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

Silvina Pagola
*College of William and Mary*

Robert D. Pike
*College of William and Mary*, rdpike@wm.edu

Kathryn deKrafft
*College of William and Mary*

Tristan A. Tronic
*College of William and Mary*

Follow this and additional works at: https://scholarworks.wm.edu/chemistrypub

Part of the Chemistry Commons

**Recommended Citation**

Pagola, Silvina; Pike, Robert D.; deKrafft, Kathryn; and Tronic, Tristan A., Poly[mu-2-aminopyrazine-kappa N-2(1): N-4-mu-cyanido-copper(I)]: a three-dimensional network from laboratory powder diffraction data (2008). *ACTA CRYSTALLOGRAPHICA SECTION C-CRYSTAL STRUCTURE COMMUNICATIONS*, 64. 10.1107/S010827010800231X

This Article is brought to you for free and open access by the Chemistry at W&M ScholarWorks. It has been accepted for inclusion in Chemistry Articles & Book Chapters by an authorized administrator of W&M ScholarWorks. For more information, please contact scholarworks@wm.edu.
Poly[μ-2-aminopyrazine-κ²N¹:N⁴-μ-cyanido-copper(I)]: a three-dimensional network from laboratory powder diffraction data

Silvina Pagola,a* Robert D. Pike,b Kathryn deKrafft b and Tristan A. Tronicb

a College of William and Mary, Physics Department, Williamsburg, VA 23187, USA, and Applied Research Center, 12050 Jefferson Avenue, Newport News, VA 23606, USA, and b College of William and Mary, Chemistry Department, Williamsburg, VA 23187, USA

Correspondence e-mail: spagol@wm.edu

Received 14 September 2007
Accepted 22 January 2008
Online 16 February 2008

In the title compound, [Cu(CN)(C₄H₅N₃)]ₙ or [Cu(μ-CN)(μ-PyzNH₂)]ₙ (PyzNH₂ is 2-aminopyrazine), the CuI center is tetrahedrally coordinated by two cyanide and two PyzNH₂ ligands. The CuI-cyano links give rise to [Cu–CN]₁ chains running along the c axis, which are bridged by bidentate PyzNH₂ 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 [Cu₆(μ-CN)₂(μ-PyzNH₂)₄].

Comment

Metal–organic networks of CuI-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 CuI-cyano units allows the preparation of new materials of a large number of structural types, where the CuI coordination often varies from 2 to 5. Furthermore, the assembly of CuI 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 CuI-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 (PyzNH₂), 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(μ-PyzNH₂)]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.Only a few 1:1 [Cu(CN)(μ-ligand)] complexes have been previously reported, all containing CuI with distorted tetrahedral coordination. In the crystal structure of [CuCN(μ-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–pdvb]₁ zigzag chains (Hanika-Heidl et al., 2003). The sheets are linked together through cyano bridges that give rise to [Cu–CN]₁ arrays of CuII atoms in [CuCN(μ-PyzNH₂)]ₙ, showing the atom-labeling scheme (H-atom labels have been omitted for clarity).

Figure 1
(a) [Cu₂(CN)₂(μ-Pyz)₄] 26-membered rings in the three-dimensional honeycomb-like arrays of [Cu(CN)(μ-Pyz)]₁. H atoms are not shown for clarity. (b) A view of the distorted tetrahedral coordination around the CuI atom in [CuCN(μ-PyzNH₂)]ₙ, showing the atom-labeling scheme (H-atom labels have been omitted for clarity).
chains running along the direction perpendicular to the plane of the sheets. This structure exhibits remarkably different Cu$^{1}$...Cu$^{1}$ 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.

$[\text{CuCN}](\mu$-2-MePyz)$_n$ (2-MePyz is 2-methylpyrazine) and $[\text{CuCN}(\mu$-4-MePym)$_n$ (4-MePym is 4-methylpyrimidine) form three-dimensional frameworks in which one-dimensional $[\text{CuCN}]_n$ chains are bridged by the linear bidentate aromatic ligands (Teichert & Sheldrick, 1999). In $[\text{CuCN}](\mu$-2-MePyz)$_n$, 22-membered rings of $[\text{CuCN}]_n(\mu$-2-MePyz)$_2$ composition form a chiral honeycomb-like two-dimensional network; these units are connected by additional 2-MePyz composition form a chiral honeycomb-like two-dimensional network made of 26-membered rings of composition $[\text{CuCN}]_n(\mu$-Pyz)$_4$. Alternatively, we can describe the three-dimensional network as formed by two interpenetrated, three-dimensional honeycomb-like arrays made of 26-membered rings of composition $[\text{CuCN}]_n(\mu$-Pyz)$_4$ (Fig. 1a). 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$^1$—N distances are 2.159 (12) and 2.134 (12) Å, whereas the cyano Cu$^1$—C and Cu$^1$—N distances are 1.920 (18) and 1.944 (19) Å, respectively, and the Cu$^1$ tetrahedral angles are 99.3 (5), 133.1 (8), 99.8 (6), 111.1 (8), 101.4 (6) and 107.2 (8)$^\circ$. 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 $[\text{CuCN}](\mu$-Pyz)$_n$ and $[\text{CuCN}(\mu$-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 $[\text{CuCN}](\mu$-PyzNH$_2$)$_n$ composition, which in turn generate the three-dimensional network of $[\text{CuCN}(\mu$-PyzNH$_2$)$_n$.

The compound crystalizes in the noncentrosymmetric and nonchiral space group $Pca_2_1$ (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 $[\text{CuCN}](\mu$-Pyz)$_n$ and $[\text{CuCN}(\mu$-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$^1$ 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

$[\text{CuCN}]_2[C_6H_5N_3]$  
$M_r$ = 184.68  
Orthorhombic, $Pca_2_1$  
$a = 11.536 (1)$ Å  
b = 6.7686 (7) Å  
c = 8.3073 (9)$ Å  
$V = 650.4 (1)$ $\text{Å}^3$  
$Z = 4$  

### Data collection

Philips Analytical X’Pert Pro MRD diffractometer  
Specimen mounting: packed powder in flat plate holder  
Specimen mounted in reflection mode  

---

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

Refinement

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

The atomic positions of the PyzNH$_2$ ligand were refined as a rigid group constraint.

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).

SP thanks to the Department of Physics of the College of William and Mary for funding. RDP gratefully acknowledges the donors of the American Chemical Society Petroleum Research Fund (grant No. 44891-B3).

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.

References