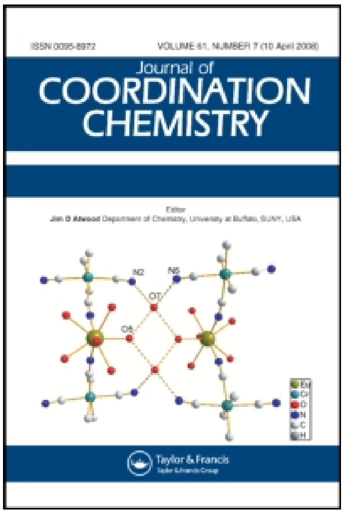

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Two 2-D copper(II) azido compounds: <i>catena</i>-poly[<i>di</i>-$\mu_{1,1}$-azido,<i>di</i>-$\mu_{N,O}$-(quinolinecarboxylato)(aqua)copper(II)] and 1-D <i>catena</i>-poly[<i>di</i>-$\mu_{N,N'}$-(quinoxaline)copper(II)nitrate]

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Two 2-D copper(II) azido compounds: *catena*-poly[*di*-$\mu_{1,1}$-azido,*di*-$\mu_{N,O}$-(quinolinecarboxylato)(aqua)copper(II)] and 1-D *catena*-poly[*di*-$\mu_{N,N'}$-(quinoxaline)copper(II)nitrate]

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We synthesized three copper(II) complexes with two structurally related polydentate ligands, quinoline-4-carboxylic acid (quCOOH) and quinoxaline (qux). The structures of these complexes were determined using X-ray single crystal crystallography. Complex **1**, $[Cu(quCOO)(N_3)(H_2O)]_n$, has a 2-D polymeric structure through di-$\mu_{1,1}$ azido groups forming (Cu_2N_2) dimeric units and di-$\mu_{N,O}$ quinoline carboxylate bridging the binuclear copper units. $[Cu(quCOO)(N_3)(H_2O)]_n \cdot 0.87MeOH$, (**2**), has the same structure as **1** in addition to MeOH molecules separating the 2-D sheets of $[Cu(quCOO)(N_3)(H_2O)]_n$. $[Cu(qux)(NO_3)_2]_n$, (**3**), has no coordinated azido groups, but the quinoxaline is a bidentate bridging ligand giving a 1-D chain, while the $\mu_{O,O'}$ chelating nitrato groups stabilize the chain structure by forming a square planar coordination sphere around copper. IR and UV–Vis spectra of the complexes are in agreement with the crystal structures.

Keywords: Copper(II); Azido compounds; Quinoline-4-carboxylate; Quinoxaline

1. Introduction

One of our research interests has been the synthesis and solid state characterization of transition metal azido compounds with both pyrazine and quinoline derivatives [1]. Cu(II) is stereochemically flexible and forms a variety of distorted stereochemistries with different ligands [2]. Quinoline carboxylates have attracted great attention because of their interesting structural features; bearing both neutral and anionic functional groups, such ligands bind to Cu(II) metal centers producing coordination frameworks with more empty space available for entrapping guest molecules than ionic frameworks [3]. Quinoxaline can also be a bidentate ligand through its pyrazine ring, forming 1-D chain structures [1b]. Pseudo halides (e.g. N_3^-; NCS^-; NCO^-) can bridge transition metal ions in many different ways [4]; azide has received intense attention as a small change in the co-ligands can lead to an astonishing variation in the structure and dimensionality of the resulting compounds [5]. Azides bridge two ionic metal centers

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either in an (end-on, $\mu_{1,1}$-N_3, EO) fashion or (end-to-end, $\mu_{1,3}$-N_3, EE) fashion (see scheme 1), depending on the steric and electronic requirements of the co-ligands present in the compound [6]. Recently, a number of azido Cu(II) compounds has been isolated and characterized in the EE bonding mode, whereas only a few compounds have been observed with EO bonding [7].

Herein we report the synthesis, X-ray crystal structures, IR spectra, elemental analyses, and electronic spectra of two new 2-D grid-like (μ-$_{1,1}$-N_3) bridged Cu(II) compounds with quinoline-4-carboxylate ligand, as well as a 1-D chain Cu(II) nitrate compound with quinoxaline (see scheme 2).

2. Experimental

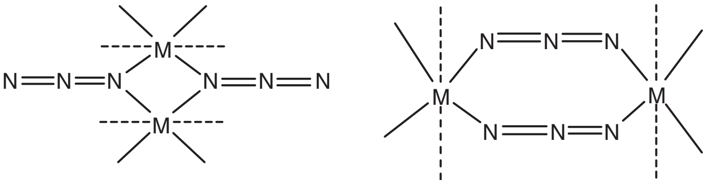
2.1. *Materials and instrumentation*

All chemicals and solvents were of analytical grade and used as received without further purification. All preparations and manipulations were performed under aerobic conditions. Infrared spectra were recorded in a Bruker IFS-125 model FT-IR spectrophotometer as KBr pellets [8]. C, H and N analyses were carried out using a Perkin–Elmer analyzer and metal analyses by complexometric titration [9] in pyridine.

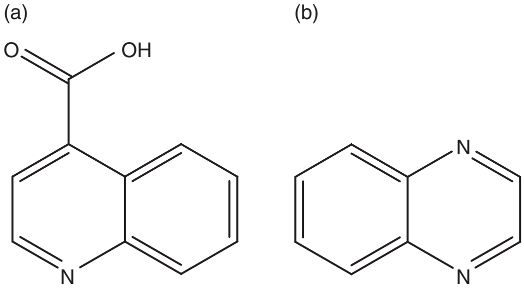
2.2. *Synthesis*

Caution: Metal azide compounds are potentially explosive and only a small amount of material should be prepared and handled with care.

2.2.1. Synthesis of [Cu(quCOO)(N_3)(H_2O)]$_n$, (1). To an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2 mmol) in 15 cm^3, quinoline-4-carboxylic acid, $C_{10}H_7NO_2$



Scheme 1. Most common bridging modes for azides illustrated by double bridged end-on, $\mu_{1,1}$-N_3, EO (left) and double bridged end-to-end, $\mu_{1,3}$-N_3, EE (right). M is commonly four, five or six coordinate.



Scheme 2. Ligands: (a) quinoline-4-carboxylic acid (quCOO); (b) quinoxaline (qux).

(0.35 g, 2 mmol) in 10 cm^3 1 : 2 ethanol/water mixture was added. Further, NaN_3 (0.65 g, 10 mmol) aqueous solution was added dropwise with continuous stirring. The clear green solution was allowed to stand at room temperature for a couple of weeks. Deep green crystals of **1** suitable for X-ray diffraction were collected and dried in air with a yield of ~60% with respect to the ligand. Analytical data: Calcd C, 40.89; H, 2.05; N, 19.07; Cu, 21.63. Found: C, 41.06; H, 2.21; N, 20.63; Cu, 20.69%. IR, KBr (cm^{-1}) (v, very; s, strong; m, medium; w, weak; br, broad): 3361 br, 2975 w, 2924 w, 2076 vs, 1612 vs, 1585 m, 1567 m, 1513 s, 1459 m, 1406 s, 1364 vs, 1296 vs, 1209 m, 1155 m, 1093 w, 1043 w, 1016 w, 879 m, 809 s, 790 m, 774 m, 752 m, 699 w, 664 s, 485 m, 441 m, 409 m, 342 m, 294 m, 270 m, 236 m.

2.2.2. Synthesis of $[Cu(quCOO)(N_3)(H_2O)]_n \cdot 0.87MeOH$, (2). To a methanolic solution (20 cm^3) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2.0 mmol), quinoline-4-COOH, $C_{10}H_7NO_2$ (0.69 g, 4 mmol) in 15 cm^3 1 : 2 methanol/water mixture was added. Further, NaN_3 (0.65 g, 10 mmol) aqueous solution was added dropwise with continuous stirring. The clear mixture was allowed to stand in a refrigerator for several days. Deep green crystals suitable for X-ray measurement were collected and dried in air, giving a yield of ~60% with respect to the metal. Analytical data: Calcd C, 41.02; H, 2.56; N, 17.88; Cu, 20.01. Found: C, 41.16; H, 2.15; N, 17.60; Cu, 19.89%. IR, KBr (cm^{-1}) (v, very; s, strong; m, medium; w, weak; br, broad): 3352 br, 2936 w, 2824 w, 2593 w, 2310 w, 2074 vs, 1839 w, 1743 w, 1692 w, 1610 vs, 1583 m, 1566 m, 1511 s, 1483 w, 1459 m, 1403 s, 1362 vs, 1292 vs, 1208 m, 1155 m, 1112 w, 1091 w, 1030 w, 1015 w, 880 m, 808 s, 789 m, 775 m, 751 m, 697 w, 664 s, 575 br, 485 m, 440 m, 408 m, 342 m, 293 m, 279 m, 233 m.

2.2.3. Synthesis of $[Cu(qux)(NO_3)]_n$, (3). An ethanolic solution of quinoxaline (0.26 g, 2 mmol), 15 cm^3 was added to an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2 mmol), 15 cm^3, causing immediate turbidity. The solution was subsequently heated and filtered, and to the filtrate an aqueous solution of NaN_3 (0.65 g, 10 mmol) was added dropwise with continuous stirring. The clear dark green solution was allowed to stand at room temperature for a couple of weeks. Black crystals of **3** suitable for X-ray diffraction were collected and dried in air in ~70% yield with respect to the ligand. Analytical data: Calcd C, 30.24; H, 1.90; N, 17.63; Cu, 19.99. Found: C, 31.09; H, 2.30; N, 18.69; Cu, 19.53%. IR, KBr (cm^{-1}) (v, very; s, strong; m, medium; w, weak; br, broad): 3437 br, 3062 br, 2923 w, 2487 w, 1861 w, 1766 w, 1554 w, 1501 s, 1467 w, 1449 w, 1383 vs, 1290 s, 1210 s, 1142 s, 1056 m, 1023 w, 1007 w, 871 w, 825 w, 800 w, 747 m, 593 br, 528 w, 411 m, 364 w, 342 m, 316 w, 293 m, 269 m, 233 s.

2.3. *X-ray crystallography*

All diffraction data were collected using a Siemens SMART CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). The crystals were cooled to 173(2) K by a flow of nitrogen gas using the LT-2A device. Full sphere of reciprocal lattices was scanned by 0.3° steps in ω with a crystal-to-detector distance of 3.97 cm. Preliminary orientation matrices were obtained from the first frames using SMART. The collected frames were integrated using the preliminary orientation matrices which were updated every 100 frames. Final cell parameters were obtained by refinement on the positions of reflections with $I > 10\sigma(I)$ after integration of all the frames using

SAINT [10]. The data were empirically corrected for absorption and other effects using SADABS [11]. The structures were solved by direct methods and refined by full-matrix least squares on all F^2 data using SHELXTL [12]. Non-H atoms were refined anisotropically, while hydrogen atoms were refined isotropically with use of geometrical restraints. Relevant crystallographic and refinement data are summarized in table 1. Molecular graphics were prepared using Diamond [13].

3. Results and discussion

Reactions between Mn(II) or Cd(II) nitrates and quinoline-4-carboxylic acid in the presence of sodium azide leads to formation of 1-D coordination polymers with formula $[M(quCOO)_2(H_2O)]_n$ [1a, 3a, 14], where the azide ion was not incorporated in the compound. Here we present a similar reaction with Cu(II) nitrates which produces two azido quinoline-4-carboxylato complexes $[Cu(quCOO)(N_3)(H_2O)]_n$ (**1**) and $[Cu(quCOO)(N_3)(H_2O)]_n \cdot 0.87MeOH$ (**2**), indicating a certain selectivity of the copper ions towards the azide ion in presence of quinoline-4-carboxylic acid. The potentially bridging *N,N′*-quinoxaline ligand forms very few complexes with Co(II), Cu(I), Cu(II), Cd(II) and Ag(I) [15], and here we present a 1-D-$[Cu(qux)(NO_3)_2]_n$ (**3**) not incorporating the azide ligand, analogous to the Mn(II) and Cd(II) compounds mentioned above.

3.1. *IR spectra*

The room temperature IR spectra of the crystalline compounds $[Cu(quCOO)(N_3)(H_2O)]_n$ (**1**) and $[Cu(quCOO)(N_3)(H_2O)]_n \cdot 0.87MeOH$ (**2**) as KBr pellets exhibit very strong bands at 2076, 1364, and 1296 cm^{-1} for **1** and 2074, 1362 and 1292 cm^{-1} for **2**. These strong bands are assigned to ν_{as} (N_3^-) and ν_s (N_3^-) stretching vibrations, respectively, indicating the presence of terminal EO bridging azides [5]. The expected bands of the ν_s (–COO^-) and ν_{as} (–COO^-) around 1710–1720 and 1640–1660 cm^{-1} for the free acid are absent in both IR spectra of **1** and **2**, instead, strong bands around 1612, 1567 and 1406 cm^{-1} for **1** and 1610, 1566 and 1403 cm^{-1} for **2** indicate that the carboxylato anions are coordinated to Cu(II) [1]. In the high energy region, **1** and **2** exhibit strong broad bands around 3361 and 3352 cm^{-1}, respectively, which correspond to the water molecules coordinated to Cu(II).

For **3**, no bands were detected around 2000–2100 cm^{-1}, indicating the absence of azide. Very strong bands at 1501 and 1383 cm^{-1} correspond to the ν_{as} (NO_3^-) and ν_s (NO_3^-), respectively, indicating the presence of monodentate (not bridging) nitrate. Other bands at 1290–411 cm^{-1} represent the quinoxaline moiety shifted to a bit higher position representing coordination through both ring nitrogens. Medium to strong bands in the far IR region can be attributed to M-L vibrations [16].

3.2. *Structures*

3.2.1. $[Cu(quCOO)(N_3)(H_2O)]_n$, (1). The atom numbering and packing diagram of **1** are shown in figures 1 and 2, respectively. The crystal was a racemic twin and was

Table 1. Crystal data and structure refinement for **1**, **2** and **3**.

	1	**2**	**3**
Empirical formula	$C_{10}H_8CuN_4O_3$	$C_{10.75}H_8CuN_4O_{3.75}$	$C_8H_6CuN_4O_6$
Formula weight	295.75	314.74	317.71
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$Cmc2_1$	$Cmc2_1$	$C2/m$
Unit cell dimensions (Å, °)			
a	18.1044(1)	17.2620(2)	13.4100(2)
b	12.8473(1)	13.5822(2)	6.8184(1)
c	11.0620(2)	11.2426(2)	12.5952(2)
β	–	–	114.722(1)°
V (Å^3)	2572.94(5)	2635.89(7)	1046.09(3)
Z	8	8	4
D_{Calcd} (mg m^{-3})	1.527	1.586	2.017
Absorption coefficient (mm^{-1})	1.703	1.672	2.122
$F(000)$	1176	1260	636
Crystal size (mm^3)	0.10 × 0.08 × 0.02	0.12 × 0.12 × 0.08	0.24 × 0.10 × 0.02
Theta range for data collection	1.94 to 25.05°	1.91 to 28.37°	3.06 to 33.01°
Index ranges	$-21 \leq h \leq 21$, $-15 \leq k \leq 15$, $-13 \leq l \leq 13$	$-23 \leq h \leq 23$, $-18 \leq k \leq 18$, $-14 <= l <= 15$	$-20 \leq h \leq 20$, $-10 \leq k \leq 10$, $-18 \leq l \leq 18$
Reflections collected	13595	17845	8671
Independent reflections	2369 [R(int) = 0.0790]	3392 [R(int) = 0.0697]	2010 [R(int) = 0.0414]
Completeness to $\theta = 25.05°$	99.9%	99.9%	94.7%
Absorption correction	Multiscan	Multiscan	Multiscan
Max. and min. transmission	0.967 and 0.741	0.878 and 0.825	0.959 and 0.687
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2369/13/175	3392/13/192	2010/0/103
Goodness-of-fit on F^2	1.042	1.028	1.057
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0513$, $wR_2 = 0.1309$	$R_1 = 0.0431$, $wR_2 = 0.0950$	$R_1 = 0.0330$, $wR_2 = 0.0899$
R indices (all data)	$R_1 = 0.0712$, $wR_2 = 0.1433$	$R_1 = 0.0644$, $wR_2 = 0.1060$	$R_1 = 0.0402$, $wR_2 = 0.0953$
Absolute structure parameter	0.56(4)	0.024(19)	–
Extinction coefficient	0.0016(3)	–	–
Largest diff. peak and hole (e Å^{-3})	0.985 and −0.373	0.692 and −0.354	1.514 and −0.904

refined as such, giving twin volume ratios as 0.56(1) : 0.44(1). The Flack parameter 0.56(4) is thus equivalent with BASF parameter in this case. Both azides lie on a crystallographic mirror plane. Hydrogen atoms belonging to water, O3, were not resolved. Selected bond distances and angles are listed in table 2. The Cu(II) is penta-coordinate with two N,O-bidentate quinoline-4-carboxylato anions, two bridging (EO) $\mu_{1,1}$-azido anions in the equatorial plane and an apical aqua forming a distorted square pyramidal geometry as shown in figure 2. The bridging di-EO azido groups form (Cu_2N_2) units which are further bridged *via* bidentate N,O-quinoline-4-caboxylato anions in a *cis*-position forming a (4,4)-2-D square grid structure. In the Cu_2N_2 units, the Cu–N distances are 1.990(5) and 2.004(5) Å and Cu–N–Cu bond angles are 101.3(3)

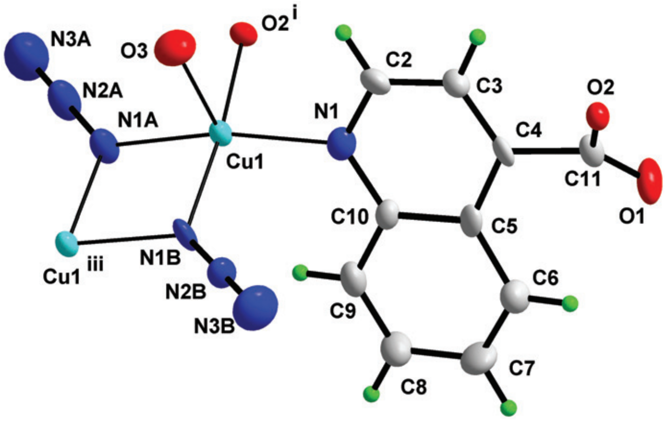


Figure 1. Numbering scheme for **1**. Atomic displacement ellipsoids drawn at 30% probability level.

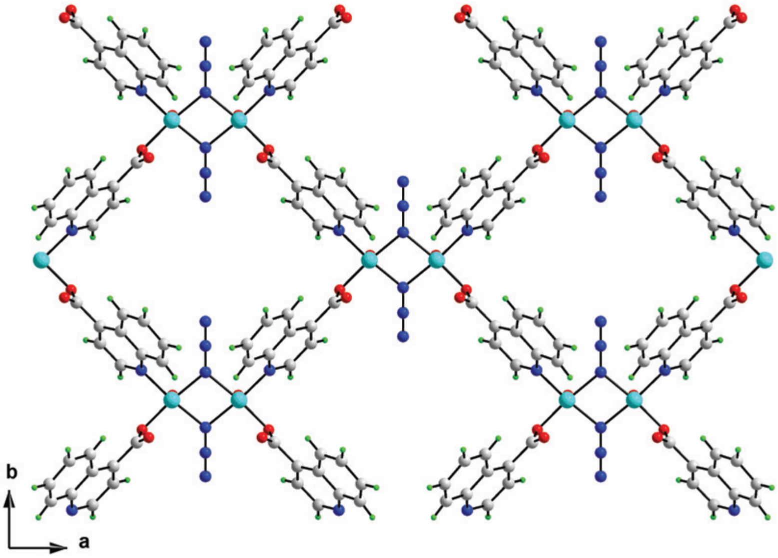


Figure 2. Packing diagram in (a,b)-plane for **1**.

and 100.3(3)°. The asymmetric azido groups have N1–N2 and N2–N3 bond distances 1.187(12), 1.213(10), and 1.116(14), 1.117(12) Å, respectively, which are all in the normal range for di-EO bridging Cu-azido complexes [4a, 6, 20]. The negatively charged oxygen and the ring nitrogen of quinoline-4-carboxylate anions coordinate to copper atom at bond distances 1.939(4) and 2.012(6) Å, respectively, close to those published, 1.937(3) and 1.999(3) Å for the non azido $[Cu(quCOO)_2]_n$ complex [4a]. The apical Cu-O(H_2O). bond distance is 2.341(6) Å. The copper atoms in the distorted square pyramidal structure are out of the basal plane by 0.085(6) Å toward O3. The two basal planes intersect at the N1A-N1B line with a dihedral angle of 3.72° and Cu–Cu separation = 3.077(1) Å. DFT calculations by Ruiz *et al.* indicate that end-on azido bridges have a minimum energy for Cu–N–Cu bond angle equal to 100° in copper(II) complexes [21], and the values for **1**, 101.3(3) and 100.3(3)°, are very close to this ideal condition. The short distance between O3 water and O1 [symmetry code: $-x+1/2$, $-y+1/2$, $z-1/2$] of 2.747(9) Å indicate the existence of a strong hydrogen bond, despite that these hydrogens cannot be located. This results in a six-connected pcu-net if we count the $Cu_2(N_3)_2$ unit as one node.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

$[Cu(quCOO)(N_3)(H_2O)]_n$, (**1**)		$[Cu(quCOO)(N_3)(H_2O)]_n \cdot 0.87$ MeOH, (**2**)	
Cu1–O2^{i}	1.939(4)	Cu1–O2^{i}	1.929(2)
Cu1–N1A	1.990(5)	Cu1–N1A	1.987(3)
Cu1–N1B	2.004(5)	Cu1–N1B	1.998(3)
Cu1–N1	2.012(6)	Cu1–N1	1.994(3)
Cu1–O3	2.341(6)	Cu1–O3	2.329(3)
O1–C11	1.233(9)	O1–C11	1.229(5)
O2–C11	1.258(9)	O2–C11	1.283(5)
O2–Cu1^{ii}	1.939(4)	O2–Cu1^{ii}	1.929(2)
N1A–N2A	1.187(12)	N1A–N2A	1.208(6)
N2A–N3A	1.116(14)	N2A–N3A	1.132(7)
N1B–N2B	1.213(10)	N1B–N2B	1.205(6)
N2B–N3B	1.117(12)	N2B–N3B	1.123(7)
O2^{i}–Cu1–N1A	95.3(2)	O2^{i}–Cu1–N1A	95.48(11)
O2^{i}–Cu1–N1B	174.3(2)	O2^{i}–Cu1–N1B	173.93(12)
N1A–Cu1–N1B	79.1(2)	N1B–Cu1–N1A	78.62(13)
O2^{i}–Cu1–N1	90.8(2)	O2^{i}–Cu1–N1	93.26(12)
N1A–Cu1–N1	168.1(4)	N1B–Cu1–N1	92.80(13)
N1B–Cu1–N1	94.8(2)	N1A–Cu1–N1	163.1(2)
O2^{i}–Cu1–O3	88.5(2)	O2^{i}–Cu1–O3	88.20(13)
N1A–Cu1–O3	90.4(5)	N1B–Cu1–O3	90.5(2)
N1B–Cu1–O3	90.6(4)	N1A–Cu1–O3	91.2(2)
N1–Cu1–O3	100.0(2)	N1–Cu1–O3	103.45(13)
N2A–N1A–Cu1	128.9(3)	N2A–N1A–Cu1^{iii}	127.7(2)
Cu1–N1A–Cu1^{iii}	101.3(3)	Cu1^{iii}–N1A–Cu1	101.51(18)
N3A–N2A–N1A	179.2(17)	N3A–N2A–N1A	179.3(12)
N2B–N1B–Cu1	129.5(2)	N2B–N1B–Cu1^{iii}	129.47(10)
Cu1–N1B–Cu1^{iii}	100.3(3)	Cu1^{iii}–N1B–Cu1	100.79(18)
N3B–N2B–N1B	179.8(17)	N3B–N2B–N1B	179.6(10)

Symmetry transformations used to generate equivalent atoms: For **1**: (i) $-x+1/2$, $y-1/2$, z; (ii) $-x+1/2$, $y+1/2$, z; (iii) $-x$, y, z; For **2**: (i) $-x+3/2$, $y+1/2$, z; (ii) $-x+3/2$, $y-1/2$, z; (iii) $-x+2$, y, z.

3.2.2. $[Cu(quCOO)(N_3)(H_2O)]_n \cdot 0.87$ MeOH, (2). The atom numbering scheme of **2** is shown in figure 3. Selected bond distances and angles are listed in table 2. Compound **2** has the same structure as **1**, with methanol between the 2-D sheets of $[Cu(quCOO)(N_3)(H_2O)]_n$ as shown in figure 4. The methanol is partially occupied with occupancy 0.868(13). In contrast to **1**, however, these crystals did not grow as twins, and therefore the absolute structure was unequivocally determined. Both azides lay on a crystallographic mirror plane. Hydrogen atoms for the methyl alcohol and water molecules were not determined. In the Cu_2N_2 units, the Cu···Cu distance is 3.0785(5) Å, the Cu–N distances are 1.987(2) and 1.998(3) Å, while Cu–N–Cu bond angles are 101.51(18) and 100.79(18)°. Hydrogen bonds between the carboxylate oxygen and coordinated water or water, methanol were found to be O3···O1 2.730, O3···O4 2.706, O4···O4 2.693 Å, respectively. All bond distances as well as bond angles are in the ranges reported for **1** and similar compounds [4a, 6, 20]. The different unit cell dimensions reflect the changes in the network to make space for the methanol molecules. Interestingly, although the methanol appears between the 2-D sheets, the inter-sheet separation remains almost the same ($c = 11.0620(2)$ Å in **1** *versus* 11.2426(2) in **2**) retaining the hydrogen bonded 3-D-network; angles in the coordination network change more significantly.

3.2.3. $[Cu(qux)(NO_3)_2]_n$, (3). The atom labeling scheme and packing diagram are shown in figures 5 and 6, respectively. Selected bond distances and angles are listed in table 3. The copper as well as both nitrate groups are situated on a crystallographic mirror plane. The Cu(II) is tetra-coordinated to two quinoxaline groups and two nitrate groups to form a distorted square planar geometry where the bond angles around Cu(II) are 90.15(4) and 89.82(4)°, and 179.25(7), 175.19(7)° through the diagonals. The two nitrate groups connect terminally to copper via an oxygen with Cu–O bond distances of 1.9767(17) and 1.9825(17) Å, respectively. The bidentate *N-N′*-quinoxaline connects two $[Cu(NO_3)_2]$ units to form an infinite 1-D chain in the *b*-axis direction, with Cu–N distance of 2.0132(14) Å with N–Cu–N angle of 175.19(7)° quite close to $[Cu(qux)(H_2O)_3](ClO_4)_2$ [15a] (Cu–N distance is 2.036(6) Å with a N–Cu–N angle 173.0(2)°), $[Cu(qux)Cl_2]_n$ [15b], and $[Cu(qux)Br_2]_n$

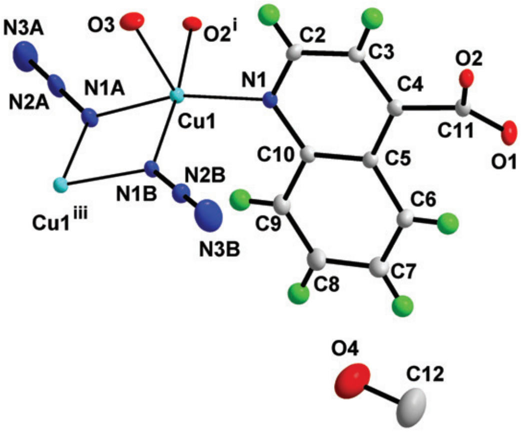


Figure 3. Numbering scheme for **2**. Atomic displacement ellipsoids drawn at 30% probability level.

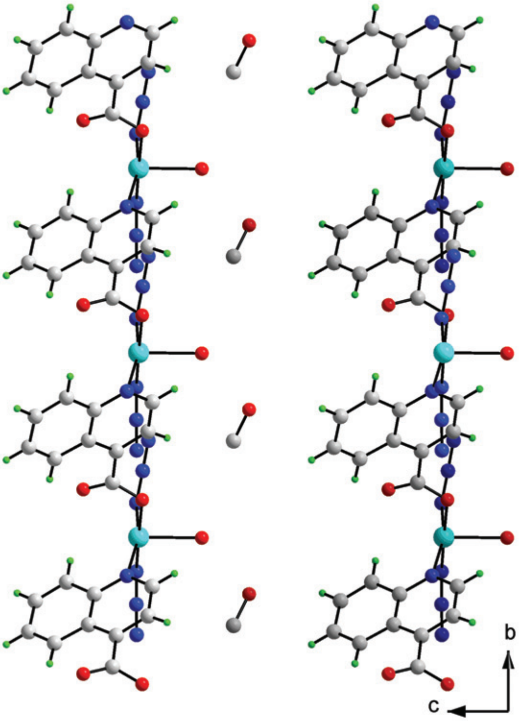


Figure 4. Packing diagram for **2**, showing MeOH molecules separating the 2-D sheets.

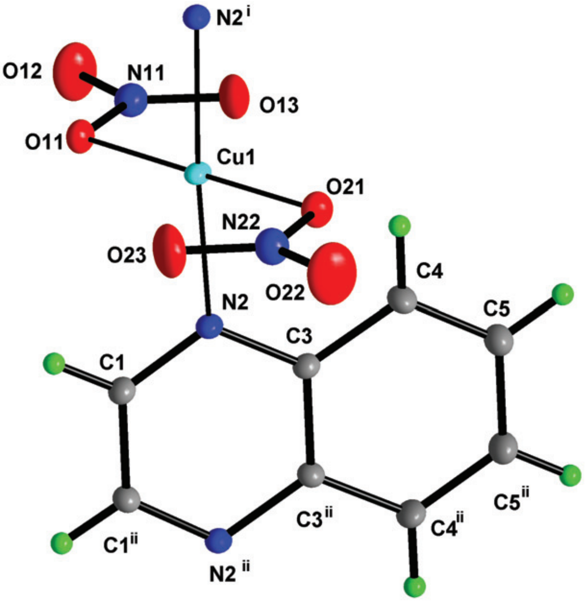


Figure 5. Numbering scheme for **3**. Atomic displacement ellipsoids drawn at 50% probability level.

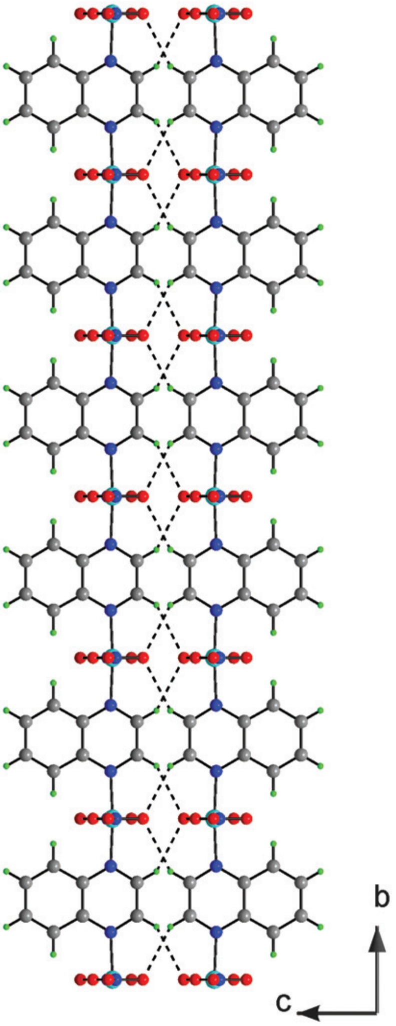


Figure 6. Two 1-D chains are connected via weak hydrogen bonds. Projection along *a*-axis for **3**.

[15e] (Cu–N distance is 2.068(2) Å with a N–Cu–N angle 174.07(8)°). The monodentate quinoxaline shows much longer bond distance Cu–N 2.479(3) Å and larger N–Cu–N 178.40(11)° for $[Cu(qux)(C_2N_3)_2]_n$ [15c] where the 1-D structure was achieved through bridging dicyanoamide groups. There is a zig-zag stacking of the neighboring chains via nitrate groups with interplanar distance of 3.409(2) Å stabilizing the structure in the direction of the *a*-axis. Weak intermolecular hydrogen bonds of the C–H ··· O type, listed in table 4 and shown in figure 6, connect two 1-D chains to form a double chain structure making R2,2(10) pattern at the first-level of the graph-set.[1]

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[1] Assignment of the H-bond descriptors are based on the graph-set theory described [22]. The full sets of the first and second-level descriptors have been obtained using the program PLUTO [22e]. For convenience, the notation Xa,d(n) has also been adopted in this article, in which (X) is the pattern descriptor, (a) the number of acceptors, (d) the number of donors and (n) the number of atoms comprising the pattern.

Table 3. Selected bond lengths (Å) and angles (°) for **3**.

Cu1–O11	1.9767(17)
Cu1–O21	1.9825(17)
Cu1–N2	2.0132(14)
O11–N11	1.305(3)
N11–O12	1.224(3)
N11–O13	1.247(3)
O21–N22	1.294(3)
N22–O22	1.217(3)
N22–O23	1.242(3)
O11–Cu1–O21	179.25(7)
O11–Cu1–N2	90.15(4)
O21–Cu1–N2	89.82(4)
N2–Cu1–N2$^{\mathrm{i}}$	175.19(7)
O12–N11–O13	124.4(2)
O12–N11–O11	118.0(2)
O13–N11–O11	117.6(2)
N22–O21–Cu1	108.26(15)
O22–N22–O23	125.4(2)
O23–N22–O21	116.1(2)

Symmetry transformations used to generate equivalent atoms: (i) x, $-y$, z; (ii) x, $-y+1$, z.

Table 4. Hydrogen bonds for **3** (Å) and (°).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
C(1)–H(1)···O(23)$^{\mathrm{iii}}$	0.95	2.59	3.386(2)	141

Symmetry transformations used to generate equivalent atoms: (iii) $-x+1$, y, $-z$.

Supplementary material

CCDC-649680, 668366 and 649682 contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internet) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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