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Synthesis and properties of a $Cu_4(SCN)_4$ cubane cluster-based coordination polymer with a diamond net

Shi-Bin Ren [a,b], Le Zhou [a], Jun Zhang [a], Cheng-Hui Li [a], Yi-Zhi Li [a], Hong-Bin Du [a,*], Xiao-Zeng You [a]

[a] *State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*
[b] *School of Pharmaceutical and Chemical Engineering, Taizhou University, Taizhou 317000, China*

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ABSTRACT

A triply-interpenetrating diamondoid coordination polymer $[Cu_4(SCN)_4(tpom)]\cdot 2H_2O$ (**1**, tpom = tetrakis(4-pyridyloxymethylene)methane) was prepared, which is built from an unprecedented pseudohalide cubane cluster $Cu_4(SCN)_4$ and tetrahedral tpom ligand. **1** exhibits high thermal stability and temperature-dependent photoluminescence behaviors resembling those of Cu_4Cl_4 complexes.

There has been considerable current interest in varieties of polynuclear complexes of transition metals with filled-shell d^{10} electronic configuration. These compounds generally possess long-lived excited states, leading to strong emissions that would allow for a better comprehension of fundamental phenomena and potential applications in sensors, light emitting diode devices, solar light harvesting and conversion [1]. Particularly interesting among these are the derivatives of Cu(I) that are often brightly luminescent even at RT. Cu(I) tends to form a variety of coordination compounds with halides ranging from zero-dimensional (0D) complexes to 3D frameworks with structural motifs such as rhomboid Cu_2X_2 dimers, cubane Cu_4X_4, and step and ladder-like $(CuX)_n$ chains (X = Cl, Br, I) [2–4]. Notably, these polyhedral Cu(I) halide clusters have been employed as building blocks for construction of novel 3D coordination polymers with intriguing structures and photoluminescent properties.

Thiocyanate (SCN^-) is a known pseudohalide, which also shows strong affinity to Cu(I) to form a number of cuprous thiocyanate complexes. In contrast with halides, however, thiocyanate is a highly ambidentate ligand, and exhibits theoretically as many as 13 coordination modes binding to metal atoms through either the nitrogen or the sulfur atom, or both (Figure S1 in the Supporting Information) [5]. As a result, there are a limited number of structural motifs known for Cu(SCN), most of which are polymeric, including rhomboid $Cu_2(SCN)_2$ dimers, 1D zig-zag chains, 2D sheets, and 3D networks as in α- and β-forms of CuSCN [6,7]. The thiocyanate analogues of the well-known Cu_4X_4 cubane clusters have not been reported so far, though its existence has been claimed in $[nBu_3PCuSCN]_4$ based on ^{13}C NMR and IR spectral data [8]. In fact, there is only one metal thiocyanate cubane cluster compound, i.e. $[(CH_3)_3PtSCN]_4$ [9], known to date [10]. We [11], among others [2–4,6,7], have been interested in coordination polymers formed by Cu(I) halides or Cu(I) thiocyanates. We herein report the synthesis of a new 3D microporous coordination polymer $[Cu_4(SCN)_4(tpom)]\cdot 2H_2O$ (tpom = tetrakis(4-pyridyloxymethylene)methane), **1**, which is, to the best of our knowledge, the first structurally characterized compound consisting of an unprecedented $Cu_4(SCN)_4$ cubane cluster.

Complex **1** was synthesized by the reaction of CuSCN, tpom and excess NH_4SCN in the mixed-solvent system of CH_3CN and H_2O under solvothermal conditions [12]. Attempts to prepare similar $Cu_4(SCN)_4$ cluster-based complexes as in **1** using pyridine (py), 4-hydropyridine and 4-cyanopyridine instead of tpom under similar conditions have so far met with failures. Complex **1** is stable in air and is insoluble in common solvents such as methanol, ethanol, acetone, acetonitrile, ether, DMF and water. The phase purity of complex **1** was confirmed by elemental analysis, IR and X-ray powder diffraction. FT-IR spectrum of **1** showed a strong peak at 2112 cm^{-1}, characteristic of the C≡N vibration from the thiocyanate. The $\nu(C{\equiv}N)$ vibration in **1** is higher than that of $Cu(SCN)_2(py)_2$ (bidentate bridge, 2074 cm^{-1}) but lower than that of β-CuSCN (tetradentate bridge, 2173 cm^{-1}), indicating the presence of the tridentate thiocyanate bridge $Cu{-}NCS{=}Cu_2$ [5,7].

X-ray single-crystal diffraction analysis [13] revealed that the structure of **1** resembles that of the recently reported $[Cu_4I_4(tpom)]\cdot H_2O$ [11b], and crystallizes in the tetragonal space group I–4. Complex **1** possesses a 3D neutral cluster-based open framework composed of the unprecedented $Cu_4(SCN)_4$ cubane cluster and

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* Corresponding author. Tel.: +86 25 83686581; fax: +86 25 83314502.
E-mail address: hbdu@nju.edu.cn (H.-B. Du).

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tetrahedral ligand tpom (Fig. 1). Both units have an exact S_4 internal symmetry. In the cubane $Cu_4(SCN)_4$ clusters, each Cu atom adopts a distorted tetrahedral coordination geometry through bonding to two S atoms from two thiocyanates and two N atoms from a tpom ligand and a thiocyanate, respectively. The Cu–S and Cu–N distances range 2.415(1)–2.508(1) and 1.964(5)–2.000(4) Å, respectively, in accordance with those of other CuSCN complexes [5,6]. The bond angles around Cu are within 102.4(1)–124.8(2)°, which confirms a distorted tetrahedral coordination geometry. Notably, the shortest diagonal Cu…Cu distance within the cubane cluster is 3.012(1) Å, longer than those of Cu_4I_4 complexes [2] but comparable to those of Cu_4Cl_4 clusters [14]. The bond valence sum calculations [15] for Cu (0.96) confirm that Cu is monovalent. It is noted that the thiocyanate in **1** acts as a tridentate bridge, and a set of four thiocyanates in parallel coordinates through both their μ_2-N and μ_3-S ends with four Cu atoms to form a cubane cluster. The Cu–N–CS angle is 149.2(4)°, much lower than those of other metal thiocyanates (between 160 and 180°). The Cu–S–CN angles vary from 96.7(2) to 97.4(2)°, which are within the normal range of 90–120°. The C—S and C—N bond distances are 1.642 (5) and 1.167(7) Å, respectively, similar to those of other metal thiocyanates [5].

The 3D framework of **1** is formed by coordination of each tetrahedral quadridentate ligand tpom *via* its N donor atoms to four respective $Cu_4(SCN)_4$ cubane clusters (Fig. 2). From the topological point of view, complex **1** possesses a sphalerite (ZnS) structure, an *AB* derivative of the diamond net (short vertex symbol 6^6) [16], with the tetrahedral $Cu_4(SCN)_4$ and quadridentate ligand tpom units as the *A* and *B* 4-connecting nodes, respectively. The structure is triply-interpenetrated, leading to elimination of almost all the free space in **1**. The rest solvent-accessible voids, in which lie disordered guest water molecules, only comprise 7.3% of the total crystal volume as calculated using PLATON [17] based on the crystal structure. The open channels in **1** are too small to allow adsorption for N_2 gas molecules, but just enough to let H_2 pass through (0.5 H_2 per unit cell at 77 K and 1 atm) as indicated by hysteresis between the H_2 adsorption and desorption isotherms (Figure S2 in the Supporting Information).

Thermogravimetric analysis of complex **1** showed that there was about 5.7% of weight loss below 250 °C (Figure S3 in the Supporting Information), corresponding to the release of the surface and occluded water molecules (calculated 3.7%). Above 300 °C, complex **1** began to lose its organic ligand (observed 41.4%, calculated 46.7%), followed by the decomposition and vaporization of the residue above 535 °C. The thermal stability of **1** was confirmed by X-ray powder diffraction (XRPD) analyses. The XRPD patterns of the synthesized samples in general match those calculated on the basis of the single-crystal structure in peak positions. The differences in reflection intensities between the calculated and experimental patterns are due to the variation in crystal orientation for the powder samples. The XRPD patterns of the samples heated at 150 and 250 °C in N_2 for 2 h, respectively, exhibit negligible changes in comparison with that of the pristine one (Figure S4 in the Supporting Information). However, **1** transformed into a black powder of Cu_2S upon heating at 300 °C in N_2 for 2 h. The results indicate that the structural skeleton of **1** remains stable up to 250 °C in nitrogen atmosphere.

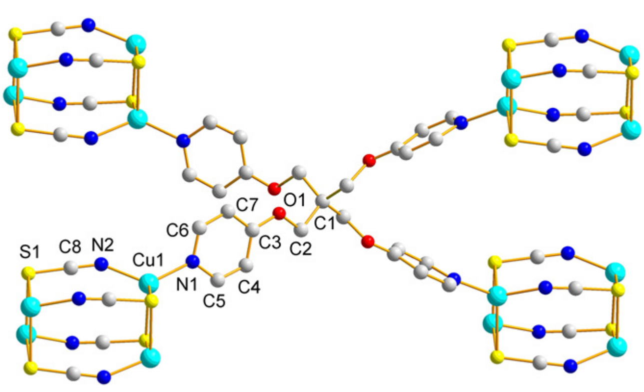

Fig. 1. Coordination environments of $Cu_4(SCN)_4$ cubane cluster and tetrahedral ligand tpom. The H atoms are omitted for clarity.

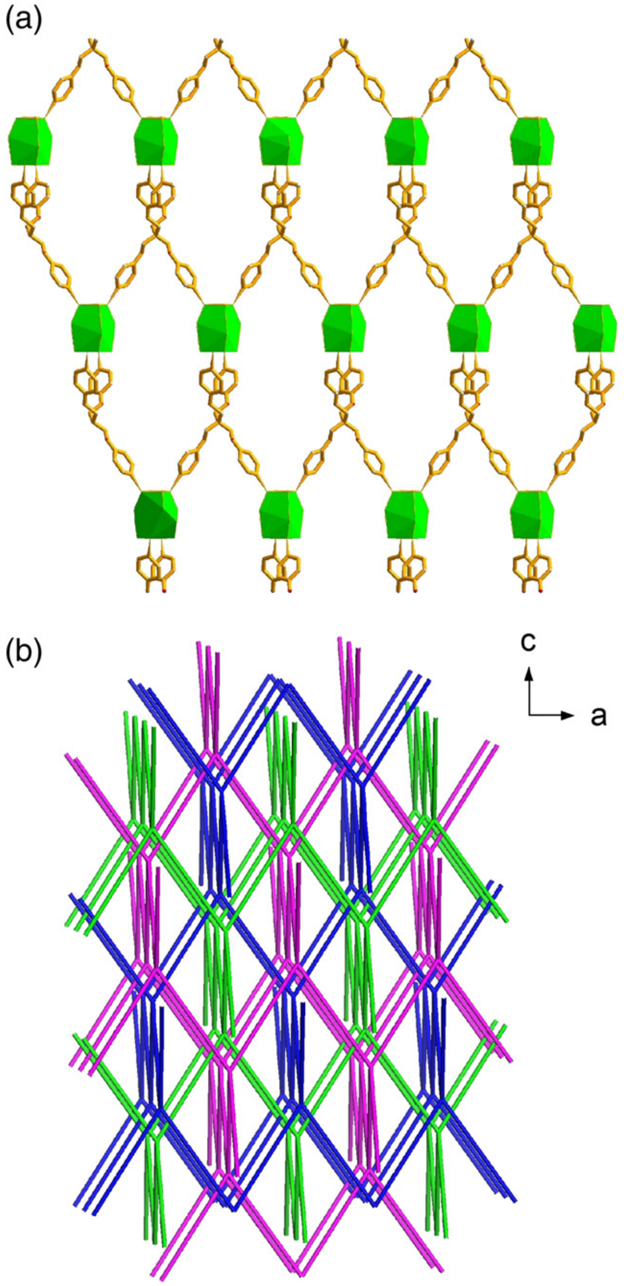

Fig. 2. Representations of (a) a single and (b) a triply-interpenetrated 6^6-***dia*** net of complex **1**. The H atoms and solvent molecules are omitted for clarity. Both $Cu_4(SCN)_4$ and tpom in (b) are represented as 4-connected nodes.

The UV–Visible diffuse-reflectance (DR) spectrum of **1** at RT shows an absorption onset at about 400 nm (Fig. 3), indicating that it is a wide-gap semiconductor with a band gap of 3.10 eV. Similar to its Cu_4X_4 analogues, complex **1** shows temperature-dependent emissive behaviors. Upon excitation at 77 K, **1** exhibits an intense, broad and asymmetric emission band centered at 470 nm. However, this emission is extremely weak at RT. In fact, there is no other measureable emission in the whole visible region at RT, unlike $[Cu_4I_4(tpom)]\cdot H_2O$ [11b] and other Cu_4I_4 complexes [1] that usually show a strong low energy emission around 600 nm and a weak higher

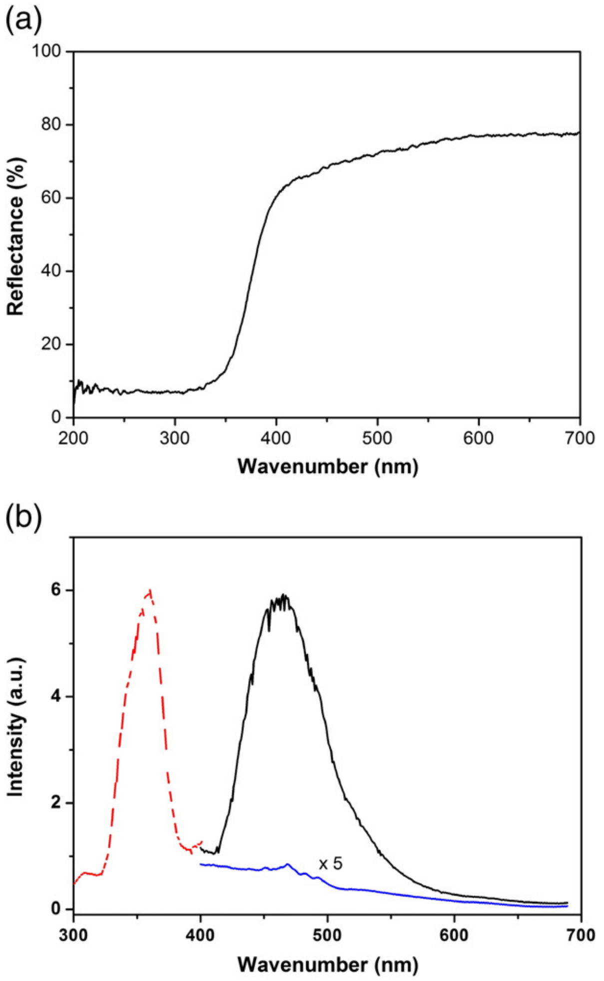

Fig. 3. (a) The solid-state UV–Vis diffuse reflectance spectrum at RT, and (b) excitation (dashed line) and emission spectra (solid line, excited at 375 nm) of **1** at 77 K (black) and RT (blue), respectively.

energy emission at *ca*. 460 nm, respectively. The low energy band of Cu_4I_4 cluster compounds has been attributed to a triplet "cluster-centered" (^{3}CC*) excited state of mixed halide-to-metal charge transfer (^{3}XMCT*) and "metal cluster centered" $d_{Cu} \rightarrow (s,p)_{Cu}$ transitions (^{3}MCC*), while the high energy emission band is assigned to a triplet state of halide to ligand charge transfer (^{3}XLCT) [1,18]. Thus, the 77 K emission band of **1** can be assigned to a ^{3}XLCT excited state in analogy to the previous assignment for $Cu_4X_4(py)_4$ (X = Cl) [1,18]. The Cu…Cu distance in **1** is longer than the sum of the van der Waals radii (2.80 Å), preventing observation of the ^{3}CC* emission band in the low energy region. The absence of emission bands at RT is probably due to quenching through the exciton transfer between the two separate π electronic systems ($Cu_4(SCN)_4(py)_4$ unit), similar to the Cu (I) iodide complexes containing *para*-substituted *trans*-stibazolic ligands [2b]. In those complexes, the extension of π-conjugation of the *trans*-stibazolic ligands leads to emission quenching when intermolecular π–π distances are shorter than 7 Å. A relatively close intermolecular π–π distance (6.06 Å) was indeed found in **1** by careful examination on the crystal structure.

In conclusion, we have synthesized a 3D cluster-based coordination polymer $[Cu_4(SCN)_4(tpom)]\cdot 2H_2O$ (tpom = tetrakis(4-pyridyloxymethylene)methane), **1**, based on the unprecedented pseudohalide cubane cluster $Cu_4(SCN)_4$ and tetrahedral quadridentate ligand tpom. **1** possesses a triply-interpenetrated diamond network with small open channels that just allow H_2 to pass through. Similar to its halide cubane cluster Cu_4Cl_4 analogues, **1** shows temperature-dependent luminescence behaviors, which upon excitation emits at RT a very weak but at 77 K a very strong blue light attributed to a ^{3}XLCT exited state. The weak Cu…Cu interactions in **1** result in no photoemission owing to the cluster-centered excited state that is often observed in various Cu_4I_4 complexes.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.01.024.

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[13] Crystal data for **1**: $C_{29}H_{28}Cu_4N_8O_6S_4$, Mw = 967.07. Tetragonal, space group I−4 (No. 82), a = 12.2839(14), c = 12.1996(14) Å, V = 1840.8(4) $Å^3$, Z = 2, $\rho_{calc} = 1.745\ g\ cm^{-1}$, $\mu = 2.559\ mm^{-1}$, $F_{000} = 972.0$, T = 291(2) K, $2\theta_{max} = 52°$, reflections collected/unique 1788/1705, $R_{int} = 0.0359$, $R_1 = 0.0412$, $wR_2 = 0.1084$, final GooF = 1.087. CCDC 761577.

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