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Poly[μ-2-aminopyrazine-κ^2N^1:N^4-μ-cyanido-copper(I)]: a three-dimensional network from laboratory powder diffraction data

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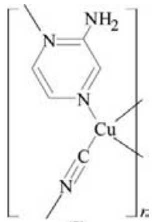
In the title compound, $[Cu(CN)(C_4H_5N_3)]_n$ or $[Cu(\mu\text{-}CN)(\mu\text{-}PyzNH_2)]_n$ ($PyzNH_2$ is 2-aminopyrazine), the Cu^I center is tetrahedrally coordinated by two cyanide and two $PyzNH_2$ ligands. The Cu^I–cyano links give rise to $[Cu\text{–}CN]_\infty$ chains running along the *c* axis, which are bridged by bidentate $PyzNH_2$ ligands. The three-dimensional framework can be described as being formed by two interpenetrated three-dimensional honeycomb-like networks, both made of 26-membered rings of composition $[Cu_6(\mu\text{-}CN)_2(\mu\text{-}PyzNH_2)_4]$.

Comment

Metal–organic networks of Cu^I–cyano and bridging diimine ligands have potential applications in gas storage and catalysis. Metal–organic materials containing luminescent metals, such as copper(I), and having suitable network porosity can potentially be used in gas molecule sensing systems, since the inclusion of small molecules into the network can alter the luminescent behavior of the material. The wide variety of bonding modes of Cu^I–cyano units allows the preparation of new materials of a large number of structural types, where the Cu^I coordination often varies from 2 to 5. Furthermore, the assembly of Cu^I and asymmetrically substituted diimine ligands can lead to chiral two- and three-dimensional networks, which could find applications in asymmetric catalysis and nonlinear optics (Teichert & Sheldrick, 1999, and references therein).

We have recently prepared a variety of new Cu^I–cyano diimine compounds by open reflux reactions and hydrothermal syntheses, and have investigated their luminescence properties (Tronic *et al.*, 2007). The ligands studied include pyrazine (Pyz), 2-aminopyrazine ($PyzNH_2$), quinoxaline, phenazine, 4,4′-bipyridyl, pyrimidine, 2-aminopyrimidine, 2,4-diaminopyrimidine, 2,4,6-triaminopyrimidine, quinazoline, pyridazine and phthalazine. As part of this study, poly[μ-2-aminopyrazine-μ-cyanido-copper(I)], $[CuCN(\mu\text{-}PyzNH_2)]_n$, (I), was prepared by an open reflux reaction. This reaction did not produce single crystals suitable for structure determination, but the structure of (I) has been solved from the X-ray powder diffraction pattern collected at room temperature.



(I)

Only a few 1:1 $[Cu(CN)(\mu\text{-ligand})]$ complexes have been previously reported, all containing Cu^I with distorted tetrahedral coordination. In the crystal structure of $[CuCN(\mu\text{-pdvb})]_n$ (pdvb is di-4-pyridyl-*trans*-1,4-divinylbenzene), the long bidentate pdvb ligand favors the formation of corrugated sheets, each sheet being composed of parallel $[Cu\text{–pdvb}]_\infty$ zigzag chains (Hanika-Heidl *et al.*, 2003). The sheets are linked together through cyano bridges that give rise to $[Cu\text{–}CN]_\infty$

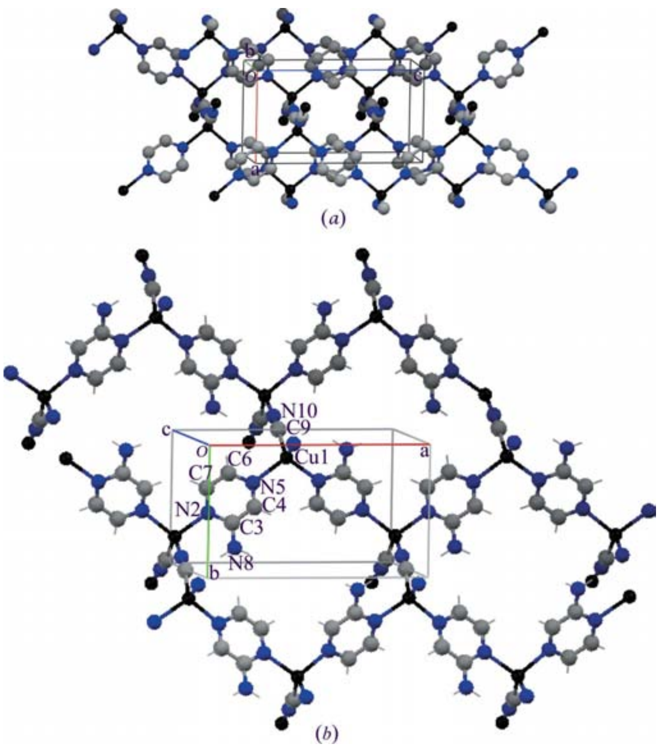


Figure 1
(*a*) $[Cu_6(CN)_2(\mu\text{-}Pyz)_4]$ 26-membered rings in the three-dimensional honeycomb-like arrays of $[Cu(CN)(\mu\text{-}Pyz)]_n$. H atoms are not shown for clarity. (*b*) A view of the distorted tetrahedral coordination around the Cu^I atom in $[Cu(CN)(\mu\text{-}PyzNH_2)]_n$, showing the atom-labeling scheme (H-atom labels have been omitted for clarity).

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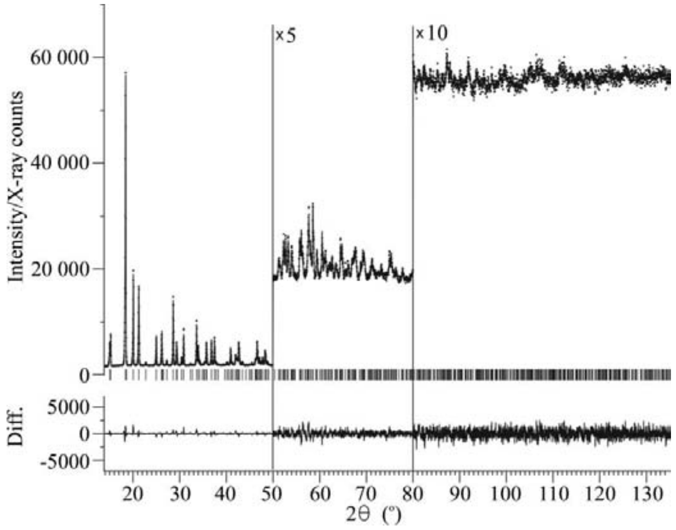

Figure 2
The final Rietveld refinement. Observed intensity (points), calculated profile (solid line) and peak positions (| symbols). The difference plot ($I_{\rm observed} - I_{\rm calculated}$) is shown at the bottom.

chains running along the direction perpendicular to the plane of the sheets. This structure exhibits remarkably different $Cu^I\cdots Cu^I$ separations of 4.804 (*via* CN^-) and 20.366 Å (*via* pdvb). The pdvb Cu—N interatomic distances are 2.249 and 2.173 Å, whereas the cyano Cu—C and Cu—N distances are 1.880 and 1.941 Å, respectively.

$[Cu(CN)(\mu\text{-2-MePyz})]_n$ (2-MePyz is 2-methylpyrazine) and $[Cu(CN)(\mu\text{-4-MePym})]_n$ (4-MePym is 4-methylpyrimidine) form three-dimensional frameworks in which one-dimensional $[Cu\text{–}CN]_\infty$ chains are bridged by the linear bidentate aromatic ligands (Teichert & Sheldrick, 1999). In $[Cu(CN)(\mu\text{-2-MePyz})]_n$, 22-membered rings of $[Cu_6(CN)_4(\mu\text{-2-MePyz})_2]$ composition form a chiral honeycomb-like two-dimensional network; these units are connected by additional 2-MePyz ligands, giving rise to a porous and chiral three-dimensional framework in $P2_12_12_1$. On the other hand, the linear ligand 4-MePym bonds to Cu^I atoms at shorter distances owing to its intramolecular geometrical disposition of N atoms, and it forms tetramers in a centrosymmetric structure containing disordered cyano C and N atoms. Furthermore, regardless of the asymmetric nature of the 4-MePym ligand, $[Cu(CN)(\mu\text{-4-MePym})]_n$ crystallizes in the nonchiral space group $P4_2/n$.

$[Cu(CN)(\mu\text{-Pyz})]_n$ forms a three-dimensional network in the $P2_1/c$ space group [a = 6.208 (2) Å, b = 9.158 (2) Å, c = 11.198 (2) Å and β = 90.89 (3)°], wherein each Cu^I center is tetrahedrally coordinated to two cyano and two Pyz units. $[Cu\text{–}CN]_\infty$ chains run along the b axis and are connected by two Pyz ligands, giving rise to 22-membered rings of composition $[Cu_6(CN)_4(\mu\text{-Pyz})_2]$. Alternatively, we can describe the three-dimensional network as formed by two interpenetrated, but otherwise symmetrically equivalent, three-dimensional honeycomb-like arrays made of 26-membered rings of composition $[Cu_6(CN)_2(\mu\text{-Pyz})_4]$ (Fig. 1*a*). Offset face-to-face π–π interactions within Pyz ligands are present, with a centroid-to-centroid distance of 4.58 (6) Å. The Pyz Cu^I—N distances are 2.159 (12) and 2.134 (12) Å, whereas the cyano Cu^I—C and Cu^I—N distances are 1.920 (18) and 1.944 (19) Å, respectively, and the Cu^I tetrahedral angles are 99.3 (5), 133.1 (8), 99.8 (6), 111.1 (8), 101.4 (6) and 107.2 (8)°. The existence of some C/N disorder (not refined) in the cyano ligands is reported for this structure (Kuhlman *et al.*, 1999).

A similar packing was found for (I). The refined unit-cell parameters (after axes permutations) are also similar, even though $[Cu(CN)(\mu\text{-Pyz})]_n$ and $[Cu(CN)(\mu\text{-PyzNH}_2)]_n$ belong to the monoclinic and orthorhombic crystal systems, respectively. Fig. 1(*b*) shows the distorted tetrahedral coordination adopted by Cu1. This figure also shows one of the two interpenetrated three-dimensional honeycomb-like arrays formed by 26-membered rings of $[Cu_6(CN)_2(\mu\text{-PyzNH}_2)_4]$ composition, which in turn generate the three-dimensional network of $[Cu(CN)(\mu\text{-PyzNH}_2)]_n$. The compound crystallizes in the noncentrosymmetric and nonchiral space group $Pca2_1$ (No. 29), and the cyano C and N positions for (I) refine as ordered. Additionally, offset face-to-face π–π interactions between the $PyzNH_2$ ligands with a centroid-to-centroid distance of 4.16 (5) Å are found.

In view of the chemical similarity of Pyz and $PyzNH_2$, and the similarity of the crystal packings of $[CuCN(\mu\text{-Pyz})]_n$ and $[CuCN(\mu\text{-PyzNH}_2)]_n$, it is reasonable that the ligand Cu—N distances found are very close for the two complexes. The differences in the tetrahedral coordination angles around Cu^I are slightly larger.

Experimental

Compound (I) was prepared by open reflux synthesis as described by Tronic *et al.* (2007). Equimolar quantities of copper(I) cyanide and KCN were suspended in water and warmed. $PyzNH_2$ was added in half of the previous molar quantity and the suspension was refluxed overnight under a nitrogen atmosphere. The reaction mixture was filtered, and the solid obtained was washed with water, ethanol and diethyl ether and dried under vacuum. A yellow powder was isolated. The C, H and N elemental compositions were measured by standard techniques, and the Cu content was determined by atomic absorption spectroscopy.

Crystal data

$[Cu(CN)(C_4H_5N_3)]$
M_r = 184.68
Orthorhombic, $Pca2_1$
a = 11.536 (1) Å
b = 6.7868 (7) Å
c = 8.3073 (9) Å
V = 650.4 (1) Å^3
Z = 4
Cu $K\alpha$ radiation
T = 298 K
Specimen shape: cylinder
27 × 27 × 2 mm
Specimen prepared at 101 kPa
Specimen prepared at 298 K
Particle morphology: fine powder, yellow

Data collection

Philips Analytical X'Pert Pro MRD diffractometer
Specimen mounting: packed powder in flat plate holder
Specimen mounted in reflection mode
Scan method: step
$2\theta_{\rm min}$ = 14.0, $2\theta_{\rm max}$ = 135.0°
Increment in 2θ = 0.03°

Refinement

R_p = 0.017
R_{wp} = 0.026
R_{exp} = 0.015
R_B = 0.083
S = 1.72
Wavelength of incident radiation: 1.5418 Å
Excluded region(s): none
Profile function: pseudo-Voigt (Thompson *et al.*, 1987), with asymmetry correction from Finger *et al.* (1994) and micro-strain broadening as reported by Stephens (1999)
149 parameters
1 restraint
H-atom parameters constrained
Preferred orientation correction: March–Dollase as implemented in *GSAS* (Larson & Von Dreele, 2000), along the (111) axis

The powder diffraction pattern was indexed without impurity peaks with the program *DICVOL04* (Boultif & Louër, 2004). Le Bail fits (Le Bail *et al.*, 1988) performed with the program *GSAS* (Larson & Von Dreele, 2000) confirmed the validity of the orthorhombic unit-cell parameters. Starting with coordinates for Cu1, the program *PSSP* (Powder Structure Solution Program; P. W. Stephens & S. Pagola; http://powder.physics.sunysb.edu/programPSSP/pssp.html), using direct-space methods and the simulated annealing algorithm, was applied to determine the location of the cyano and PyzNH$_2$ ligands. The atomic positions of the PyzNH$_2$ ligand were refined as a rigid body [geometry from Cambridge Structural Database (Allen, 2002) entry AMPYRZ (Chao *et al.*, 1976)], and H-atom positions were calculated with the program *WinGX* (Farrugia, 1999). A positive-definite set of anisotropic displacement parameters could be determined for the Cu1 atom, whereas the values of the remaining non-H-atom isotropic displacement parameters were refined subject to a group constraint. U_{iso}(H) values were constrained to a value of 1.2 times the equivalent isotropic displacement parameter of the attached non-H atom.

A bond-length restraint of 1.160 (1) Å was included in order to obtain a reasonable cyano bond length, although no restraints were necessary for PyzNH$_2$ Cu—N distances or angles. The possibility of disorder in the cyano C9 and N10 atoms was investigated by switching C- and N-atom identities. It was concluded that the cyano C and N positions are ordered.

The following parameters were constrained to equivalent values for the three histograms: lattice parameters, 2θ zero error, transparency, sample displacement error, profile parameters, atomic positions, isotropic and Cu1 anisotropic displacement parameters, preferred orientation and absorption coefficients. The standard deviations of the crystallographic parameters have been corrected following the procedure reported by Scott (1983). A plot of the observed and calculated powder diffraction intensities and their difference (at the bottom) is shown in Fig. 2.

Data collection: *X'Pert Data Collector* (Philips, 2002); cell refinement: *GSAS* (Larson & Von Dreele, 2000); data reduction: *GSAS*; program(s) used to solve structure: *EXPO2004* (Altomare *et al.*, 2004) and *PSSP* (http://powder.physics.sunysb.edu/programPSSP/pssp.html); program(s) used to refine structure: *GSAS*; molecular graphics: *Mercury* (Macrae *et al.*, 2006) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3122). Services for accessing these data are described at the back of the journal.

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