

**(Azido- κN)bis(di-2-pyridylamine)-
copper(II) hexafluorophosphate and
(azido- κN)bis(di-2-pyridylamine)-
copper(II) chloride tetrahydrate**Sujittra Youngme,^{a*} Jaturong Phatchimkun,^a Chaveng
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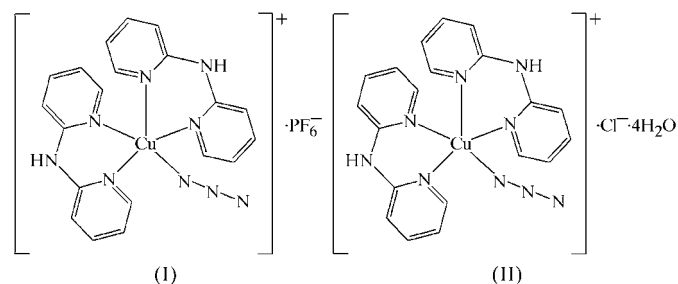
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The two new title complexes, $[\text{Cu}(\text{N}_3)(\text{dpyam})_2]\text{PF}_6$ (dpyam is di-2-pyridylamine, $\text{C}_{10}\text{H}_{11}\text{N}_3$), (I), and $[\text{Cu}(\text{N}_3)(\text{dpyam})_2]\text{Cl}\cdot 4\text{H}_2\text{O}$, (II), respectively, have been characterized by single-crystal X-ray diffraction. Both complexes display a distorted square-pyramidal geometry. Each Cu atom is coordinated in the basal plane by three dpyam N atoms and one azide N atom in equatorial positions, and by another N atom from the dpyam group in the apical position. In complex (I), the one-dimensional supramolecular architecture is assembled *via* hydrogen-bonding interactions between the amine N atom and terminal azide N atoms and the F atoms of the PF_6^- anion. For complex (II), hydrogen-bonding interactions between the amine N atom, the Cl^- anion and water O atoms result in a two-dimensional lattice.

Comment

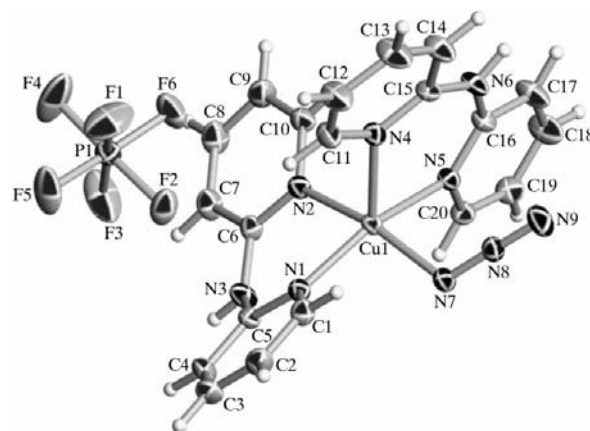
The synthesis of pseudohalide-bridged complexes continues to be a subject of much interest, and intensive investigations have taken place as a result of their diverse structures and potential



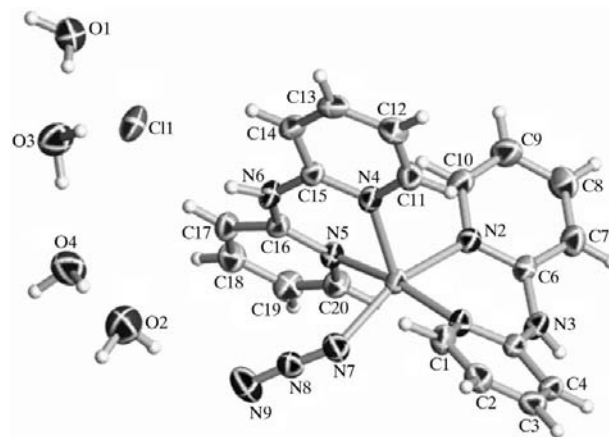
applications in magnetic materials. Pseudohalide ligands (OCN^- , SCN^- , N_3^- , *etc.*) can coordinate to transition metal

atoms in different ways, for example, as a terminal ligand or as a bridge (Talukder *et al.*, 2004). One-, two- or three-dimensional supramolecular architectures assembled *via* intermolecular non-covalent interactions are of considerable interest for the crystal engineering of new functional solid-state materials, as well as for their fascinating structures (Gao *et al.*, 2001). Hydrogen bonding, which combines directionality, selectivity and strength, has been noted as the most versatile organizing force for supramolecular assembly (Chen *et al.*, 2001). We report here the two new title complexes, $[\text{Cu}(\text{N}_3)(\text{dpyam})_2]\text{PF}_6$, (I), and $[\text{Cu}(\text{N}_3)(\text{dpyam})_2]\text{Cl}\cdot 4\text{H}_2\text{O}$, (II). The dpyam ligand has been selected primarily because it also has an N–H hydrogen-bond donor function that might produce one-, two- or three-dimensional supramolecular architectures.

The crystal structures of (I) and (II) (Figs. 1 and 2) consist of a $[\text{Cu}(\text{N}_3)(\text{dpyam})_2]^+$ cation and PF_6^- and Cl^- anions,

**Figure 1**

The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii. Only one of the disordered components of the PF_6^- anion is shown.

**Figure 2**

The molecular structure of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

respectively. The Cu atoms of both molecules exhibit five-coordination of the CuN₄N' chromophore (see scheme). The coordination around each Cu atom consists of three dpyam N atoms and one azide N atom in equatorial positions, and another N atom from dpyam in the apical position. Both complexes exhibit a slightly distorted square-pyramidal environment, the geometric τ values (Addison *et al.*, 1984) being 0.061 for (I) and 0.148 for (II). The average Cu–N distances (Tables 1 and 3) in the equatorial positions are 2.017 (1) Å for (I) and 2.009 (1) Å for (II). The axial Cu–N distances are longer, at 2.153 (2) Å for (I) and 2.169 (2) Å for (II). The Cu atoms are displaced by 0.264 (1) Å for (I) and 0.255 (1) Å for (II) from the mean basal plane towards the apical position. The dpyam ligands are not planar, with dihedral angles between the two pyridine rings of 34.4 (1) and 16.1 (1)° for (I), and 35.3 (1) and 14.6 (1)° for (II).

There are extensive hydrogen-bonding interactions in both structures. In complex (I), intermolecular N–H...F and N–H...N(azide) hydrogen-bonding interactions (Table 2) produce a one-dimensional chain (Fig. 3). The crystal packing of complex (II) is stabilized by intermolecular N–H...Cl, O–H...N(azide), O–H...Cl and O–H...O hydrogen

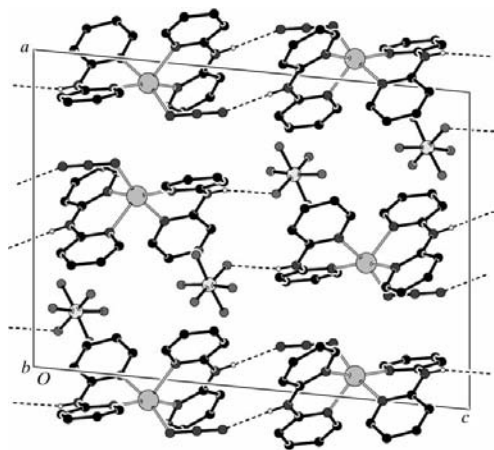


Figure 3
A packing diagram for (I), with hydrogen bonds (dashed lines), showing the one-dimensional structure.

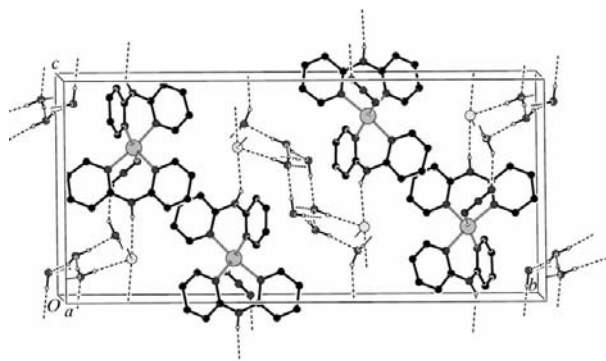


Figure 4
A packing diagram for (II), with hydrogen bonds (dashed lines), showing the two-dimensional structure.

bonds (Table 4), leading to a two-dimensional supramolecular structure (Fig. 4).

The chromophores of (I) and (II) are very similar except for the four additional water molecules in the structure of complex (II), which create a two-dimensional hydrogen-bonded network in (II).

Experimental

Complex (I) was prepared by adding a warm solution of di-2-pyridylamine (0.17 g, 1.00 mmol) in methanol (15 ml) to a hot aqueous solution (10 ml) containing Cu(CH₃COO)₂·H₂O (0.091 g, 0.5 mmol) and NaN₃ (0.065 g, 1.0 mmol). An aqueous solution (15 ml) of KPF₆ (0.184 g, 1.0 mmol) was then added, giving a clear green solution. The resulting solution was evaporated slowly at room temperature. After several days, green needle-shaped crystals of (I) which had formed were filtered off, washed with mother liquor and air-dried (yield *ca* 90%). Green needle-shaped crystals of (II) were obtained by adding a warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 ml) to a boiling aqueous solution (15 ml) of CuCl₂·2H₂O (0.085 g, 0.5 mmol). NaN₃ (0.130 g, 2.0 mmol) was then added to the reaction mixture. After several days, crystals of (II) which had formed were filtered off, washed with mother liquor and air-dried (yield *ca* 85%). The electronic reflectance spectra of both complexes involve main peaks at 14 050 and 14 000 cm⁻¹, and lower energy shoulders at 11 010 and 11 110 cm⁻¹ for (I) and (II), respectively. These spectroscopic characteristics of the compounds are consistent with a distorted square-pyramidal geometry with a small τ value. The transitions may be assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition for the low-energy shoulder and the $d_{xz} \sim d_{yz} \rightarrow d_{x^2-y^2}$ transition for the high-energy peak. The strongest intensity features in the spectra of (I) and (II) appear at 2042 and 2040 cm⁻¹, respectively, together with sharp and medium intensity peaks at 2035 and 2034 cm⁻¹, respectively, attributed to $\nu_{as}(N_3)$. For the IR spectrum of sodium azide, a single strong peak at 2033 cm⁻¹ is observed. Hence, in the present compounds, the shift towards higher wavenumbers of the ν_{as} stretching of the azide indicates that it must be coordinated.

Compound (I)

Crystal data

[Cu(N₃)(C₁₀H₁₁N₃)₂]PF₆
M_r = 592.94
 Monoclinic, *P*2₁/*n*
a = 14.1074 (8) Å
b = 8.5839 (5) Å
c = 19.4144 (11) Å
 β = 95.6350 (10)°
V = 2339.7 (2) Å³

Z = 4
D_x = 1.683 Mg m⁻³
 Mo *K*α radiation
 μ = 1.08 mm⁻¹
T = 298 (2) K
 Needle, green
 0.31 × 0.21 × 0.11 mm

Data collection

Siemens SMART CCD area detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)
T_{min} = 0.769, *T_{max}* = 0.884

19955 measured reflections
 5804 independent reflections
 4381 reflections with *I* > 2σ(*I*)
R_{int} = 0.027
 θ_{max} = 28.3°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.043
wR (*F*²) = 0.111
S = 1.05
 5635 reflections
 397 parameters
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.9007P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.22 \text{ e \AA}^{-3}$

Table 1

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

Cu1—N1	2.0046 (19)	Cu1—N5	2.0361 (19)
Cu1—N7	2.009 (2)	Cu1—N4	2.1534 (19)
Cu1—N2	2.0166 (19)		
N1—Cu1—N7	88.15 (8)	N2—Cu1—N5	89.82 (8)
N1—Cu1—N2	88.00 (8)	N1—Cu1—N4	108.15 (8)
N7—Cu1—N2	166.76 (8)	N7—Cu1—N4	96.51 (8)
N1—Cu1—N5	163.10 (8)	N2—Cu1—N4	96.73 (8)
N7—Cu1—N5	90.18 (8)	N5—Cu1—N4	88.75 (8)

Table 2

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H5...F3 ⁱ	0.86 (2)	2.20 (2)	3.045 (12)	168 (2)
N3—H5...F3A ⁱ	0.86 (2)	2.14 (2)	2.963 (8)	161 (2)
N6—H15...N9 ⁱⁱ	0.86 (2)	2.27 (2)	3.130 (3)	179 (3)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z$.**Compound (II)***Crystal data*

[Cu(N₃)(C₁₀H₁₁N₃)₂]Cl·4H₂O
M_r = 555.49
 Monoclinic, *P*₂₁/*c*
a = 7.0560 (2) Å
b = 27.8360 (13) Å
c = 12.8780 (6) Å
 β = 99.009 (2)°
V = 2498.18 (18) Å³

Z = 4
D_x = 1.477 Mg m⁻³
 Mo *K*α radiation
 μ = 1.03 mm⁻¹
T = 298 (2) K
 Needle, green
 0.50 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius MACH3
 diffractometer
 ψ scan
 12357 measured reflections

6685 independent reflections
 4900 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.032
 θ_{\max} = 29.1°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.046
wR(*F*²) = 0.147
S = 1.10
 6407 reflections
 348 parameters
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2 + 0.2714P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.012$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.82 \text{ e } \text{Å}^{-3}$

In (I), H atoms attached to N3 and N6 were located in a difference Fourier map and refined with a DFIX (*SHELXTL*; Sheldrick, 2000*b*) restraint of N—H = 0.86 (1) Å. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The F atoms of the hexafluorophosphate group showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.5. In (II), H atoms attached to water O atoms were located in difference Fourier maps and refined with a DFIX restraint of O—H = 0.90 (1) Å. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and N—H = 0.86 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C,N).

Data collection: *SMART* (Bruker, 2000) for (I); *MACH3* (Enraf–Nonius, 1993) for (II). Cell refinement: *SAINT* (Bruker, 2000) for (I);

Table 3

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

Cu1—N1	1.999 (2)	Cu1—N2	2.028 (2)
Cu1—N5	2.003 (2)	Cu1—N4	2.169 (2)
Cu1—N7	2.007 (2)		
N1—Cu1—N5	169.35 (9)	N7—Cu1—N2	160.47 (10)
N1—Cu1—N7	86.36 (9)	N1—Cu1—N4	102.54 (8)
N5—Cu1—N7	88.99 (9)	N5—Cu1—N4	87.86 (8)
N1—Cu1—N2	87.37 (8)	N7—Cu1—N4	103.42 (10)
N5—Cu1—N2	93.91 (8)	N2—Cu1—N4	95.99 (8)

Table 4

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1W...O3	0.90 (3)	1.96 (3)	2.855 (4)	172 (1)
O1—H2W...O3 ⁱ	0.90 (2)	1.95 (2)	2.847 (4)	178 (1)
O2—H3W...Cl ⁱⁱ	0.90 (3)	2.30 (3)	3.203 (4)	174 (1)
O2—H4W...N9	0.91 (4)	2.12 (4)	2.964 (5)	153 (5)
O3—H5W...O4	0.92 (4)	1.84 (4)	2.751 (4)	171 (4)
O3—H6W...Cl1	0.89 (3)	2.27 (3)	3.151 (3)	170 (3)
O4—H7W...O2	0.89 (3)	1.96 (3)	2.843 (5)	174 (3)
O4—H8W...O1 ⁱⁱ	0.90 (4)	1.89 (4)	2.768 (4)	164 (1)
N3—H5...Cl ⁱⁱⁱ	0.86	2.56	3.256 (2)	139
N6—H15...Cl1	0.86	2.49	3.297 (2)	157

Symmetry codes: (i) $-x + 2, -y, -z$; (ii) $x - 1, y, z$; (iii) $x, y, z + 1$.

MACH3 for (II). Data reduction: *SAINT* for (I); *MolEN* (Fair, 1990) for (II). For both compounds, program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3027). Services for accessing these data are described at the back of the journal.

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