cm^{-3}, R = 0.062 and R_w = 0.076 for 2841 unique reflections.
18 Crystal data for **2**: $C_{34}H_{32}ClCuN_6O_5$, M = 703.67, monoclinic, Cc, a = 9.590(7), b = 27.429(3), c = 13.416(4) Å, β = 105.80(3)°, U = 3396(2) Å^3, Z = 4, D_{cal} = 1.376 g cm^{-3}, R = 0.055 and R_w = 0.063 for 2700 unique reflections.
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