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A novel ligand-unsupported 3D framework polymer of trimeric copper(I)) and its NLO property

Yao Kang, Yuan-Gen Yao,* Ye-Yan Qin, Jian Zhang, Yu-Biao Chen, Zhao-Ji Li, Yi-Hang Wen, Jian-Kai Cheng and Rui-Feng Hu
State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China.
E-mail: yyg@ms.fjirsm.ac.cn

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A novel 3-D coordination polymer with trimeric copper (I) unit, $[Cu_3(CN)(IN)_2]_n$ (IN = isonicotinate), was hydrothermally synthesized by the reaction of $Cu(NO_3)_2·3H_2O$ with isonicotinic and terephthalic acids. The structure was characterized to be a twofold interpenetrated 3-D coordination network polymer with two-coordinated copper(I). It has a powder SHG efficiency about that of KDP.

Hydrothermal synthesis has been widely employed to construct assemblies of metal complexes in recent years. The reactivity of some organic compounds in hydrothermal conditions can be reinforced by autocatalysis from some water soluble hydrolysis products.[1] Thus, a great many transition metal coordination polymers with unique structures and specific properties such as adsorption,[2] ion-exchange,[3] heterogeneous catalysis[4] and NLO materials,[5] have been synthesized by this strategy.

In most cases, reduction and oxidation reaction mechanisms were not invoked under hydrothermal conditions. However, a recent literature review[6,7] revealed that some organonitrogen species had intriguing reactivity as reducing agents that could reduce Cu(II) to Cu(I). Few coordination polymers[6,8] were reported for Cu(II) reduction to Cu(I). Herein we report a novel coordination polymer: $[Cu_3(CN)(IN)_2]_n$ **(1)** (IN = isonicotinate); it is a twofold interpenetrated 3-D coordination polymer.

The hydrothermal reaction of $Cu(NO_3)_2·3H_2O$ with isonicotinic, terephthalic acid, ethanol and water in a molar ratio 2:1:1:2:500 at 160 °C for 60 h produced yellow crystals of **1**, although its yield was very low. Terephthalic acid proved to be a necessary reagent to obtain the title complex, because without it we obtained only the black-green crystals of $[Cu_2(IN)_3]_n$ (**2**), reported by Chen.[9]

A single-crystal X-ray diffraction† study of **1** reveals 3-D open frameworks consisting of three copper(I) atoms, two IN ions and one cyanic ion (Fig. 1). The XPS spectrum indicates the valence of the Cu of compound **1** to be 1 (peaks at 932.7 and 952.6 eV (Cu(I) character)). Three Cu(I) atoms constitute an isosceles triangle *via* two Cu–Cu interactions, the distances are [Cu(2)–Cu(1)] 2.793(1) Å and [Cu(2)–Cu(3)] 2.698(1) Å, respectively. The distance between Cu(1) and Cu(3) is 5.138 Å. The angles are 20.315° [Cu(2)–Cu(1)–Cu(3)], 21.064°[Cu(2)–Cu(3)–Cu(1)] and 138.621°[Cu(1)–Cu(2)–Cu(3)], respectively.[10] The Cu1 ion is four-coordinated, bridged by one cyanic ion, one nitrogen atom from IN ion and two oxygen atoms from IN ion. These four atoms form a distorted tetrahedral coordination around Cu1. Both the Cu2 and Cu3 are two-coordinated. The Cu2(I) ion is coordinated to two oxygen atoms of two IN ions and the Cu3(I) ion is coordinated to a nitrogen atom of IN ion and a carbon (or nitrogen) atom of cyanide ion. The infrared spectrum of the title compound exhibited bands at 2123 cm^{-1}, which is attributed to the stretch vibration of CN. The existence of cyanide is also substantiated by the elemental analysis‡. At present, the formation mechanism of cyanide during this reaction is not clear and this interesting reaction was not pursued further due to the intricate hydrothermal condition. In our experiment we had not obtained the title product when sodium cyanide was added. We presume that CN ion is formed by the acid-catalyzed decomposition of isonicotinic acid.[1,11]

M(I)–M(I)(M = Cu, Ag, Au) interactions in reported complexes are generally ligand-supported, the M(I)–M(I) geometry is maintained by bridging or capping ligands. Ligand-unsupported M(I)–M(I) (M = Cu, Ag, Au) interactions are scarce and only a few examples of ligand-unsupported Cu(I)–Cu(I) interactions have been reported in the literature,[12] when there are d^{10}–d^{10} metal–metal interactions. The structural feature of complex **1** is different from those reported in the literature,[12] where both the ligand-supported and the ligand-unsupported M(I)–M(I) interactions exist simultaneously. Cu1(I)–Cu2(I) is ligand-supported with bridging $–CO_2$ from IN ion, but Cu2(I)–Cu3(I) is ligand-unsupported and both Cu2 and Cu3 are two-coordinated. The metal–ligand bond lengths of Cu2 and Cu3 are shorter and the ligand coordination on Cu2 and Cu3 is not linear, the bond lengths are 1.855(5) Å (Cu2–O2), 1.863(5) Å (Cu2–O4), 1.888(7) Å (Cu3–N2) and 1.820(7) Å (Cu3–CN or NC) and the angles are 170.1(8)° (NC?–CN?–Cu3) and 176.5(8)° (CN?–NC?–Cu1), respectively. Only a few examples[13,14] of two-coordinated copper(I) are reported, in which the copper(I) ions are coordinated by either oxygen or cyanide; 1D or 2D network coordination polymers were generally constructed. The structure of complex **1** is evidently different from those of the polymers reported. It is a 3-D network polymer with distortion cubic $Cu_{24}(IN)_8(CN)_3$ building unit, which is built up by two planes of $Cu_{12}(IN)_4$ (9 × 9 Å) building blocks and four planes of $Cu_9(IN)_2(CN)_2$ (8 × 11 Å) building blocks. The dihedral angle between the two planes is approximately 77.86°. Fig. 2 shows that the whole structure is a twofold interpenetrated 3-D network polymer. Unlike many other solids[15] with interpenetrating network, the extent of interpenetration in this complex fills all the available voids, so no small molecules or solvent molecules are encaged. The shortest distance inside the cavity formed by the molecular accumulation is about 4.5 Å).

In order to confirm its acentricity and to evaluate if it is a potential second-order NLO candidate compound, we have per-

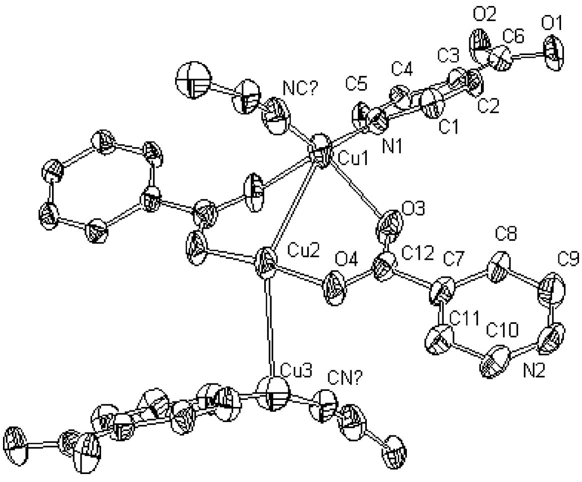

Fig. 1 The molecular structure of **1** showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 2.236(6), Cu(1)–O(3) 2.273(5), Cu(1)–N(1) 1.989(6), Cu(1)–N(C?) 1.872(9), Cu(2)–O(4) 1.863(5), Cu(2)–O(2) 1.855(5), Cu(3)–C(N?) 1.820(7), Cu(3)–N(2) 1.888(7),; Cu(3)–Cu(2)–Cu(1) 138.62(5), N(C?)–C(N?)–Cu(3) 170.1(8), C(N?)–N(C?)–Cu(1) 176.5(8).

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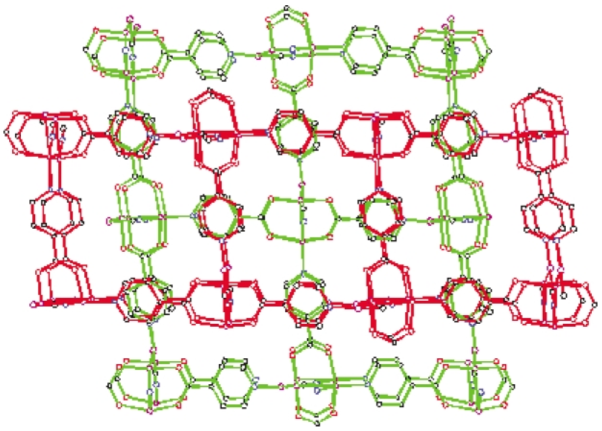

Fig. 2 View of the 3D twofold interpenetrating network structure of **1** along [010].

formed powder second harmonic generation (SHG) measurements[16] of complex **1** in a similar way as described by Kurtz at λ = 1064 nm. Qualitative experimental results show the powder SHG intensity of complex **1** is about that of KDP (potassium dihydrogen phosphate). This new solid is totally transparent in the visible region, and insoluble in common solvents. To our knowledge, this is the first example of the second-order NLO behavior of Cu(I). More significantly, tri- or multinuclear Cu(I) polymers with twofold interpenetrated 3-D network are readily obtainable by the hydrothermal assembly. The complex also exhibits remarkable thermal stability. TGA analyses show that it has an onset temperature for decomposition above 270 °C. The stability of the complex makes it a potential candidate for practical applications.

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Notes and references

† *Crystal data* for **1**: $C_{13}H_8Cu_3N_3O_4$, Orthorhombic. Space group. *Pca*2 (1). *a* = 13.7541(4), *b* = 7.2352(3), *c* = 14.7958(7) Å. *V* = 1472.38(10) Å^3, Z = 4. D_c = 2.079 g cm^{-3}. λ = 0.7107 Å, *F* (000) = 904 1590 reflections out of 1815 unique reflections measured at 293 K on a Siemens SMART/CCD diffractometer using the θ scan mode (2.75 < θ < 25.00°) afforded on convergence final *R*-factors of *R*1 = 0.0452 and *wR*2 = 0.0906 (208 parameters refined, *S* = 1.016 and $(\Delta/\delta^2)_{max}$ = 0.002). The structure was solved by direction methods and difference Fourier synthesis. Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were located by direct methods with geometrical calculation but their positions and thermal parameters were fixed during the structure refinement. The cyano group was crystallographically disordered. The positions of the N atom and the C atom of the cyano group were modelled with each position having an occupancy of 50% of each atom type. The temperature factors were then simultaneously refined. The crystallographic calculations were conducted using the SHELXL-97 programs. CCDC 230029. See http://www.rsc.org/suppdata/cc/b4/b401345j/ for crystallographic data in .cif or other electronic format.

‡ Elemental analysis (%) calcd for $C_{13}H_8Cu_3N_3O_4$: H 1.76, C 34.00, N 9.16; found: H 1.36, C 33.84, N 8.72%; IR data (KBr, cm^{-1}): 2123m, 1605s, 1547s, 1417m, 1383s, 1228w, 1055w, 924w, 864w, 845w, 771w, 704m, 573w.

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