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catena-Poly[[bis(2-methylpyrazine-κN^4)copper(II)]-di-μ-bromido]

Robert T. Butcher,[a] Brendan Twamley[b] and Mark M. Turnbull[a]*

[a]Carlson School of Chemistry and Biochemistry, Clark University, 950 Main St., Worcester, MA 01610, USA, and [b]Dept. of Chemistry, Trinity College Dublin, The University of Dublin, College Green, Dublin 2, Ireland. *Correspondence e-mail: mturnbull@clarku.edu

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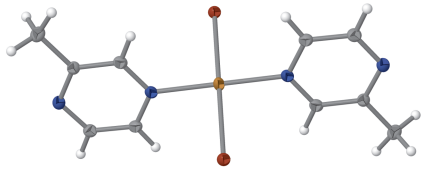
Keywords: crystal structure; copper(II); bihalide bridged chain; methylpyrazine.

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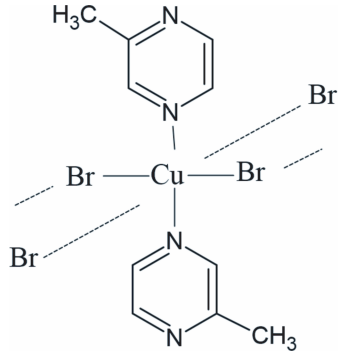
Structural data: full structural data are available from iucrdata.iucr.org

The reaction of 2-methylpyrazine with copper(II) bromide *via* gel diffusion yielded crystals of the title compound, $[CuBr_2(C_5H_6N_2)_2]_n$. The compound crystallizes in the monoclinic $P2_1/n$ space group and the metal atom (site symmetry $\overline{1}$) adopts a square-planar $CuBr_2N_2$ coordination geometry. Short Cu···Br contacts, nearly perpendicular to the Cu coordination plane, link the molecules into chains propagating parallel to the *a*-axis direction, which are well separated by the bulk of the methylpyrazine ligands.

3D view



Chemical scheme



Structure description

Pyrazine has been used ubiquitously in coordination chemistry, in particular with Cu^{II} (Landee & Turnbull, 2013). The two nitrogen atoms provide a linear coordination bridge for good control of geometry in coordination polymers. Substituted pyrazine ligands have also been used frequently, but may introduce a change in local geometry depending upon the number and position of the substituents. In cases where the substituted pyrazine is monodentate, coordination occurs uniformly to the distal nitrogen atom, except in cases where the substituent may coordinate in which case chelation is observed to the proximal nitrogen atom, as in the case of pyrazine-2-carboxylate (Klein *et al.*, 1981, 1982; Konar *et al.*, 2014).

2-Methylpyrazine is one of the most commonly employed monosubstituted pyrazine ligands with more than eighty complexes of first row transition metals alone; fifty of those involve copper (Groom *et al.*, 2016). Cu^{II} coordinates to methylpyrazine in both bridging (Otieno *et al.*, 1993; Abu-Youssef *et al.*, 2008) and terminal (Maekawa *et al.*, 1992; Navas *et al.*, 1993; Amaral *et al.*, 2001; Otieno *et al.*, 2002; Manson *et al.*, 2008; Barquín *et al.*, 2010; Araujo-Martinez *et al.*, 2023) modes, again with the terminal methylpyrazine molecules coordinated through the distal nitrogen atom. We find only three examples in the literature of terminal methylpyrazine molecules coordinated through the proximal

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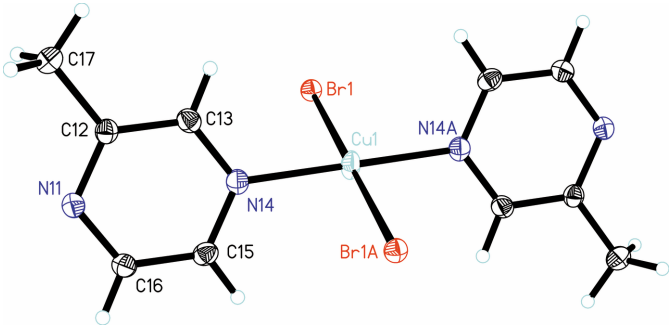


Figure 1
The molecular unit drawn as 50% probability ellipsoids. Hydrogen atoms are shown as spheres of arbitrary size. Only the asymmetric unit and copper coordination sphere are labelled. Atoms with suffix A are generated by the symmetry operation −x + 1, −y, −z + 1.

nitrogen atom, namely bis(μ-iodo)bis(2-methylpyrazine)bis-(triphenylphosphine)dicopper(I) and its triphenylarsine equivalent (Kikuchi *et al.*, 2026), plus the silver(I) complex *catena*-[(μ2-methylpyrazine)bis(μ_2-tricyanomethanide)bis-(methylpyrazine)disilver(I)] (Abrahams *et al.*, 2003).

In the course of our investigations of complexes of substituted pyrazines with Cu^{II}, we prepared the title compound, which crystallizes in the monoclinic space group $P2_1/n$ with the Cu^{II} ion located on an inversion centre. The molecular unit is shown in Fig. 1. The Cu1—N14 bond length is 2.021 (2) Å (Table 1) and comparable to known compounds with methylpyrazine coordinated to the distal nitrogen atom (Otieno *et al.*, 2002; Araujo-Martinez *et al.*, 2023) but somewhat shorter (∼0.05 Å) than the equivalent bond in compounds where the methylpyrazine is bridging (Otieno *et al.*, 1993). When bridging, it is common for the position of the methyl group to be disordered (Amaral *et al.*, 2001; Liu *et al.*, 2017; Kikuchi *et al.*, 2023), rendering the distal and proximal nitrogen atoms equivalent and the bond length moot. The Br1—Cu1—N14 bond angle is 90° within error and all *trans* bond angles are 180° as required by symmetry. The pyrazine ring is virtually planar, as expected (mean deviation of constituent atoms = 0.006 Å) and the ring is canted 60.6 (2)° relative to the Cu coordination plane.

Table 1
Selected geometric parameters (Å, °).

Cu1—N14	2.021 (2)	Cu1—Br1	2.4196 (3)
N14—Cu1—Br1	89.84 (6)		

In the extended structure, the molecular units are linked into chains parallel to the *a*-axis direction *via* short Cu···Br contacts forming bihalide bridges (see Fig. 2). The Cu1···$Br1^{i}$ distance is 3.1912 (3) Å [symmetry code: (i) 2 − *x*, −*y*, 1 − *z*) and the Br1—Cu1—$Br1^{i}$ angle is 92.141 (10)°. The Cu1—Br1···$Cu1^{ii}$ angle supplementary [87.859 (10)°; symmetry code: (ii) 1 + *x*, *y*, *z*] as required by symmetry. The long Cu···Br contact lies only 2.2 (1)° from the normal to the Cu^{II} coordination plane. The chains are well separated by the bulk of the methylpyrazine ligands (see Fig. 3), suggesting that the chains would be well isolated magnetically. The structure of the bihalide bridges within the chains suggests weak antiferromagnetic interactions. Sadly, insufficient material was isolated to measure the magnetic properties.

Synthesis and crystallization

Single crystals suitable for single-crystal X-ray diffraction were made by a gel diffusion technique. The bottom gel layer

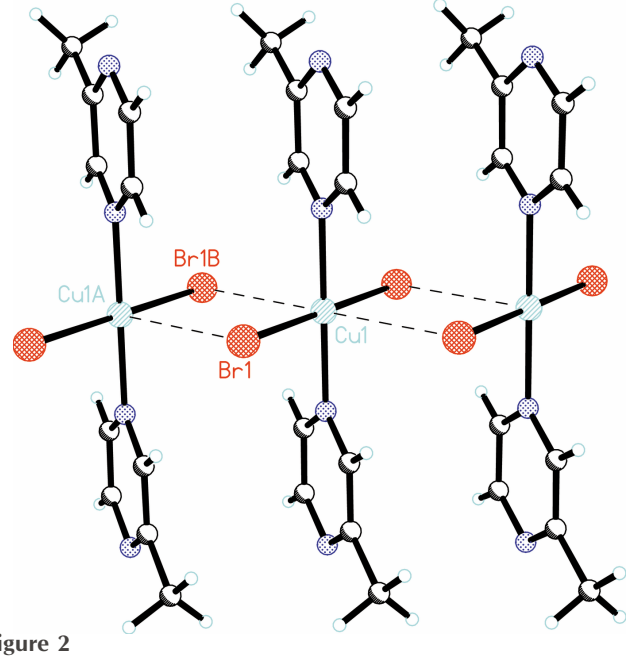


Figure 2
The chain structure of the compound shown as arbitrary spheres (*a* axis horizontal).

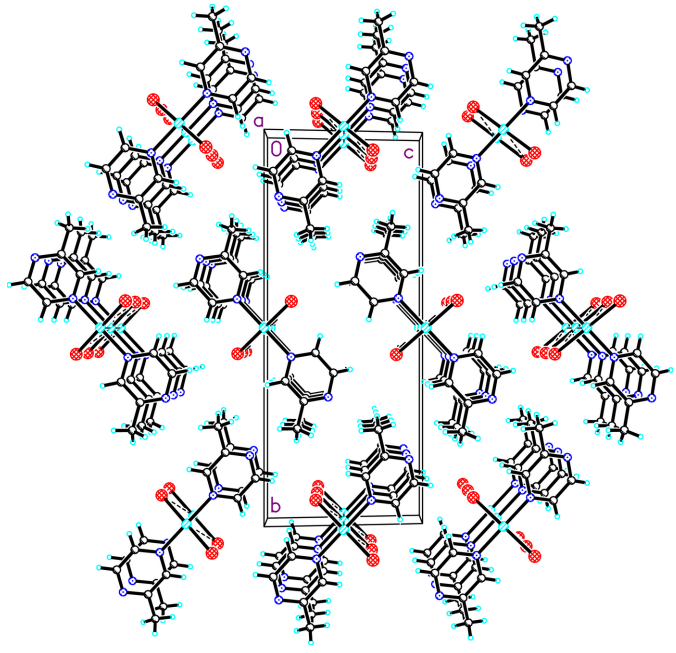


Figure 3
Packing of the chains viewed down the *a* axis. Atoms are shown as arbitrary spheres.

was prepared by dissolving copper(II) bromide (1.001 g, 4.49 mmol) and 1 ml of tetramethyl orthosilicate (TMOS) in 9 ml of H_2O. The mixture was stirred for 5 min. and allowed to harden overnight. The second layer was made by adjusting the pH of 18 ml H_2O and 2 ml TMOS with 20 drops of 2% ammonium hydroxide. This mixture was carefully poured over the top of the first layer, and also allowed to harden overnight. The third layer was prepared by dissolving 2-methylpyrazine (375.8 mg, 3.99 mmol) and 1 ml of TMOS in 10 ml of H_2O, stirring for 5 minutes, and pouring the solution over the top of the previous two layers. The layered gels were allowed to sit for 8 months yielding green needles approximately 1.10 × 0.06 × 0.04 mm in size on the surface of the gel. The crystals were harvested by filtration and washed with 30 ml of diethyl ether. IR (KBr) ν: 3083*w*, 1595*w*, 1482*w*, 1443*m*, 1400*m*, 1302*m*, 1259*w*, 1164*m*, 1081s, 1026*m*, 981*w*, 909*w*, 830*s*, 737*m*, 668*s*, 567*w*, 503*w* cm^{-1}.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. A very large crystal was used (1 mm long) due to the braided nature of the sample. Once cut, the de-braided end was kept out of the beam path. No decomposition was observed during data collection.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[CuBr_2(C_5H_6N_2)_2]$
M_r	411.60
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	90
a, b, c (Å)	3.9321 (4), 20.274 (2), 8.2685 (9)
β (°)	99.602 (2)
V (Å^3)	649.93 (12)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	7.81
Crystal size (mm)	1.10 × 0.06 × 0.04
Data collection	
Diffractometer	Bruker SMART APEX
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.042, 0.730
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8934, 1837, 1674
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.703
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.074, 1.08
No. of reflections	1837
No. of parameters	80
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.68, −0.62

Computer programs: *SMART* and *SAINT-Plus* (Bruker, 2006), *SHELXS2014* (Sheldrick, 2008), *SHELXL2019/2* (Sheldrick, 2015), *XP* (Bruker, 2004) and *publCIF* (Westrip, 2010).

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full crystallographic data

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catena-Poly[[bis(2-methylpyrazine-κN^4)copper(II)]-di-μ-bromido]

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Crystal data

$[CuBr_2(C_5H_6N_2)_2]$
M_r = 411.60
Monoclinic, $P2_1/n$
a = 3.9321 (4) Å
b = 20.274 (2) Å
c = 8.2685 (9) Å
β = 99.602 (2)°
V = 649.93 (12) Å^3
Z = 2
$F(000)$ = 398
D_x = 2.103 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6357 reflections
θ = 2.9–30.0°
μ = 7.81 mm^{-1}
T = 90 K
Rod, green
1.10 × 0.06 × 0.04 mm

Data collection

Bruker SMART APEX diffractometer
ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.042, T_{max} = 0.730
8934 measured reflections
1837 independent reflections
1674 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 30.0°, θ_{min} = 2.0°
h = −5→5
k = −28→28
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.074
S = 1.08
1837 reflections
80 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 0.3P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

Special details

Refinement. Data were measured using omega scans (0.3 ° per frame for 15 s). All non-hydrogen atoms were refined anisotropically.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.500000	0.000000	0.500000	0.01973 (12)

Br1	0.92174 (5)	0.06601 (2)	0.67603 (3)	0.01551 (9)
N11	0.3718 (5)	0.17387 (10)	0.0988 (2)	0.0173 (4)
C12	0.2992 (6)	0.18368 (11)	0.2500 (3)	0.0159 (4)
C13	0.3393 (6)	0.13326 (11)	0.3659 (3)	0.0173 (4)
H13	0.291403	0.141949	0.472767	0.021*
N14	0.4438 (6)	0.07281 (9)	0.3308 (2)	0.0167 (4)
C15	0.5144 (7)	0.06290 (11)	0.1796 (3)	0.0178 (4)
H15	0.587954	0.020597	0.150055	0.021*
C16	0.4813 (6)	0.11378 (12)	0.0659 (3)	0.0182 (4)
H16	0.538781	0.105545	−0.039345	0.022*
C17	0.1775 (7)	0.25094 (12)	0.2889 (3)	0.0224 (5)
H17A	0.369251	0.282275	0.296126	0.034*
H17B	0.093376	0.249652	0.393945	0.034*
H17C	−0.009587	0.264898	0.202115	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0253 (2)	0.0148 (2)	0.0164 (2)	−0.00535 (15)	−0.00449 (16)	0.00416 (15)
Br1	0.01469 (13)	0.01564 (13)	0.01582 (14)	−0.00124 (7)	0.00148 (9)	−0.00008 (7)
N11	0.0192 (9)	0.0164 (9)	0.0164 (10)	−0.0007 (7)	0.0035 (8)	0.0013 (7)
C12	0.0153 (10)	0.0153 (10)	0.0168 (11)	−0.0015 (8)	0.0018 (8)	0.0004 (8)
C13	0.0181 (11)	0.0186 (10)	0.0150 (10)	−0.0032 (8)	0.0024 (8)	−0.0007 (8)
N14	0.0183 (10)	0.0161 (9)	0.0144 (10)	−0.0035 (7)	−0.0015 (7)	0.0003 (7)
C15	0.0184 (11)	0.0166 (11)	0.0173 (11)	0.0008 (8)	−0.0003 (8)	−0.0023 (8)
C16	0.0202 (11)	0.0185 (11)	0.0162 (11)	−0.0007 (8)	0.0043 (9)	−0.0008 (8)
C17	0.0267 (12)	0.0175 (11)	0.0238 (13)	0.0025 (9)	0.0062 (10)	−0.0007 (9)

Geometric parameters (Å, º)

Cu1—N14^{i}	2.020 (2)	C13—H13	0.9500
Cu1—N14	2.021 (2)	N14—C15	1.340 (3)
Cu1—Br1^{i}	2.4196 (3)	C15—C16	1.387 (3)
Cu1—Br1	2.4196 (3)	C15—H15	0.9500
N11—C16	1.335 (3)	C16—H16	0.9500
N11—C12	1.343 (3)	C17—H17A	0.9800
C12—C13	1.392 (3)	C17—H17B	0.9800
C12—C17	1.498 (3)	C17—H17C	0.9800
C13—N14	1.340 (3)		
N14^{i}—Cu1—N14	180.0	C15—N14—Cu1	121.37 (16)
N14^{i}—Cu1—Br1^{i}	89.85 (6)	C13—N14—Cu1	121.34 (16)
N14—Cu1—Br1^{i}	90.15 (6)	N14—C15—C16	120.7 (2)
N14^{i}—Cu1—Br1	90.15 (6)	N14—C15—H15	119.7
N14—Cu1—Br1	89.84 (6)	C16—C15—H15	119.7
Br1^{i}—Cu1—Br1	180.0	N11—C16—C15	122.5 (2)
C16—N11—C12	116.8 (2)	N11—C16—H16	118.7
N11—C12—C13	121.0 (2)	C15—C16—H16	118.7

N11—C12—C17	117.4 (2)	C12—C17—H17A	109.5
C13—C12—C17	121.6 (2)	C12—C17—H17B	109.5
N14—C13—C12	121.7 (2)	H17A—C17—H17B	109.5
N14—C13—H13	119.1	C12—C17—H17C	109.5
C12—C13—H13	119.1	H17A—C17—H17C	109.5
C15—N14—C13	117.3 (2)	H17B—C17—H17C	109.5

Symmetry code: (i) $-x+1, -y, -z+1$.