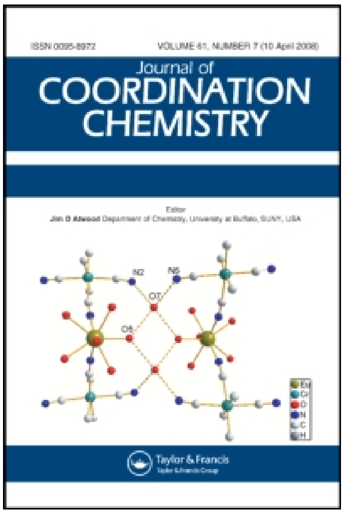

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Synthesis and crystal structure of a two-dimensional bi-layered supramolecular network compound $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$ ($C_7H_8N_4O$ = pyridine-3-carbaldehyde semicarbazone)

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A two-dimensional bi-layered supramolecular compound $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$ has been synthesized by the solvothermal method, and characterized via IR and CHN elemental analysis. The single crystal X-ray data of this compound reveal the complex to be dimeric as a result of terminal $-NH_2$ group of the semicarbazone moiety bridging, which is relatively rare. On this bi-copper(I) complex, another remarkably structural feature is that each Cu atom adopts an unsymmetrical T-shaped geometry comprised of three N atoms from three pyridine-3-carbaldehyde semicarbazone ligands. The molecules are linked into a two-dimensional bi-layered framework by intermolecular $N–H\cdots O$ hydrogen bonds.

Keywords: Crystal structure; Supramolecular structure; Pyridine-3-carbaldehyde Semicarbazone; Hydrothermal method

1. Introduction

Considerable efforts have been devoted to crystal engineering of supramolecular architectures assembled by means of coordination covalent bonding, hydrogen bonding, $\pi \rightarrow \pi$ interactions and other weak intermolecular interactions [1], because of their intriguing structural diversity [2, 3] and crystal packing motifs along with potential functions such as photoluminescence [3], magnetic [4] and nonlinear

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optical [5] properties. For obtaining supramolecular sheets, hydrogen bonding is one of the principal intermolecular forces for molecular aggregation and recognition in nature. By choosing versatile ligands with functional groups (for example, –COOH, –NH–, –C(O or S)NH_2, etc.), stable intermolecular hydrogen bonding can be formed, often thereby providing novel supramolecular architectures with new properties [6–8]. Semicarbazone (or thiosemcarbazone) ligands are a good candidate, because the hydrogen atoms attached to the amino nitrogen atoms of the semicarbazone or thiosemicarbazone moiety have the ability to form donor hydrogen bonds through which diverse supramolecular networks [9, 10] can be achieved. However, a semicarbazone or thiosemicarbazone moiety attached to the 3- or 4-position has received even less attention [11]. Herein the crystal structure of a two-dimensional bi-layered supramolecular network compound, $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$, is reported.

2. Experimental

$[Cu(CH_3CN)_4]ClO_4$ [12] was prepared by literature method and other reagents were used as received commercially without further purification. IR spectra were recorded on a Nicolet FT-IR Spectrophotometer with KBr pellets (range: 4000–400 cm^{-1}) and elemental analysis for C, H and N was carried on a Varlo ERBA1106EL analyzer.

2.1. *Synthesis of* $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$

The Schiff-base ligand pyridine-3-carbaldehyde semicarbazone (H-Pysc) was prepared according to the method described by Beraldo *et al.* [11]. Single crystals of the title complex suitable for X-ray crystallographic analysis were obtained by solvothermal reaction of $[Cu(CH_3CN)_4]ClO_4$ (0.2 mmol), H-Pysc (0.5 mmol), ethanol (2 mL) and water (0.5 mL). The reagents were placed in a thick pyrex tube (ca 20 cm long). The tube was cooled with liquid N_2 and the air was evacuated. The sealed tube was heated at 85°C for 3 d to yield yellow block-shaped crystals in about 61% yield (based on Cu atom). Anal. Found: C, 34.02; H, 3.32; N, 22.53. Calc for $C_{28}H_{32}Cl_2Cu_2N_{16}O_{12}$: C, 34.19; H, 3.26; N, 22.79%. IR (KBr pellets, cm^{-1}): 3304(vs), 3205(s), 3113(m), 1682(s), 1621(m), 1574(m), 1417(w), 1243(m), 1198(vs), 1089(vs), 1012(s), 602(m).

Safety note: The perchlorate salt {$[Cu(CH_3CN)_4]ClO_4$} is potentially explosive, only small amount of this material should be prepared and it should be handled with great caution.

2.2. *X-ray crystallography*

The diffraction data were collcted on a Siemens SMART CCD area detector diffractometer in the range $2.57 \leq \theta \leq 28.31°$ for $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$ at 293(2) K with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A total of 6189 reflections were collected, of which 4564 were unique. The structures were solved by direct methods (SHELXS-97) [13] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [14]. Data were corrected for absorption with SADABS [15]. All non-hydrogen atoms were located with successive difference Fourier syntheses and refine anisotropically, all H atoms were located in a difference map and refined with isotropic thermal parameters. The final difference density map showed

Table 1. Crystal data and structure refinement for $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$.

Identification code	$[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$
Empirical formula	$C_{14}H_{16}ClCuN_8O_6$
Formula weight	982.68
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.5444(6)
b	8.7190(7)
c	16.2409(13)
α	76.601(2)
β	84.352(2)
γ	68.560(1)
Volume (Å^3)	967.2(1)
Z	2
Calculated density (Mg m^{-3})	1.687
Absorption coefficient (mm^{-1})	1.319
$F(000)$	500
Crystal size (mm^3)	0.30 × 0.18 × 0.12
θ range for data collection (°)	2.57 to 28.31
Limiting indices	$-9 \le h \le 10$, $-11 \le k \le 10$, $-19 \le l \le 21$
Reflections collected/unique	6189/4564 [$R(\text{int}) = 0.0230$]
Completeness to theta = 28.31	94.9%
Absorption correction	Empirical
Max. and min. transmission	0.8577 and 0.6930
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4564/0/335
Goodness-of-fit on F^2	1.133
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0720$, $wR_2 = 0.1346$
R indices (all data)	$R_1 = 0.1081$, $wR_2 = 0.1494$
Largest difference peak and hole $\Delta\rho$ (e Å^{-3})	0.511 and −0.432

Table 2. Selected bond lengths (Å) and angles (°) for $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$.

Cu1–N1	1.902(3)	Cu1–N5	1.901(4)	Cu1–N4^A	2.498(4)
N1–Cu1–N5	161.86(15)	N1–Cu1–N4^A	97.81(15)		
N5–Cu1–N4^A	99.97(14)				

Symmetry code, A: $2-x$, $2-y$, $-z$.

a maximum peak and hole of 0.511, −0.432 e Å^{-3} for $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$. The crystal data and details of crystal structure determinations are summarized in table 1 and selected bond lengths and angles are listed in table 2.

3. Results and discussion

The crystal structure of this compound consists of dimeric units of $[Cu_2(C_7H_8N_4O)_4]^{2+}$ cations and uncoordinated perchlorate counter-anions (figure 1). The $[Cu_2(C_7H_8N_4O)_4]^{2+}$ cation can be considered as a dimer constructed of two three-coordinated copper units bridged by the terminal $-NH_2$ group of the semicarbazone moiety, leading to a centrosymmetric metallomacrocycle with

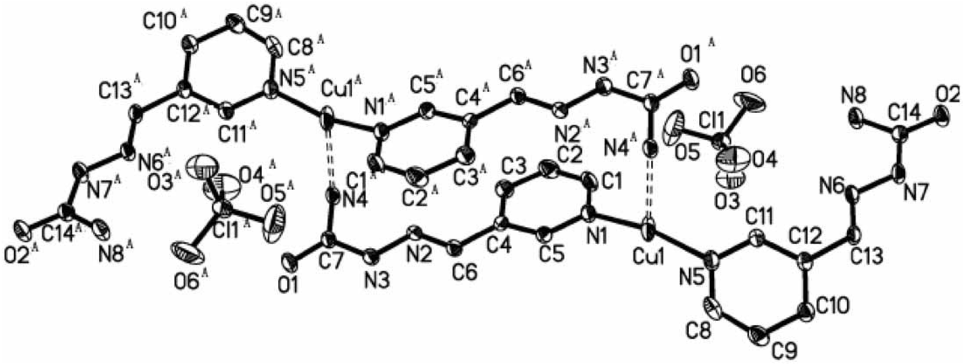

Figure 1. ORTEP drawing of $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$ with the atom labeling scheme (30% probability thermal ellipsoids; Symmetry code, A: $2-x$, $2-y$, $-z$).

Table 3. Hydrogen bonds in the crystal structure of $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$.

D–H···A	D···H (Å)	H···A (Å)	D···A (Å)	∠DHA (°)	Sym. trans.
N7–H7^A···O1	0.75(4)	2.25(5)	2.989(5)	173(4)	$-1+x$, $-1+y$, $1+z$
N4–H4^A···O2	0.79(5)	2.03(5)	2.820(5)	177(4)	$1+x$, $1+y$, $-1+z$
N8–H8^B···O2	0.83(5)	2.11(5)	2.925(6)	168(5)	$1-x$, $-y$, $1-z$
N3–H3^A···O3	0.72(5)	2.47(6)	3.150(6)	157(5)	$1-x$, $2-y$, $-z$
N4–H4^B···O6	0.76(5)	2.37(4)	2.884(6)	127(4)	$1-x$, $2-y$, $-z$
N4–H4^B···N2	0.76(5)	2.28(5)	2.624(5)	108(4)	
N8–H8^A···N6	0.76(5)	2.27(5)	2.674(6)	114(4)	

a chair-like configuration. Each copper is coordinated by three N atoms from three pyridine-3-carbaldehyde semicarbazone ligands, forming an irregular T-shaped geometry. Two Cu–N(pyridine) distances are 1.902(3) and 1.901(4) Å for Cu1–N1 and Cu1–N5, respectively, comparable to those reported for $[Cu(L_1–Pr)][BF_4]$ {Cu–N1, 1.912(5) Å; Cu–N3, 1.910(5) Å} [16], $Cu(pze)BF_4${Cu–N1, 1.877(5) Å; Cu–N2, 1.874(5) Å} [17], $Cu^I_2(ISOID)(Etpy)_2(pz)$ {Cu1–N1, 1.901(3) Å} [18] and $[Cu_2(napy)_2(Me_2CO)](PF_6)_2$ {Cu2–N4, 1.920(9) Å} [19]. The Cu1–N4^A distance is rather long [2.498(4) Å] and could be considered as a 'weak' bond. This phenomenon also appears in other T-shaped Cu(I) complexes [19, 20] with the middle bond distance longer than the other terminal bond distances. The N1–Cu1–N5 angle (161.86(15)°) is larger than the other angles {97.81(15)° for N1–Cu1–N4^A and 99.97(14)° for N5–Cu1–N4^A}, compared with the corresponding angles in the structural analogue, $[Cu_2(napy)_2(Me_2CO)](PF_6)_2$ [19]. The closest Cu···O6 {O6 atom at (x, $1+y$, z)} distance is 2.951(6) Å and is longer than the sum of Van der Waals' radii (Cu–O, 2.900 Å) [21], showing that the perchlorate counterions are uncoordinated. The coordinated pyridine-3-carbaldehyde semicarbazone may be considered as quasi-planar, the angle between the least-squares planes through the pyridine ring and the semicarbazone moiety is 13.5(3)°, similar to the angle observed for H_3FoPyS [11] (13.01°). The coordination mode of semicarbazone moiety is significantly different from other semicarbazones, which are bidentate coordinating to the metal ion by the carbonylic oxygen atom and azomethine nitrogen atom in $[Cu(H_2daps)(H_2O)_2$ [22], $[Cu(SALSC)Cl]\cdot 2H_2O$ [23] and $[Cu(HBnz_2)Cl]\cdot H_2O$ [24], and is relatively rare.

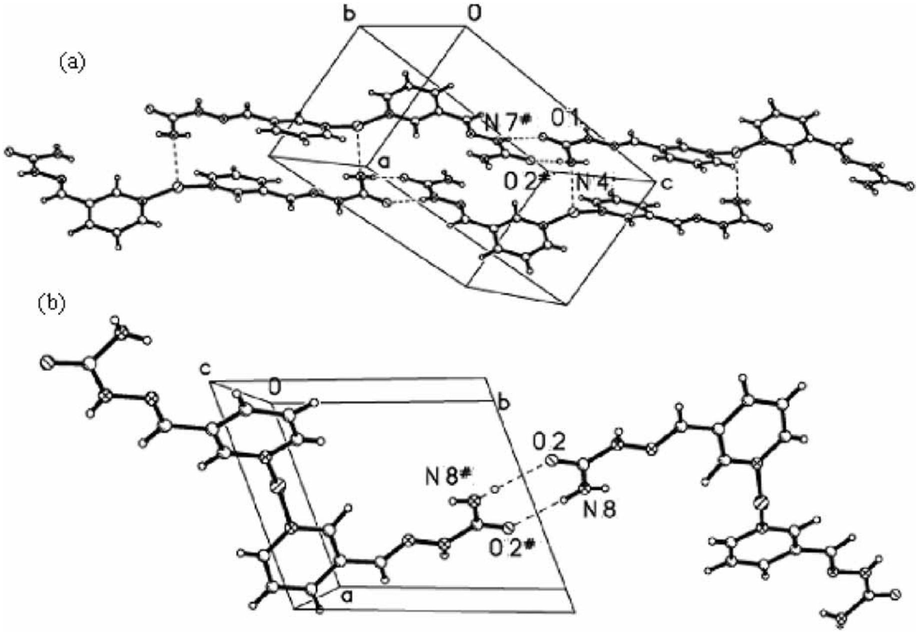

Figure 2. Part of the crystal structure of $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$, (a) showing the formation of a bi-chain along $[11\bar{1}]$ {Atoms marked with a hash (#) is at the symmetry positions $(1+x, 1+y, -1+z)$} and (b) showing the formation of a chain along [010] {Atoms marked with a hash (#) is at the symmetry positions $(1-x, -y, 1-z)$}.

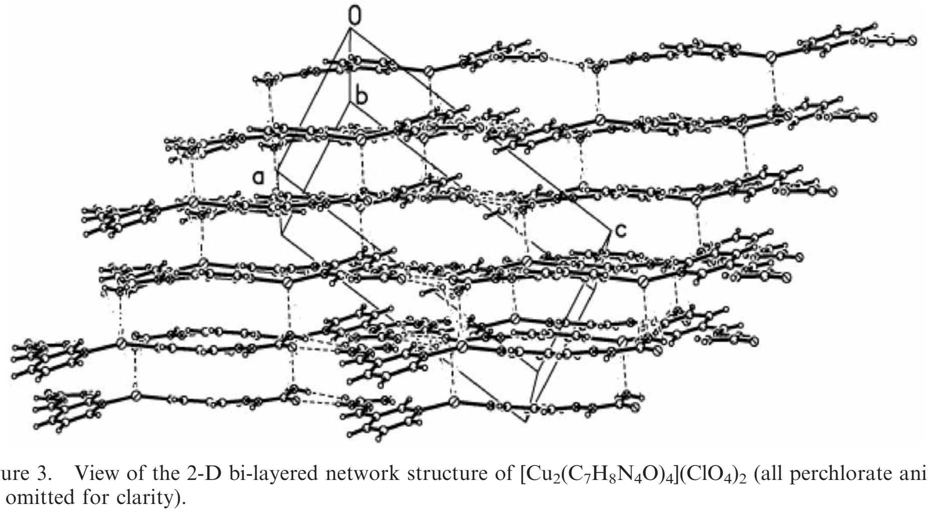

Figure 3. View of the 2-D bi-layered network structure of $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$ (all perchlorate anions are omitted for clarity).

The dimeric units of $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$ are fully ordered, a pair of N7–$H7^A \cdots$O1 hydrogen bonds (see table 3) reinforces another pair of N4–$H4^A \cdots$O2 hydrogen bonds in linking together the two dimeric units, so forming two $R_2^2(8)$ motifs [25], which are further interconnected into a one-dimensional bi-chain running parallel to the $[11\bar{1}]$ direction (figure 2a). In addition, N8 in the molecules at (x, y, z) and $(1-x, -y, 1-z)$ acts as a hydrogen-bond donor to O2 in the molecules at $(1-x, -y, 1-z)$ and (x, y, z), respectively, so giving rise to a similar $R_2^2(8)$ motif, which are further interconnected into a one-dimensional chain running parallel to the [010] direction (figure 2b). The combination of the $[11\bar{1}]$ and [010] chains then generates a 2-D bi-layered network within the (101) plane (figure 3). The O3 and O6 atoms of a uncoordinated perchlorate counter-anion accept two hydrogen bonds in intermolecular interactions with the N3–H3^{A} and N4–H4^{B} groups of a neighboring semicarbazone moiety, respectively, which fix perchlorate anions within the 2-D bi-layered network.

Supplementary material

Crystallographic data for the structure of $[Cu_2(C_7H_8N_4O)_4](ClO_4)_2$ has been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 288269. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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