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A novel polymeric copper(I) complex with an unusual azide bridge. Synthesis and crystal structure of $[Cu(pyza)(\mu\text{-}1,1,3\text{-}N_3)]_\infty$ (pyza = pyrazinecarboxamide)

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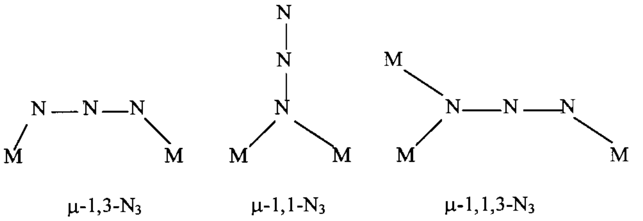
The first polymeric copper(I) complex with a μ-1,1,3-N_3 bridge $[Cu(pyza)(\mu\text{-}1,1,3\text{-}N_3)]_\infty$ (pyza = pyrazinecarboxamide) has been synthesized and characterized.

The azide ion, N_3^- is known to coordinate to metals in both terminal and bridging modes. As a bridging ligand it can link a pair of metal centers in either an end-on (μ-1,1) or an end-to-end (μ-1,3) bonded fashion. The azide ligand may link a third metal atom giving rise to a μ-1,1,3 mode (see below).



Bi-, and poly-nuclear copper azide systems are of considerable interest due to the broad range of their structural and magnetic properties.[1] However, the vast majority of studies have focused on copper(II) azide complexes.[2] On the other hand, reports on copper(I) complexes are scarce and only two structures, namely those of $[(Ph_2P)_2Cu(\mu\text{-}1,3\text{-}N_3)Cu(PPh_3)_2]$[3] and $[Cu(\mu\text{-pyz-}N,N)(\mu\text{-}1,3\text{-}N_3)]_n$ (pyz = pyrazine),[4] which exhibit μ-1,3-N_3 bridges, and that of $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}1,1\text{-}N_3)][ClO_4]\cdot Et_2O$ [Ph_2Ppypz = 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine] which possesses a μ-1,1-N_3 bridge,[5] have been established. To our knowledge, there is as yet no known example of a polynuclear copper(I) complex with a μ-1,1,3-N_3 bridge. We report here the first structure of this kind in the polymeric copper(I) complex $[Cu(pyza)(\mu\text{-}1,1,3\text{-}N_3)]_\infty$ (pyza = pyrazinecarboxamide).

The reaction between copper(I) azide and pyrazinecarboxamide resulted in the formation of a deep red-brown complex in high yield.† Copper(I) azide has been rarely used in coordination chemistry due to its insolubility in common solvents. Significantly, concentrated solutions of sodium or potassium azide can be used to dissolve polymeric $Cu^I(N_3)$. Importantly, using this procedure allowed us to avoid the isolation of any Cu^{II} impurities, and single crystals of $[Cu(N_3)L]_\infty$‡ were grown by mixing with pyrazinecarboxamide in EtOH. This synthesis was found to be reproducible.

The IR spectrum of $[Cu(pyza)(\mu\text{-}1,1,3\text{-}N_3)]_\infty$ shows the characteristic asymmetric N_3 stretching vibrations at 2070 cm^{-1}, which is substantially higher than that of the Ph_2Ppypz complex with μ-1,1-N_3 bridges (2037 cm^{-1}) as well as those of the binuclear copper(I) complex of Ph_3P (2055 cm^{-1}) or the polymeric complex of pyrazine (2041 cm^{-1}),[4] both with μ-1,3-N_3 bridges. This value, however, along with the symmetric N_3 stretch band at 1322 cm^{-1} is indicative of an asymmetric azido ligand. The carbonyl and amide stretching vibrations appear almost at the same positions as in the spectrum of free pyrazinecarboxamide, suggesting that the $CONH_2$ group is not involved in bond formation.

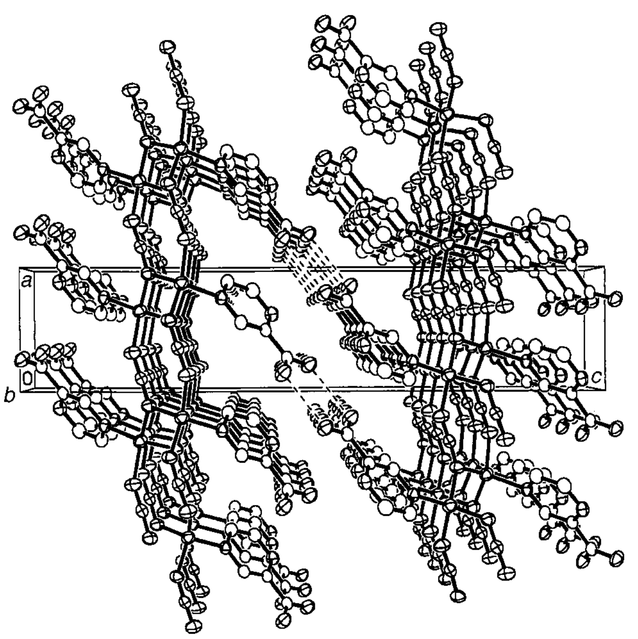


Fig. 1 A view of $[Cu(N_3)(L)]_\infty$ down the *b* axis showing the arrangement of the Cu^I–azido-sublattice as 2-D layers oriented normal to the *c* axis. The 2-D layers are connected *via* N–H···O hydrogen bonds formed by adjacent pyrazineamide ligands (L).

The polymer $[CuL(N_3)]_\infty$ exists as a 3-D network consisting of sheets of $[Cu^I(N_3)]_\infty$ linked by pyrazinecarboxamide (Fig. 1). Within the $[Cu(N_3)]_\infty$ sheets each copper(I) center is coordinated by three symmetry-related azide ligands, thus the azido groups behave as μ-1,1,3 bridges forming a 2-D layer structure oriented parallel to the *ab* plane of the monoclinic unit cell. This arrangement leads to the formation of ten-membered Cu–NNN–Cu–N–Cu–NNN rings (Fig. 2). Owing to the rigid rod-like nature of $(N_3)^-$ each ten-membered ring adopts a pseudo-chair conformation, similar to that found in the structure of $[Cu_2(NCS)_2(pyz)]_\infty$.[6] The remaining fourth coordination site of each Cu^I center is occupied by a nitrogen atom [N(2)] of a pyrazinecarboxamide ligand. The 2-D layers are connected *via* N–H···O hydrogen bonds formed by adjacent pyrazinecarboxamide molecules.

The structural motif observed in the complex $[Cu(N_3)L]_\infty$ represents both a new arrangement of polymeric $Cu^I(N_3)$ and also a new 3-D network. The preparation of this compound

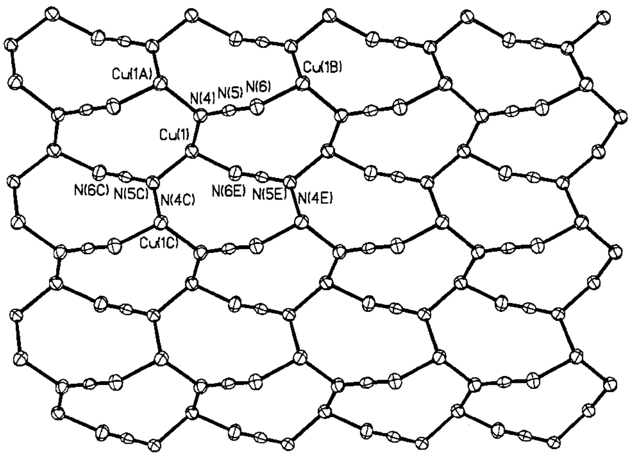


Fig. 2 A view of the $[Cu^{I}(N_3)]_{\infty}$ sheet showing the ten-membered pseudo-cyclohexane rings. Selected bond lengths (Å) and angles (°): Cu(1)···Cu(1A)[Cu(1C)] 3.484(1), Cu(1)···Cu(1B) 5.533(2), Cu(1)–N(4) 2.098(3); Cu(1)–N(4C) 2.030(3), Cu(1)–N(6E) 2.007(4), not shown: Cu(1)–N(2) 2.067(3) and N(3)···O(1D) 2.890(5); N(2)–Cu(1)–N(4) 101.60(14), N(4)–Cu(1)–N(4C) 116.07(7), N(4C)–Cu(1)–N(2) 107.33(13), N(2)–Cu(1)–N(6E) 114.2(2), N(4C)–Cu(1)–N(6E) 114.5(2), N(4)–Cu(1)–N(6E) 102.63(14) [symmetry codes: A $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; B $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; C $\frac{3}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$; D $3-x, 1-y, -z$; E $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$].

illustrates a new and potentially versatile approach to the construction of uncharged inorganic coordination networks and we are currently pursuing this methodology towards the synthesis of such new materials.

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Notes and references

† Preparation of $[Cu(pyza)(\mu\text{-}1,1,3\text{-}N_3)]_{\infty}$. To an aqueous suspension of CuN_3 (2 mmol) a saturated solution of NaN_3 was added until a clear solution was obtained. Pyrazinecarboxamide (3 mmol) dissolved in ethanol (10 ml) was then added and the final mixture allowed to stand for several days to deposit deep red-brown needle-like crystals of the complex. Yield, *ca.* 80% [Found (Calc.): C, 27.1 (26.26); H, 2.3 (2.21); N, 36.5 (36.73); Cu, 27.2 (27.78%)]. IR (KBr disc): $\nu(N_3)$ 2070, 1322 cm^{-1}. Electronic spectrum (solid Nujol mull): 409 (br), 628 (br) nm ($Cu^{I}\rightarrow L$ CT).

‡ Crystal data. $[Cu(pyza)(\mu\text{-}1,1,3\text{-}N_3)]_{\infty}$, $C_5H_5N_6OCu$, $M = 228.69$, monoclinic, space group $P2_1/n$, $a = 5.528(2)$, $b = 5.442(2)$, $c = 25.999(9)$ Å, $\beta = 90.59(3)°$, $V = 782.1(4)$ Å^3, $Z = 4$, μ(Mo-Kα) = 2.757 mm^{-1}, $T = 298(2)$ K. 1543 unique reflections ($R_{int} = 0.0242$) were collected. At final convergence $R1$ [1296 data with $I > 2\sigma(I)$] = 0.0427, $wR2$ (all 1528 data) = 0.1132 for 125 parameters. CCDC reference number 186/1396. See http://www.rsc.org/suppdata/dt/1999/1535/ for crystallographic files in .cif format.

1 E. I. Solomon, M. J. Baldwin and M. D. Lowery, *Chem. Rev.*, 1992, **92**, 521.

2 See for example, (*a*) L. K. Thompson, S. S. Tandon and M. E. Manuel, *Inorg. Chem.*, 1995, **34**, 2356; (*b*) J. H. Satcher, Jun., M. W. Droege, T. J. R. Weakly and R. T. Taylor, *Inorg. Chem.*, 1995, **34**, 3317; (*c*) A. Escuer, R. Vicente, F. A. Mautner and M. A. S. Goher, *Inorg. Chem.*, 1997, **36**, 1233.

3 R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 1971, **10**, 1289.

4 M. A. S. Goher and F. A. Mautner, *Polyhedron*, in the press.

5 S.-M. Kuang, Z.-Z. Zhang, Q.-G. Wang and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1997, 4477.

6 A. J. Blake, N. R. Champness, M. Crew, L. R. Hannon, S. Parsons and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 1998, 1533.

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