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Uncommon isonicotinamide supramolecular synthons in copper(II) complexes directed by nitrate and perchlorate anions

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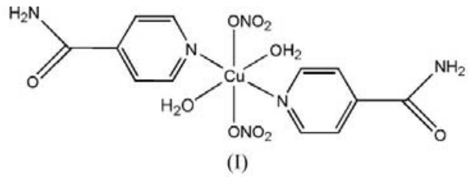
The title compounds, *trans*-diaquabis(nitrato-κO)bis(pyridine-4-carboxamide-κN^1)copper(II), $[Cu(NO_3)_2(C_6H_6N_2O)_2(H_2O)_2]$, (I), and *trans*-diaquatetrakis(pyridine-4-carboxamide-κN^1)copper(II) bis(perchlorate), $[Cu(C_6H_6N_2O)_4(H_2O)_2](ClO_4)_2$, (II), are composed of mononuclear coordination entities involving Cu^{II} ions and isonicotinamide. In (I), the centrosymmetric tetragonally distorted octahedral copper(II) environment contains *trans*-related isonicotinamide and water molecules in the equatorial plane and two nitrate ions occupying the axial sites. In (II), the equatorial plane of the C_2-symmetric distorted octahedron is built up of four isonicotinamide ligands, while water molecules occupy the axial positions. The complex molecules of (I) and (II) are linked into three-dimensional supramolecular frameworks by O—H···O and N—H···O hydrogen bonds. The nitrate and perchlorate ions are building blocks that disturb the robust $R_2^2(8)$ amide supramolecular motif commonly found in crystal structures of copper–isonicotinamide complexes.

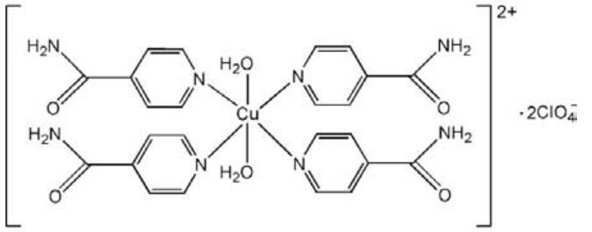
Comment

Amides, essential components of living organisms, have an ability to coordinate strongly with various transition metal ions (Uçar *et al.*, 2006). Isonicotinamide (pyridine-4-carboxamide, isn), a pyridine derivative with an amide group (–CO-NH$_2$) in the γ-position, is known to be an antitubercular, antipyretic, fibrinolytic and antibacterial medicinal agent (Ahuja & Prasad, 1976; Yurdakul *et al.*, 2003). However, sometimes metal complexes involving a ligand possessing biological activity show enhanced properties, and from that point of view isn is a promising ligand for binding to various metal centres. Interestingly, mixed salts of isn have found extensive use as drugs in many biological and medicinal processes (Murray *et al.*, 1990). Besides its importance in living organisms, isn and its derivatives are also interesting ligands for the construction of sophisticated hybrid organic–inorganic supramolecular networks based on organized strong covalent interactions (Bhogala *et al.*, 2004; Lian *et al.*, 2007; Moncol *et al.*, 2007; Zhao & Mak, 2004) and on weak noncovalent interactions (Aakeröy *et al.*, 2000, 2003; Moncol *et al.*, 2007). Among the weak interactions, hydrogen bonding is a general protocol for structure-directing master–key interactions.

The behaviour of pyridinecarboxamides towards biologically relevant *d*-block metals has been widely investigated. The structures of copper(II) complexes with picolinamide and nicotinamide have been thoroughly discussed (Brown *et al.*, 1971; Batsanov *et al.*, 1986; Emsley *et al.*, 1986; Cantarero *et al.*, 1988; Sieroń & Bukowska-Strżyzewska, 1997, 1998, 1999; Kozlevčar *et al.*, 1999; Cakir *et al.*, 2003; Sieroń, 2004; Uçar *et al.*, 2004; Du *et al.*, 2006; Valigure *et al.*, 2006; Ruan *et al.*, 2007; Moncol *et al.*, 2007). Regarding isn complexes, there are a few interesting reports in the literature for the acetate (Tsintsadze *et al.*, 1985; Zhang *et al.*, 2005), chloroacetate (Aakeröy *et al.*, 2003; Moncol *et al.*, 2007), trichloroacetate (Moncol *et al.*, 2007), formate (Tsintsadze *et al.*, 1986), fluorobenzoate (Aakeröy *et al.*, 2003), squarate (Uçar *et al.*, 2005), benzenedicarboxylate (Li *et al.*, 2005; Zhou, 2007), aspirinate (Ma & Moulton, 2007*a*), oxalate (Li *et al.*, 2007), hydroxybenzoyloxybenzoate (Ma & Moulton, 2007*b*) and iodo (Aakeröy *et al.*, 2000) complexes. As part of our ongoing research (Đaković & Popović, 2007; Đaković, Popović, Giester & Rajić-Linarić, 2008*a*,*b*; Đaković, Popović & Smrečki-Lolić, 2008) on heteroleptic pyridinecarboxamide complexes of the late 3*d*-block metals, the title compounds, (I) and (II), have been synthesised and their crystal structures are reported here.



(I)



(II)

The crystal structure of (I) consists of neutral *trans*-diaquadinitratobis(pyridine-4-carboxamide)copper(II) molecules with the Cu^{II} ions located on a crystallographic inversion centre. The tetragonally distorted octahedral coordination is formed by two *trans*-related isn ligands and two water molecules in the equatorial plane, plus two nitrate ions in the axial positions, thus constituting an N_2O_4 core (Fig. 1). Isn acts as a conventional ligand through the pyridine-ring N atom, while the nitrate ion exhibits its *O*-monodentate coordination mode, the most frequently observed in nitrate complexes of Cu^{II} [Cambridge Structural Database (CSD), Version 5.30 of 2008; Allen, 2002].

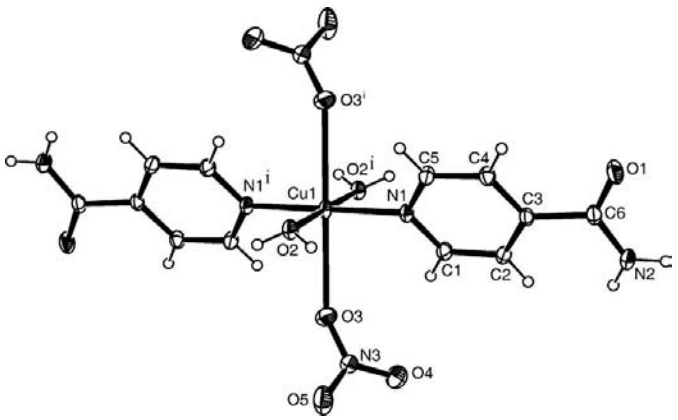


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

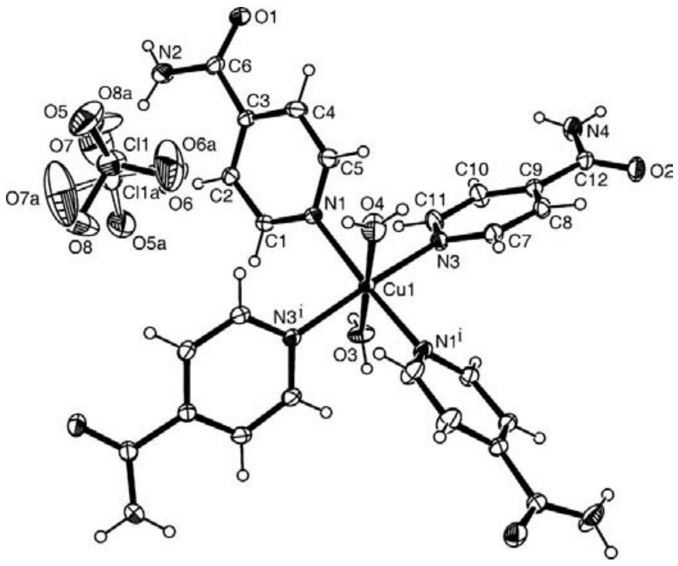


Figure 2
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.]

Isonicotinamide, possessing three potential donor sites, can adopt diverse coordination modes. However, due to the carboxamide group in the *para* position, in most of its complexes isn is only a monodentate ligand, coordinated to the metal centre through the pyridine-ring N atom. According to the CSD, there are just five isn complexes (out of 73) where a different coordination mode is observed. In four of these, one being a copper(II) complex (Moncol *et al.*, 2007) and three silver(I) complexes (Zhao & Mak, 2004; Lian *et al.*, 2007; Bhogala *et al.*, 2004), isn bridges two metal ions *via* the pyridine-ring N and carboxamide O atoms, exhibiting its μ_2-isn-*N*:*O* bridging function, while monodentate isn-*O* coordination is found in only one structurally characterized complex, *viz.* $[Ca(isn\text{-}O)_2(H_2O)_4]Cl_2$ (Cole & Holt, 1989).

In complex (I), the Cu1—O3 bond is significantly longer than the Cu1—O2 bond, regardless of the negative charge on the nitrate ligand (Table 1), but it still falls within the range of 2.2–2.9 Å known for axial Cu—O bond lengths (Wells, 1975). A search of the CSD revealed 31 crystal structures of six coordinated copper complexes simultaneously having water and nitrate in the coordination environment, and in the majority of these the O atoms of the water molecules and nitrate ions occupy equatorial and axial sites, respectively, as is the case in (I). Furthermore, the same feature is also observed for some other coordinated oxoanions, *e.g.* SO_4^{2-}, PO_4^{3-} and ClO_4^- (Cordes *et al.*, 2006; Manna *et al.*, 2007; Youngme *et al.*, 2005). Interestingly, when the oxoanions are replaced by carboxylate or squarate (sq) ligands, the reverse positions of the ligands are mostly observed, *i.e.* O atoms from water molecules occupy the expected axial sites. Although, according to the Cu—O bond length, the nitrate ion is considered to be covalently bound, the presence of a strong absorption band in the IR spectrum at 1384 cm^{-1}, and the absence of absorption in the regions 1540–1480 and 1290–1250 cm^{-1}, suggest the presence of a free nitrate anion in (I) (Nakamoto, 1997).

In (I), the Cu1—N1 bond is somewhat shorter than in most isn copper(II) complexes with a distorted octahedral coordination of the Cu^{II} ion, regardless of the coordination mode of isn {2.046 (6) Å in $[Cu(CH_3COO)_2(isn\text{-}N)_2(H_2O)_2]$ (Tsintsadze *et al.*, 1985); 2.034 (7) Å in $[Cu(HCOO)_2(isn\text{-}N)_2(H_2O)_2]$ (Tsintsadze *et al.*, 1986); 2.045 (2) Å in $[Cu(C_7H_4FO_2)_2(isn\text{-}N)_2(H_2O)_2]$ (Aakeröy *et al.*, 2003); 2.003 (1) Å in $[Cu(sq)_2(isn\text{-}N)_2(H_2O)_2]\cdot 2H_2O]_n$ (Uçar *et al.*, 2005); 2.015 (4) and 2.014 (4) Å in $[Cu(ClCH_2CO_2)_2(\mu_2\text{-}isn\text{-}N{:}O)_2]$ (Moncol *et al.*, 2007); 2.006 (2) Å in $[Cu(CCl_3CO_2)_2(\mu_2\text{-}isn\text{-}N{:}O)_2]$ (Moncol *et al.*, 2007)}. The pyridine ring of the isn ligand forms a dihedral angle of 60.8 (1)° with the equatorial plane of the CuN_2O_4 octahedron, thus minimizing steric repulsion between the coordinated ligands. The mean plane through the carboxamide group is not coplanar with the mean plane of the pyridine ring, but forms an angle with it of 11 (1)°, probably due to the complex hydrogen-bonding pattern in which the carboxamide group participates.

In complex (II), the substitution of nitrate with perchlorate leads to significant differences in both the molecular and crystal structures. In contrast with (I), the crystal structure of (II) consists of $[Cu(isn)_4(H_2O)_2]^{2+}$ complex cations, with the perchlorate anions as counter-ions. The Cu^{II} coordination is best described as distorted octahedral, with the Cu^{II} ion and two water-ligand O atoms lying on a twofold rotation axis at ($\frac{1}{2}$, y, $\frac{1}{4}$). The coordination is completed by four isn-*N* ligands lying on a plane perpendicular to the twofold axis (Fig. 2). Each of the two symmetrically related isn ligands is slightly tilted towards the twofold axis, causing a slight tetrahedral disposition of the isn-*N* ligands around the metal centre. The bond angles around the Cu^{II} centre lie within the ranges 85–94 and 170–173° for the formally *cis* and *trans* pairs of N-ligating atoms, respectively (Table 3). The Cu—N and Cu—O bond lengths (Table 3) lie within the normal ranges for equatorial Cu—N and axial Cu—O bonds in Cu^{II}(isn) complexes, respectively. Interestingly, the two axial Cu—O bonds differ

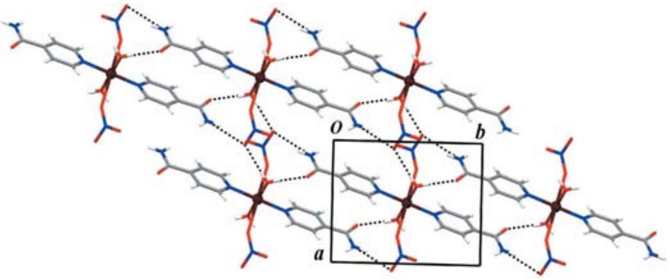


Figure 3
The hydrogen-bonded sheet structure of (I), viewed down the *c* axis. Hydrogen bonds are represented by dashed lines. For details, see Table 2.

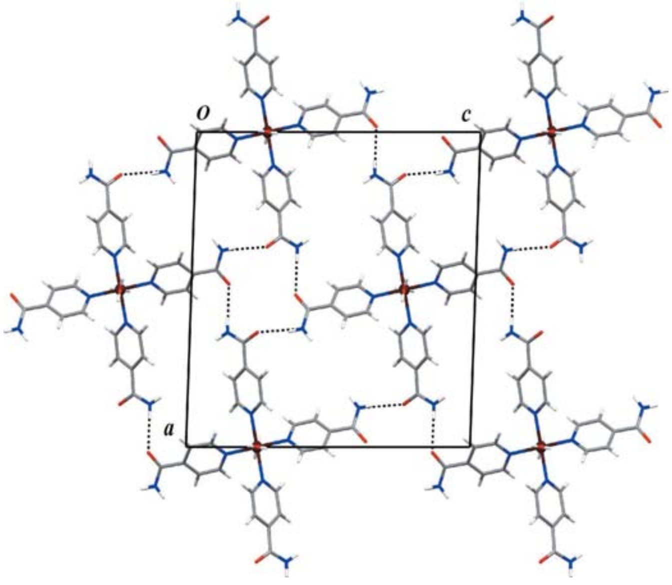


Figure 4
Projection of the structure of (II) on to the (010) plane, showing the two-dimensional cationic sheets generated by the amide N—H$\cdots$O hydrogen-bonded $R_4^4(16)$ and $R_2^2(28)$ motifs. The perchlorate ions have been omitted for clarity. Hydrogen bonds are represented by dashed lines.

significantly (66σ), and this is the first example where this difference is so pronounced. To date, there are 14 structurally characterized complexes of the $[\mathrm{Cu^{II}}(L)_4(\mathrm{H_2O})_2]$ type (L = pyridine-like ligand) in the CSD and in six of them a significant difference in axial Cu—O bonds is observed. The greatest difference reported so far is 28σ in the $[\mathrm{Cu(py)_4(H_2O)_2}]^{2+}$ cation (py is pyridine; Holzbock *et al.*, 1997). During the refinement process, it became apparent that the perchlorate ion in (II) was disordered. The disorder in the positions of the perchlorate atoms Cl1, O5, O6, O7 and O8 (Cl1*A*, O5*A*, O6*A*, O7*A* and O8*A*) was resolved and two distinct orientations of the anion were identified, with an occupancy factor of 0.595 (5) Å for the major component.

Although isonicotinamide can be employed as a practical ‘supramolecular reagent’, an effective tool for consistently assembling coordination complexes of $\mathrm{Cu^{II}}$ with widely differing geometries and ligands (Aakeröy *et al.*, 2000, 2003; Moncol *et al.*, 2007; Ma & Moulton, 2007*b*; Li *et al.*, 2007), in (I) and (II) isn forms neither self-complementary N—H$\cdots$O hydrogen bonds to yield head-to-head amide–amide dimers, designated by graph-set motif $R_2^2(8)$ (Bernstein *et al.*, 1995; Etter, 1990), nor catameric-type hydrogen-bonds with a $C(4)$ motif. In (I), the nitrate ions and water molecules of two additional neighbouring complex molecules enter the above-mentioned supramolecular synthon and expand the $R_2^2(8)$ ring into a new centrosymmetric hydrogen-bonded $R_6^4(14)$ motif. These rings are further fused by four more centrosymmetric hydrogen-bond ring motifs, *viz.* two $R_4^2(22)$ and two $R_2^2(18)$, forming layers in the (001) plane (Fig. 3). These layers are self-assembled into a three-dimensional supramolecular architecture through N—H$\cdots$O hydrogen bonds involving the amide group and the nitrate ion. Pertinent parameters of the hydrogen-bonding geometry are presented in Table 2. In addition to hydrogen bonds, there is also one weak interaction between the nitrate ion and the π-system of the py ring, which contributes to the overall stability of the crystal structure. The N—O$\cdots Cg^{\mathrm{iii}}$ distance is 3.435 (2) Å [Cg is the centroid of the N1/C1–C5 ring; symmetry code: (i) $-x, -y+1, -z+1$].

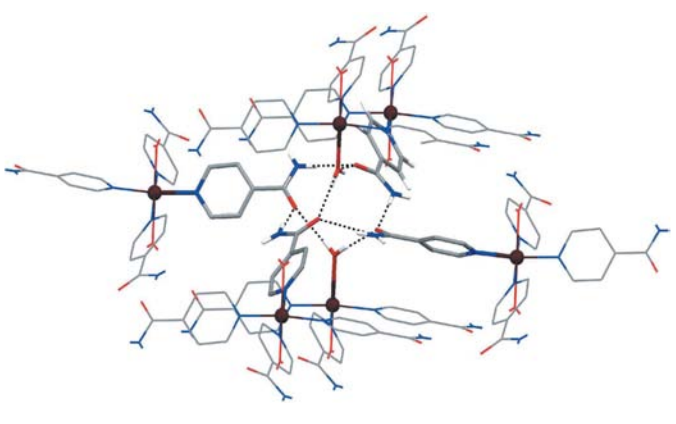
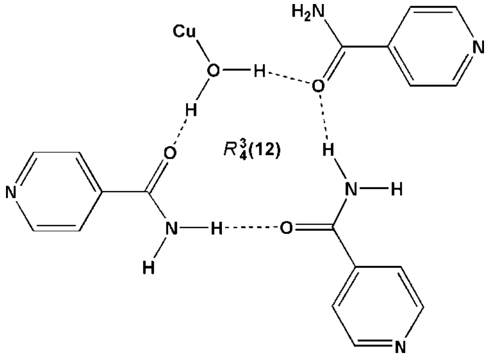


Figure 5
A view of the $R_4^3(12)$ hydrogen-bonded motif involved in the connection of the two-dimensional cationic sheets of (II) to form a three-dimensional hydrogen-bonded framework. Aromatic H atoms and some isonicotinamide ligands not involved in the formation of the $R_4^3(12)$ motif have been omitted for clarity. Hydrogen bonds are represented by dashed lines.



In (II), complex cations are linked together through four N—H$\cdots$O hydrogen bonds to form cationic sheets parallel to the (010) planes (Fig. 4), similar to those described for $[\mathrm{Ni(isn)_4(H_2O)_2}](\mathrm{ClO_4})_2\cdot 2\mathrm{H_2O}$ (Aakeröy *et al.*, 1999). In each of these parallel sheets, two hydrogen-bonding motifs involving amide groups are formed, *i.e.* $R_4^4(16)$ and $R_2^2(28)$ rings. Neighbouring cationic sheets are arranged in such a way that the Cu^{II} centres of each layer sit just above the $R_4^4(16)$ holes of the layer below. Consequently, the watermolecules coordinated to the Cu^{II} ions in the layers above and below the cationic sheets are involved in the constitution of more complicated $R_4^3(12)$ hydrogen-bonding motifs (see second scheme). Interestingly, four rings of this type are fused together, extending the two-dimensional sheets into a three-dimensional hydrogen-bonded network (Fig. 5). The bigger holes in the cationic sheets described by the $R_2^2(28)$ motif are only partially blocked by neighbouring sheets, providing enough space to accommodate the perchlorate ions. The details of the hydrogen-bonding geometry are listed in Table 4.

Experimental

For the preparation of compound (I), warm aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2 mmol in 10 ml) and isonicotinamide (0.48 g, 4 mmol in 20 ml) were mixed together and stirred at room temperature. The mother liquor was left to stand and allowed to evaporate slowly for a few days to give blue crystals of (I) suitable for X-ray analysis (yield 0.72 g, 77%). The crystals detonate without melting when warmed up to 511 K. IR (KBr pellet, ν, cm^{-1}): 3424 (*s*), 3185 (*m*), 1706 (*s*), 1624 (*w*), 1611 (*m*), 1554 (*w*), 1420 (*m*), 1384 (*vs*), 1231 (*w*), 1064 (*w*), 1027 (*w*), 862 (*w*), 846 (*w*), 761 (*w*), 720 (*vw*), 668 (*w*), 644 (*w*), 482 (*w*).

For the preparation of compound (II), a water solution of $NaClO_4$ (0.28 g, 2 mmol in 10 ml) was added dropwise with stirring to a warm aqueous mixture of $Cu(CH_3COO)_2 \cdot H_2O$ (0.20 g, 1 mmol in 10 ml) and isonicotinamide (0.24 g, 2 mmol in 10 ml). The resulting dark-blue solution was left to stand undisturbed and allowed to evaporate slowly for a few days to give blue crystals of (II) (yield 0.28 g, 70%). The crystals detonate without melting when warmed up to 534 K. IR (KBr pellet, ν, cm^{-1}): 3424 (*s*), 3326 (*s*), 3181 (*s*), 1705 (*vs*), 1684 (*s*), 1624 (*s*), 1612 (*s*), 1554 (*s*), 1506 (*m*), 1491 (*w*), 1457 (*w*), 1419 (*s*), 1394 (*s*), 1224 (*m*), 1144 (*vs*), 1110 (*vs*), 1087 (*vs*), 1027 (*m*), 1002 (*m*), 941 (*w*), 862 (*w*), 847 (*m*), 760 (*m*), 668 (*w*), 636 (*s*), 627 (*s*), 551 (*m*), 482 (*m*).

IR spectra were recorded as KBr pellets within the range 4000–400 cm^{-1} using a Perkin–Elmer 1600 Series FT–IR spectrometer. Thermal measurements were performed using a simultaneous TG–DT analyser (Mettler–Toledo TGA/SDTA 850e).

Compound (I)

Crystal data

$[Cu(NO_3)_2(C_6H_6N_2O)_2(H_2O)_2]$
$M_r = 467.86$
Monoclinic, $P2_1/c$
$a = 7.5367\ (2)$ Å
$b = 9.8819\ (3)$ Å
$c = 11.7402\ (4)$ Å
$\beta = 96.280\ (3)^\circ$
$V = 869.13\ (5)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.33\ mm^{-1}$
$T = 296$ K
0.59 × 0.02 × 0.01 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire3 detector
Absorption correction: multi-scan (*CrysAlis Pro*; Oxford Diffraction, 2007)
$T_{min} = 0.874$, $T_{max} = 0.987$
11568 measured reflections
2536 independent reflections
2188 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—O2	1.984 (1)	Cu1—N1	1.992 (1)
Cu1—O3	2.507 (1)		
O2—Cu1—O3	84.36 (4)	O2—Cu1—N1^{i}	89.98 (4)
O2—Cu1—N1	90.02 (4)	O3—Cu1—N1	90.27 (4)
O2—Cu1—O3^{i}	95.64 (4)	O3—Cu1—N1^{i}	89.73 (4)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H12O$\cdots$O1^{ii}	0.81 (2)	1.90 (2)	2.702 (1)	175 (2)
O2—H22O$\cdots$O5^{iii}	0.74 (2)	2.03 (2)	2.764 (2)	174 (2)
N2—H12N$\cdots$O3^{iv}	0.84 (3)	2.50 (3)	3.123 (2)	132 (2)
N2—H22N$\cdots$O4^{v}	0.84 (2)	2.12 (2)	2.910 (2)	158 (2)
N2—H12N$\cdots$O5^{iv}	0.84 (3)	2.21 (3)	2.988 (2)	154 (2)

Symmetry codes: (ii) $x, y+1, z$; (iii) $-x, -y+1, -z+1$; (iv) $x, y-1, z$; (v) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.069$
$S = 1.09$
2536 reflections
149 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Compound (II)

Crystal data

$[Cu(C_6H_6N_2O)_4(H_2O)_2](ClO_4)_2$
$M_r = 786.99$
Monoclinic, $C2/c$
$a = 18.7783\ (3)$ Å
$b = 9.5648\ (2)$ Å
$c = 18.2630\ (2)$ Å
$\beta = 92.0900\ (10)^\circ$
$V = 3278.05\ (9)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.91\ mm^{-1}$
$T = 296$ K
0.60 × 0.38 × 0.30 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire3 detector
Absorption correction: multi-scan (*CrysAlis Pro*; Oxford Diffraction, 2007)
$T_{min} = 0.628$, $T_{max} = 0.761$
26135 measured reflections
3576 independent reflections
3224 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.089$
$S = 1.05$
3576 reflections
293 parameters
366 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Aromatic H atoms were fixed in geometrically calculated positions and refined using a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms on the carboxamide N atom of (I) and water O atoms of (I) and (II) were placed in the positions indicated by difference electron-density maps and their positions were allowed to refine together with individual isotropic displacement parameters. H

Table 3
Selected geometric parameters (Å, °) for (II).

Cu1—O3	2.415 (2)	Cu1—N1	2.0280 (15)
Cu1—O4	2.652 (3)	Cu1—N3	2.0428 (15)
O3—Cu1—O4	180.00	O4—Cu1—N3	93.78 (5)
O3—Cu1—N1	95.04 (5)	N1—Cu1—N3	89.12 (6)
O3—Cu1—N3	86.22 (5)	$N1^{i}$—Cu1—N3	91.55 (6)
O4—Cu1—N1	84.96 (5)		

Symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H12⋯$O5A^{ii}$	0.85 (3)	2.07 (3)	2.882 (4)	159 (3)
N2—H13⋯$O2^{iii}$	0.84 (2)	2.07 (2)	2.898 (2)	174 (3)
N4—H14⋯$O8A^{iv}$	0.85 (2)	2.38 (3)	3.128 (7)	148 (3)
N4—H15⋯$O1^{v}$	0.87 (2)	2.09 (2)	2.940 (2)	167 (2)
O3—H16⋯$O1^{iv}$	0.82 (3)	2.04 (3)	2.831 (2)	163 (3)
O4—H17⋯$O2^{vi}$	0.79 (3)	2.10 (3)	2.889 (3)	176 (3)

Symmetry codes: (ii) $-x+\frac{3}{2}, -y+\frac{3}{2}, -z+1$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iv) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+\frac{3}{2}, -y+\frac{3}{2}, -z$; (vi) $-x+1, -y+1, -z$.

atoms on the carboxamide N atoms in (II) were found in a difference map at the final stage of refinement and refined semi-freely with N—H = 0.86 Å. The atoms of the perchlorate anion were located in a difference Fourier map and refined to an ideal tetrahedron [SADI instruction in *SHELXL97* (Sheldrick, 2008); s.u. = 0.02 Å]. The anisotropic displacement parameters of adjacent atoms were restrained to be similar (SIMU instruction in *SHELXL97*; s.u. = 0.04 Å^2), and the main directions of movement of covalently bonded atoms were likewise restrained (DELU instruction in *SHELXL97*; s.u. = 0.01 Å^2) (Müller *et al.*, 2006). The occupancy ratio was refined freely during subsequent anisotropic least-squares refinements.

For both compounds, data collection: *CrysAlis Pro* (Oxford Diffraction, 2007); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GT3009). Services for accessing these data are described at the back of the journal.

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