Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.101$
$S = 0.744$
6942 reflections
524 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.61$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0060 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.023 (13)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—O1	1.918 (3)	Cu2—O3	1.941 (3)
Cu1—N3	2.004 (4)	Cu2—N5	1.992 (4)
Cu1—N2	2.020 (4)	Cu2—N6	1.997 (4)
Cu1—N1	2.033 (4)	Cu2—N4	2.031 (4)
Cu1—O1*W*	2.234 (4)	Cu2—O2*W*	2.382 (3)
C16—N3—C13—C14	8.5 (7)	C33—N6—C30—C31	38.0 (5)
N3—C13—C14—C15	−29.2 (8)	N6—C30—C31—C32	−40.2 (5)
C13—C14—C15—C16	38.3 (9)	C30—C31—C32—C33	27.0 (5)
C13—N3—C16—C15	15.3 (5)	C30—N6—C33—C32	−20.6 (5)
C14—C15—C16—N3	−32.8 (7)	C31—C32—C33—N6	−4.2 (5)

The absolute structure was determined from the known absolute configuration of one of the ligands (L-proline) in the complex. The Flack (1983) parameter was refined without Friedel data. In the development of the molecular model from X-ray data, H atoms were located in difference Fourier maps and included in the model at calculated positions and allowed to refine using a riding model, except for the water H atoms (on O4*W*), which could not be found. $U_{\rm iso}$ values for H atoms were assigned values 120% of the $U_{\rm eq}$ values of the attached non-H atoms or 150% in the case of water H atoms.

Data collection: *P*3 *Software* (Siemens, 1989). Cell refinement: *P*3 *Software*. Data reduction: *XDISK* in *P*3 *Software*. Program(s) used to solve structure: *SHELXS*93 (Sheldrick, 1993). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *P*3 *Software*. Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1195). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1243–1246

$[Cu_2\{$1,4-bis[(3-methyl-2-pyridyl)amino]phthalazine–H$\}(N_3)_3]$ at 40 K

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Abstract

The structure of the title compound, μ-azido-1:2κ^2N^1-[μ-4-(3-methyl-2-pyridyl-2κN-amino)-1-(3-methyl-2-pyridyl-1κN-imino)-1,2-dihydrophthalazin-2-yl-1:2κ^2N^2:N^3]-bis[(azido-κN^1)copper(II)], $[Cu_2(C_{20}H_{17}N_6)(N_3)_3]$, (I), determined from data recorded at 40 (1) K using a new open-flow He gas cryostat, is presented here as part of an extended study program on dicopper(II) azide-bridged compounds. Each pair of Cu$^{\rm II}$ centres in (I) is equatorially bridged by a μ_2-1,1-azide, with a bridge angle of 107.2 (1)°. The dinuclear centres form tetranuclear clusters through two μ_2-1,3-azide bridges, which in turn form chains along the *a* axis. Two C—

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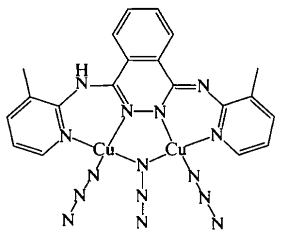
H···N intermolecular interactions interlink these chains along the [110] and [1$\bar{1}$0] directions.

Comment

The measurement of X-ray diffraction data at temperatures lower than 80 K has up to now required the use of closed-cycle helium refrigerators. Although this has become a well established technique for temperatures down to 10 K (Larsen, 1995; Copley *et al.*, 1997, and references therein), it has its drawbacks, *i.e.* the equipment is expensive, it is not obtainable as an 'off-the-shelf' product and it needs considerably more maintenance than an N_2 open-flow device. Moreover, the sample is not visible during data collection, being mounted inside one, two or three evacuated beryllium heat shrouds. A natural extension of these two approaches would be a combination of them, *i.e.* an open-flow He gas cryostat. The two main limitations with this kind of cooling device are the cost of He gas and the prevention of frosting. The use of CCD area detectors, which reduces data collection times dramatically, brings the cost of the He gas used into the range of other consumable items. The problems associated with frosting have been addressed in the careful design of a new temperature-controlled cryostat (Cosier, 1998).

Herein, as the first example of the capabilities of the new device, we describe the 40 K structure of $[Cu_2\{1,4\text{-bis(3-methyl-2-pyridyl)aminophthalazine} - H\}(N_3)_3]$, (I), determined from single-crystal X-ray data recorded using this controllable Oxford Cryosystems open-flow He gas cryostat combined with a diffractometer equipped with a Bruker SMART CCD area detector. The cryostat comprises a small closed-cycle helium refrigerator which is used to cool down a heating stage. He gas flowing around this stage is cooled down and finally escapes through a specially designed nozzle into the atmosphere and onto the sample. A temperature calibration using the known phase transition of terbium vanadate (Will *et al.*, 1972) indicates that the minimum temperature currently attainable is 30 (1) K. The total data collection time for the present experiment was 8 h and the amount of He gas used was about 16 l at 200 bar (1 bar = 10^5 Pa).



(I)

The structure of (I) was determined as part of an extended study program on dicopper azide-bridged compounds (Thompson & Tandon, 1996; Tandon *et al.*, 1994, 1995; Thompson *et al.*, 1995).

The molecular structure of (I) (Fig. 1) shows that each pair of five-coordinate copper(II) centres is bridged equatorially by an intramolecular μ_2-1,1-azide, with a bridge angle of 107.2 (1)°. These dinuclear centres form tetranuclear clusters through two μ_2-1,3-azide bridges [Cu1—N7—N8—N9···Cu2^{i} and Cu1^{i}—N7^{i}—N8^{i}—N9^{i}···Cu2; symmetry code: (i) $-x$, $2-y$, $-z$] *via* axial interactions [Cu2···N9^{i} 2.349 (2) Å]. The five-coordination of Cu1 is completed by a Cu1···N12^{ii} axial interaction of 2.586 (2) Å [symmetry code: (ii) $1-x$, $2-y$, $-z$], which involves the same azide that forms the μ_2-1,1-azide bridge between Cu1 and Cu2, and forms chains of tetranuclear clusters along the *a* axis (Fig. 2). These chains are interlinked along the [110] and [1$\bar{1}$0] directions by two C—H···N intermolecular interactions (Table 2). The ligand is slightly folded, with dihedral angles between the phthalazine mean plane and the pyridine mean planes of 33.6 (1) and 26.4 (1)°. The basal N_4 sets are almost planar, with N—Cu—N angles ranging from 84.7 (1) to 95.2 (1)°, but while Cu1 lies close to its surrounding N_4 mean plane [Cu1···N_4 0.015 (1) Å], Cu2 is slightly displaced from its plane, by 0.157 (1) Å towards the axial azide N9^{i} atom.

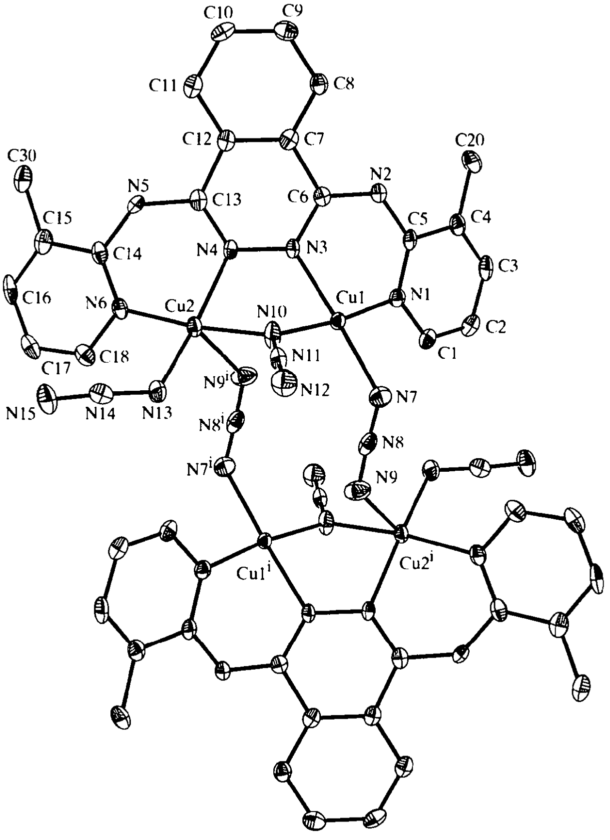


Fig. 1. *SHELXTL* (Siemens, 1995) drawing of (I) showing 70% probability displacement ellipsoids for non-H atoms. H atoms bound to carbon have been omitted for clarity.

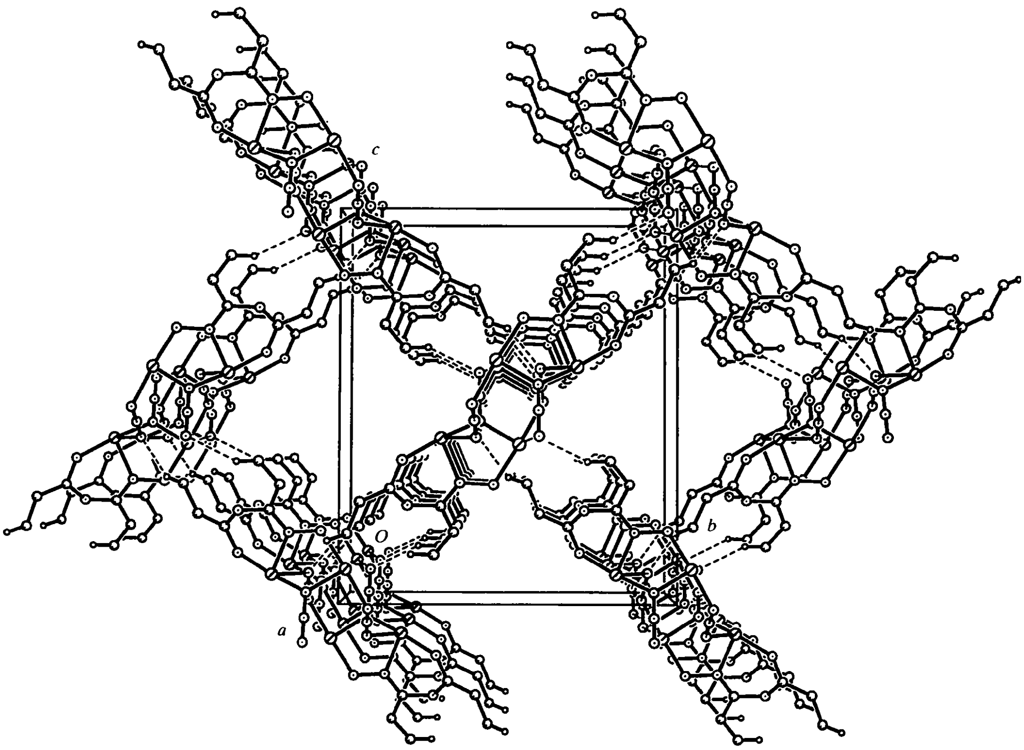


Fig. 2. View down the *a* axis showing the chains of tetranuclear clusters along the *a* axis joined by hydrogen bonds along [011] and [0$\bar{1}$1]. Atoms not involved have been omitted for clarity.

It would be expected that complex (I) should exhibit magnetic properties which could be modelled adequately by the Bleaney–Bowers equation (Bleaney & Bowers, 1952) for the magnetic susceptibility of a copper(II) binuclear centre. However, attempts to fit the experimental variable-temperature magnetic data to this equation using normal values of the parameters proved impossible (Thompson, 1998). Since the magnetic coupling in a μ_2-1,1-azide-bridged system has been shown to be dependent on the azide-bridge angle (Thompson & Tandon, 1996), one possible explanation for the anomalous behaviour is that the azide-bridge angle changes over the temperature range in which the magnetic data were collected. To investigate whether a structural change is responsible for this unusual magnetic behaviour of (I), X-ray diffraction data should be collected at several temperatures in order to map these structural changes. Variable-temperature data collections can take weeks using a standard four-circle diffractometer fitted with a Displex refrigerator or they are limited to temperatures above 80 K using an N_2 cooler. The new helium device and a CCD diffractometer make a very powerful combination and allow rapid data collections in the critical temperature range for these magnetic complexes. The unit-cell volume of (I) shows only a 1.8% reduction between room temperature and 40 K, which would indicate very small or even no change between the structures at these temperatures. The results of the complete variable-temperature magneto-structural study are being prepared for publication.

Experimental

$Cu(CH_3COO)_2 \cdot H_2O$ (0.300 g, 1.50 mmol) was dissolved in hot methanol (20 ml) and added to a solution of 1,4-bis-[(3-methyl-2-pyridyl)amino]phthalazine (0.100 g, 0.3 mmol) in hot dichloromethane (25 ml) and the mixture refluxed for 5 min. A solution of NaN_3 (0.050 g, 0.77 mmol) dissolved in hot methanol (10 ml) was added dropwise with stirring and the resulting dark-khaki-green solution heated for a further 2 min and filtered hot. Dark-red crystals, suitable for structural studies, formed on standing overnight. The crystals were filtered off, washed with a dichloromethane/methanol mixture and air dried (yield 70%).

Crystal data

$[Cu_2(C_{20}H_{17}N_6)(N_3)_3]$
M_r = 594.57
Monoclinic
$P2_1/c$
a = 8.904 (2) Å
b = 14.657 (3) Å
c = 17.190 (3) Å
β = 92.266 (5)°
V = 2241.6 (8) Å^3
Z = 4
D_x = 1.762 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 362 reflections
θ = 13.62–23.63°
μ = 1.944 mm^{-1}
T = 40 (2) K
Irregular prism
0.3 × 0.2 × 0.2 mm
Dark red

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan using *SADABS* (Sheldrick, 1996; Blessing, 1995)
$T_{min} = 0.583$, $T_{max} = 0.678$

10 681 measured reflections
3983 independent reflections
3363 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 26.10°$
$h = -10 \rightarrow 10$
$k = -18 \rightarrow 17$
$l = -20 \rightarrow 17$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.069$
$S = 1.056$
3980 reflections
339 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 1.5415P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu2—N13	1.968 (2)	Cu1—N12^{ii}	2.586 (2)
Cu2—N10	1.972 (2)	N3—N4	1.392 (3)
Cu2—N6	1.976 (2)	N7—N8	1.197 (3)
Cu2—N4	2.027 (2)	N8—N9	1.173 (3)
Cu2—N9^{i}	2.349 (2)	N9—Cu2^{i}	2.349 (2)
Cu1—N3	1.966 (2)	N10—N11	1.219 (3)
Cu1—N1	1.983 (2)	N11—N12	1.154 (3)
Cu1—N7	1.991 (2)	N13—N14	1.215 (3)
Cu1—N10	1.997 (2)	N14—N15	1.162 (3)
N13—Cu2—N10	89.76 (9)	N3—Cu1—N12^{ii}	96.17 (8)
N13—Cu2—N6	95.20 (9)	N1—Cu1—N12^{ii}	96.63 (8)
N10—Cu2—N6	173.27 (9)	N7—Cu1—N12^{ii}	84.44 (8)
N13—Cu2—N4	164.90 (9)	N10—Cu1—N12^{ii}	81.29 (9)
N10—Cu2—N4	84.74 (8)	N4—N3—Cu1	117.51 (14)
N6—Cu2—N4	89.33 (8)	N3—N4—Cu2	116.17 (14)
N13—Cu2—N9^{i}	105.15 (9)	N8—N7—Cu1	123.1 (2)
N10—Cu2—N9^{i}	85.52 (9)	N9—N8—N7	176.5 (3)
N6—Cu2—N9^{i}	97.53 (9)	N8—N9—Cu2^{i}	129.4 (2)
N4—Cu2—N9^{i}	88.47 (8)	N11—N10—Cu2	124.2 (2)
N3—Cu1—N1	88.44 (8)	N11—N10—Cu1	126.7 (2)
N3—Cu1—N7	176.88 (9)	Cu2—N10—Cu1	107.23 (10)
N1—Cu1—N7	94.53 (9)	N12—N11—N10	179.2 (3)
N3—Cu1—N10	85.31 (9)	N14—N13—Cu2	123.2 (2)
N1—Cu1—N10	173.15 (9)	N15—N14—N13	176.8 (3)
N7—Cu1—N10	91.77 (9)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H111···N12^{i}	0.95	2.395	3.266 (4)	152.3
C30—H302···N9^{i}	0.98	2.541	3.441 (4)	152.7

Symmetry code: (i) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

H atoms were allowed to ride on their parent C atoms with $U_{iso}(H) = xU_{eq}(C)$, with $x = 1.5$ for methyl H atoms and $x = 1.2$ for the other H atoms. Idealized C—H distances were fixed at 0.95 Å, while idealized tertiary C—H distances were fixed at 0.98 Å. The idealized CH_3 groups were allowed to rotate about their *X*—C bond. The only H atom bonded to an N atom was located from a difference Fourier map, its coordinates were refined and its U_{iso} value kept at $1.2U_{eq}(N)$.

Data collection: *SMART* (Siemens, 1996*a*). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1996*b*). Program(s) used to solve structure: *SHELXTL* (Siemens, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1313). Services for accessing these data are described at the back of the journal.

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