

A heterometallic polymeric complex: [Cu₂(N₃)₂(medpt)₂{Ni(CN)₄}]_n [medpt is bis(3-aminopropyl)methylamine]¹

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The structure of the title compound, *catena*-poly[[di- μ -azido- $\kappa^4 N^1: N^1$ -bis[[bis(3-aminopropyl)methylamine- $\kappa^3 N$]copper(II)]]- μ -cyano-[dicyanonickel(II)]- μ -cyano], [Cu₂(N₃)₂(medpt)₂{Ni(CN)₄}]_n [medpt is bis(3-aminopropyl)methylamine, C₇H₁₉N₂] or [Cu₂Ni(CN)₄(N₃)₂(C₇H₁₉N₃)₂]_n, is a one-dimensional heterometallic covalent chain where Ni(CN)₄²⁻ functions as a molecular ion bridge. The Ni atom sits on the centre of inversion. The chain undergoes hydrogen-bonding interactions, forming a three-dimensional supramolecular network.

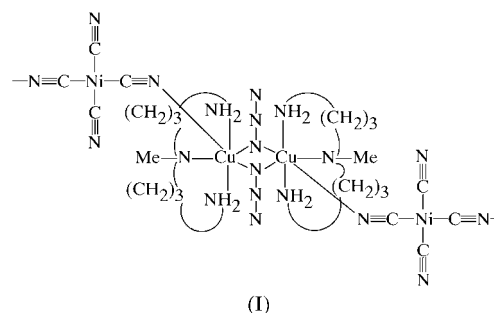
Comment

There are currently several successful examples of self-assembly towards the construction of cyano-bridged complexes, in which cyanometallate anions, *e.g.* Ag(CN)₂⁻, Cu(CN)₃²⁻, Au(CN)₄⁻, M(CN)₄²⁻ (*M* is Ni^{II}, Pt^{II} and Cd^{II}) and M(CN)₆³⁻ (*M* is Cr^{III}, Fe^{III}, *etc.*) (Iwamoto, 1996; Bowmaker *et al.*, 1998; Chesnut & Zubieta, 1998; Falvello & Tomas, 1999; Mondal *et al.*, 2000; Du *et al.*, 2000; Niel *et al.*, 2001; Shorrocks *et al.*, 2003; Colacio *et al.*, 2003), behave as bridging moieties to build a multidimensional structure with a second coordination centre, and the resulting complexes demonstrate unique magnetic, host-guest and other properties.

One of the most prominent characteristics of CN⁻ is its ability to act as either a terminal or a bridging ligand. When it acts as a bridging ligand between metal atoms, it usually gives rise to polymeric compounds with a one-, two- or three-dimensional network and often containing guest solvent molecules and/or a complementary ligand. Usually, the second coordination centres are transition metal ions, since $\sigma \rightarrow \pi$ back-bonding stabilizes the resulting complex (Muga *et al.*, 1997). The rigidity and stability of such frameworks allow for shape- and size-selective inclusion of organic solvents, water

molecules, aromatic amines, *etc.*, to fill up the void space, thus stabilizing the crystal structure. Maji *et al.* (2001) reported a novel porous framework, [[Cu₂(medpt)₂Ni(CN)₄](ClO₄)₂].2.5H₂O, where all the CN groups of the Ni(CN)₄²⁻ anion are involved in bridging. This compound retains single crystallinity upon removal of guest water molecules and the dehydrated species selectively binds organic molecules.

With regard to the Hoffman-type and analogous inclusion compounds, the Hoffman-en-type network [Cd(en)Ni(CN)₄].2*G* (*en* is ethylenediamine; *G* is C₄H₄N, C₄H₄S or C₆H₆) has a host structure similar to that of the Hoffman-type network [Cd(NH₃)₂Ni(CN)₄].2*G* (*G* is C₄H₅N, C₄H₄S, C₆H₆ or PhNH₂) (Iwamoto *et al.*, 1974). Similar behaviour was reported for [Ni(en)₂Ni(CN)₄].2.5H₂O (Černák *et al.*, 1990), where the role of the water molecules was interpreted using a molecular mechanics investigation. Yuge & Iwamoto (1994) reported phenol and aniline as guest molecules accommodated among [M(en)₂Ni(CN)₄]_n chains (*M* is Ni, Cu, Zn or Cd). Moreover, the azide ligand has been used extensively to design molecular-based magnets displaying a huge structural variety, spanning dinuclear, tetranuclear, cubane, and one-, two- and three-dimensional compounds (Ribas *et al.*, 1999). During our ongoing research on mixed bridging ligands, we synthesized the title compound, (I), and this paper reports the synthesis and crystal structure of this novel one-dimensional heterometallic polymeric complex, [Cu₂(medpt)₂(N₃)₂Ni(CN)₄]_n [medpt is bis(3-aminopropyl)methylamine].



The present X-ray crystal-structure determination reveals that (I) is a one-dimensional heterometallic chain (Fig. 1). In the chain, each pseudo-octahedral Cu^{II} centre is linked to another Cu^{II} centre by a double end-on bridging azide ligand, and these dimeric units are linked alternately by the *trans* cyanide group of a square-planar Ni(CN)₄²⁻ dianion to form a one-dimensional heterometallic chain along the *c* axis. The Ni^{II} atom sits on the inversion centre.

All donor N atoms of the triamine (atoms N5, N6 and N7) and one N atom (N1) from the μ -(1,1)-bridging azide ligand form the equatorial plane, where the Cu1–N bond lengths are in the range 2.006 (4)–2.130 (4) Å. The *trans* axial sites of both Cu^{II} centres are occupied by atom N8 of a cyanide group of the Ni(CN)₄²⁻ anion [Cu1–N8 = 2.223 (4) Å] and another N atom [N1ⁱ; symmetry code: (i) 1 – *x*, 2 – *y*, 1 – *z*] from the end-on bridging azide ligand, with a long Cu1–N bond distance [3.013 (4) Å]. Similarly long Cu–N(azide) distances are also observed in several other systems (Goher *et al.*, 1998; Mautner & Goher, 1994). The Cu1...Cu1 and Cu1...Ni1

¹ Contribution No. IND44.

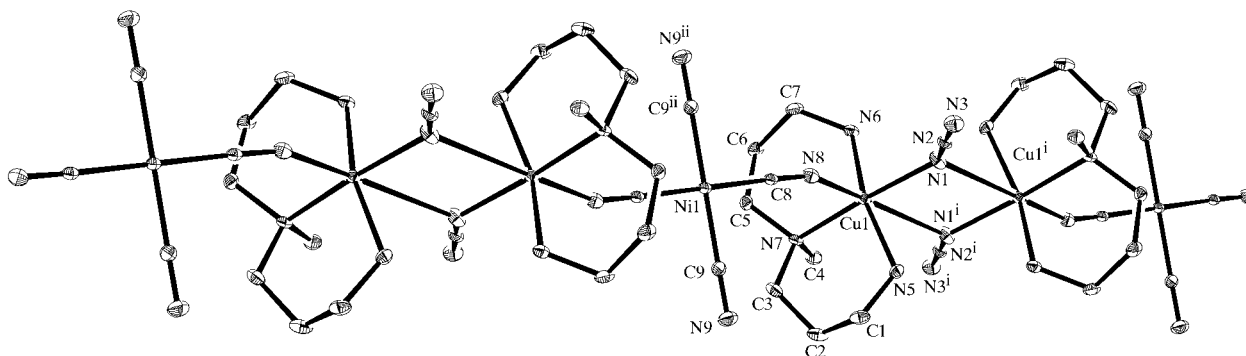


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids. [Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $-x, 2 - y, -z$]

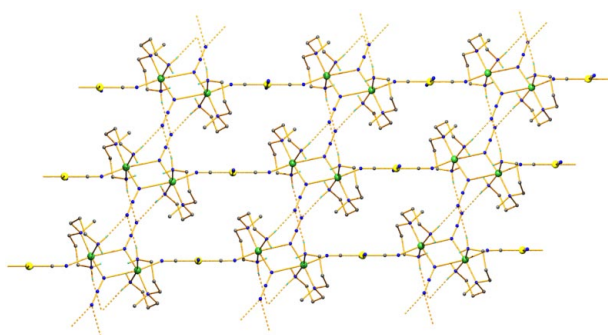


Figure 2
The formation of two-dimensional sheets in the bc plane via bifurcated hydrogen bonds joining the chains through atom N3 of the bridging azide ligand.

distances are 3.987 and 5.103 Å, respectively. At the Cu^{II} centre, both six-membered chelate rings formed by the medpt ligand possess chair conformations.

When these heterometallic chains line up in the bc plane, bifurcated hydrogen bonds (Table 2) from atom N3 join the parallel chains, resulting in a two-dimensional sheet (Fig. 2)

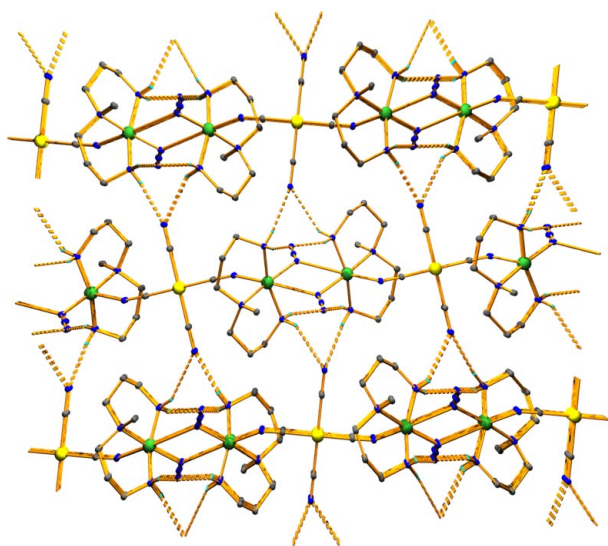


Figure 3
The supramolecular three-dimensional continuum formed by joining the two-dimensional sheets through bifurcated hydrogen bonds generated from the pendant N9 atom of the CN ligand.

with graph-set motif $R_2^1(8)$. The H atoms bound to atoms N6 and N5 are also involved in a bifurcated hydrogen-bonding system with the terminal cyano atom N9. This hydrogen-bonding motif, with graph set $R_4^2(8)$, joins the two-dimensional sheets from above and below to form a three-dimensional supramolecular array (Fig. 3).

Experimental

A methanol solution (5 ml) of medpt (2 mmol, 0.290 g) was added dropwise to an aqueous solution (10 ml) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2 mmol, 0.741 g). To the resulting deep-blue solution, $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (1 mmol, 0.276 g) dissolved in water (5 ml) was added. Instantaneously, a crystalline sky-blue complex separated out and was treated with an aqueous solution (5 ml) of NaN_3 (1 mmol, 0.065 g), resulting in a deep-green solution. This was filtered and the filtrate was kept in a CaCl_2 desiccator (yield: 60%). Found: C 32.46, H 5.64, N 33.52, Cu 19.56%; calculated for $\text{C}_{18}\text{H}_{38}\text{Cu}_2\text{N}_{16}\text{Ni}$: C 32.51, H 5.76, N 33.71, Cu 19.11%. Spectroscopic data, IR (ν , cm^{-1}): 3178, 3270, 3300 (N–H), 2859, 2929, 2893, 2963 (CH_2), 2117, 2137 (N₃), 2036 (CN).

Crystal data

$[\text{Cu}_2\text{Ni}(\text{CN})_4(\text{N}_3)_2(\text{C}_7\text{H}_{19}\text{N}_3)_2]$
 $M_r = 664.43$
 Monoclinic, $P2_1/n$
 $a = 7.4094$ (9) Å
 $b = 14.5472$ (16) Å
 $c = 12.8512$ (19) Å
 $\beta = 97.757$ (11)°
 $V = 1372.5$ (3) Å³
 $Z = 2$

$D_x = 1.608$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 38 reflections
 $\theta = 2.8$ – 20.0°
 $\mu = 2.26$ mm⁻¹
 $T = 160$ (2) K
 Plate, green
 0.38 × 0.18 × 0.08 mm

Data collection

Bruker P4 diffractometer
 ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.595$, $T_{\max} = 0.835$
 3235 measured reflections
 2404 independent reflections
 1791 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -8 \rightarrow 1$
 $k = -1 \rightarrow 17$
 $l = -15 \rightarrow 15$
 3 standard reflections every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.043$
 $wR(F^2) = 0.115$
 $S = 1.04$
 2404 reflections
 169 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 3.3185P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.64$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.72$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Cu1—N5	2.006 (4)	Cu1—N8	2.222 (4)
Cu1—N6	2.009 (4)	Cu1—N1 ⁱ	3.013 (4)
Cu1—N1	2.075 (4)	Ni1—C8	1.868 (4)
Cu1—N7	2.130 (3)	Ni1—C9	1.871 (5)
N5—Cu1—N6	162.23 (16)	N1 ⁱ —Cu1—N8	171.33 (13)
N5—Cu1—N1	86.62 (15)	Cu1—N1—Cu1 ⁱ	101.55 (14)
N6—Cu1—N1	87.43 (15)	N3—N2—N1	177.1 (5)
N5—Cu1—N7	93.06 (14)	C1—N5—Cu1	121.6 (3)
N6—Cu1—N7	90.63 (14)	C7—N6—Cu1	116.6 (3)
N1—Cu1—N7	172.35 (15)	C4—N7—Cu1	109.2 (3)
N5—Cu1—N8	98.08 (15)	C3—N7—Cu1	113.6 (3)
N6—Cu1—N8	99.19 (15)	C5—N7—Cu1	112.3 (3)
N1—Cu1—N8	96.12 (15)	C8 ⁱⁱ —Ni1—C9 ⁱⁱ	89.23 (18)
N7—Cu1—N8	91.50 (14)	C8—Ni1—C9 ⁱⁱ	90.77 (18)
N2—N1—Cu1	123.2 (3)	C8 ⁱⁱ —Ni1—C9	90.77 (18)
N1—Cu1—N1 ⁱ	78.45 (13)	C8—Ni1—C9	89.23 (18)
N1 ⁱ —Cu1—N5	75.01 (14)	N8—C8—Ni1	177.9 (4)
N1 ⁱ —Cu1—N6	87.41 (13)	N9—C9—Ni1	179.3 (4)
N1 ⁱ —Cu1—N7	94.07 (13)	C8—N8—Cu1	155.0 (3)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N5—H5A...N9 ⁱ	0.90	2.56	3.298 (6)	140
N5—H5B...N3 ⁱⁱ	0.90	2.62	3.489 (5)	163
N6—H6A...N9 ⁱⁱⁱ	0.90	2.30	3.154 (6)	158
N6—H6B...N3 ^{iv}	0.90	2.37	3.252 (5)	167

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

H atoms bonded to C and N atoms were placed in geometrically calculated positions, with C—H distances in the range 0.97–0.99 Å and N—H distances of 0.90 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N}) [1.5U_{\text{eq}}(\text{C})$ for the methyl H atoms].

Data collection: XSCANS (Bruker, 1999); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: PLATON (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1710). Services for accessing these data are described at the back of the journal.

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