

Di- μ -iodo-bis[[1,1'-methylenebis(3,5-dimethyl-1*H*-pyrazole- κ N²)]copper(I)]

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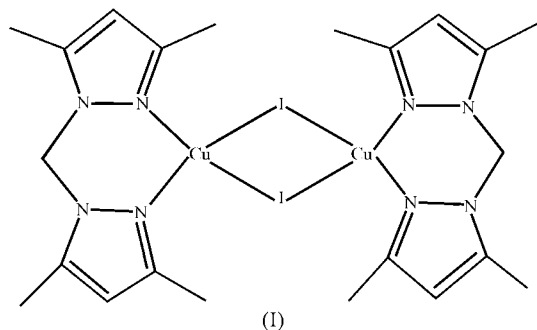
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In the title compound, [Cu₂I₂(C₁₁H₁₆N₄)₂], each of the two crystallographically equivalent Cu atoms is tetrahedrally coordinated by two N atoms from one 1,1'-methylenebis(3,5-dimethyl-1*H*-pyrazole) ligand and two bridging iodide anions. The molecule has a crystallographic center of symmetry located at the mid-point of the Cu...Cu line. One H atom of the CH₂ group of the 1,1'-methylenebis(3,5-dimethyl-1*H*-pyrazole) ligand interacts with an iodide ion in an adjacent molecule to afford pairwise intermolecular C—H...I contacts, thereby forming chains of molecules running along the [101] direction.

Comment

Cuprous halide (CuX) is known to easily form neutral adducts with various N-atom donor ligands (*L*). Some of these compounds show interesting catalytic properties (Mar Diaz-Requejo *et al.*, 2003; Caballero *et al.*, 2003) and rich luminescent properties (Lindsay & Ford, 1996; Vital & Ford, 2001; Rasika Dias *et al.*, 2003). The most commonly encountered



stoichiometry in CuX/*L* complexes is a dinuclear one, [CuXL₂] (X = Cl, Br and I). For example, for X = I, a number of dinuclear complexes with different N-atom donor ligands [e.g. 1,10-phenanthroline, *N,N*-bis(pyrazol-1-ylmethyl)benzyl-

amine, 2,6-bis(3-pyridyloxy)pyrazine and 2,2-diethylpyrazine] have been reported (Healy *et al.*, 1985; Sheu *et al.*, 1995; McMorran & Steel, 2002; Näther *et al.*, 2003). Although the N-atom donor ligand 1,1'-methylenebis(3,5-dimethyl-1*H*-pyrazole) or bis(3,5-dimethylpyrazolyl)methane (dmpzm; Julia *et al.*, 1982) has often been employed to react with transition metals to form interesting coordination compounds, for example, [Hg(CN)₂(dmpzm)] (Cingolani *et al.*, 1987), [NiCl₂(dmpzm)]₂ (Jansen *et al.*, 1980) and [PdL'(dmpzm)]₂·(ClO₄)₂·CH₃COCH₃·H₂O (*L'* is *p*-toluenethiolate; Sanchez *et al.*, 2000), there is no report of the cuprous halide adducts of this ligand. We report here the crystal structure of the title cuprous iodide complex, (I), of dmpzm.

Complex (I) (Fig. 1) crystallizes in space group *C2/c* and the asymmetric unit contains one dmpzm ligand, one Cu^I cation and one iodide ion. The structure contains a dimetallo-cyclic Cu₂I₂ species with a crystallographic center of symmetry at the mid-point of the Cu...Cu line. Each Cu atom is coordinated by two N atoms of one dmpzm ligand and two bridging iodide ions, forming a distorted tetrahedral geometry with bond angles at the Cu atom ranging from 104.60 (10) to 117.89 (11)^o (Table 1). Each dmpzm ligand coordinates to one Cu center in an *N,N'*-bidentate fashion, forming a six-membered chelate ring. The dinuclear Cu₂I₂ core is asymmetric, as the Cu1—I1 and Cu1—I1ⁱ bond distances are 2.5719 (10) and 2.6933 (10) Å, while the Cu1—I1—Cu1ⁱ and I1—Cu1—I1ⁱ bond angles are 62.69 (2) and 117.31 (2)^o [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$]. The Cu—I bond lengths bracket the mean value of 2.615 (1) Å in the similar [CuIL]₂ complex (*L* is 1,10-phenanthroline; Healy *et al.*, 1985) but are shorter than that in [CuIL]₂ [2.7297 (9) Å; *L* is 2,6-bis(3-pyridyloxy)pyrazine; McMorran & Steel, 2002]. The Cu...Cu distance [2.7412 (13) Å] within the Cu₂I₂ core is shorter than that in [CuIL]₂ [2.803 (2) Å; *L* is 2,6-bis(3-pyridyloxy)pyrazine; McMorran & Steel, 2002] but longer than that in [CuIL]₂ [2.609 (2) Å; *L* is 1,10-phenanthroline; Healy *et al.*, 1985].

The two Cu centers and the four N atoms (N1, N1ⁱ, N4 and N4ⁱ) lie close to the Cu₂N₄ plane (the maximum deviation

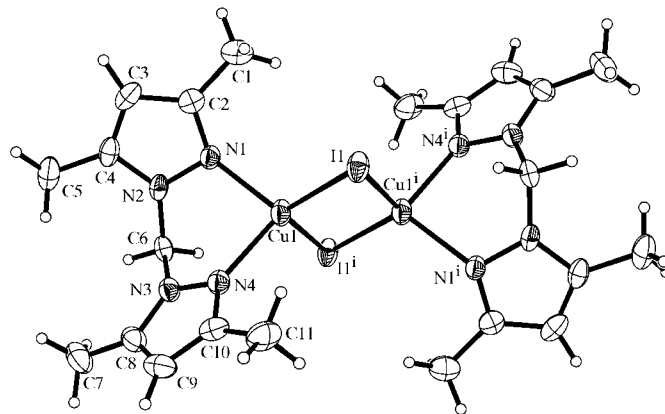
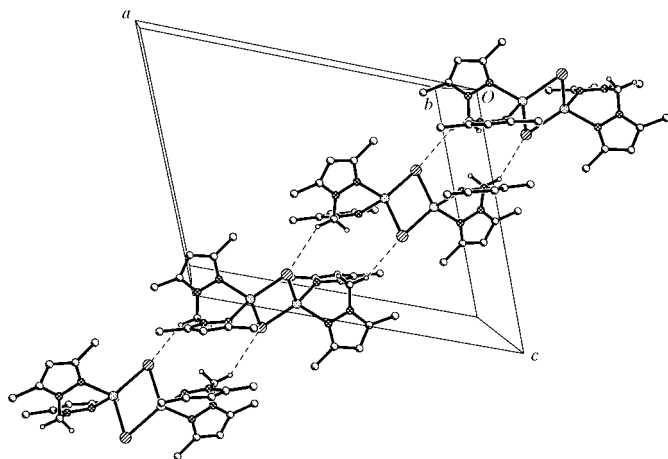


Figure 1

A perspective view of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.]

**Figure 2**

A packing diagram of (I), viewed approximately down the *b* axis, showing chains of molecules linked by pairwise C—H...I interactions running along the [101] direction.

from this plane is 0.18 Å). This plane is perpendicular to the Cu₂I₂ core. The Cu1—N1 and Cu1—N4 distances are almost identical, and the mean Cu—N bond length [2.097 (4) Å] is longer than that observed in [CuIL]₂ [2.0303 (18) Å; *L* is 2,6-bis(3-pyridyloxy)pyrazine; McMorran & Steel, 2002] and shorter than that in [CuIL]₂ [2.167 (9) Å; *L* is 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl; Oshio *et al.*, 1996]. Each ligand in the title compound adopts an extended and twisted *exo-anti* conformation. Atom C6 of one of the methylene groups in the dinuclear complex lies 1.89 Å below the Cu₂N₄ plane, while the symmetry-related atom in the other ligand lies the same distance above the plane.

Atom H6*B* of the CH₂ group of each dmpzm ligand interacts with atom I1 in an adjacent molecule to afford pairwise intermolecular C—H...I contacts, thereby forming chains of molecules running along the [101] direction (Fig. 2 and Table 2).

Experimental

An acetonitrile solution (10 ml) of dmpzm (0.020 g, 0.1 mmol) was added to CuI (0.019 g, 0.1 mmol) in acetonitrile (10 ml). The mixture was stirred at room temperature for 1 h and then filtered. Slow evaporation of the filtrate gave rise to colorless crystals of (I) (yield 0.051 g, 92% based on Cu). The crystal used for the crystal structure determination was obtained directly from the above preparation. Analysis found: C 33.47, H 4.18, N 14.19%; calculated for C₂₂H₃₂Cu₂I₂N₈: C 33.22, H 4.38, N 13.75%. IR (KBr, cm⁻¹): 3008 (*w*), 2942 (*w*), 2920 (*w*), 1633 (*m*), 1558 (*m*), 1465 (*m*), 1427 (*m*), 1384 (*s*), 1287 (*s*), 1270 (*m*), 1035 (*m*), 792 (*m*), 676 (*m*).

Crystal data

[Cu₂I₂(C₁₁H₁₆N₄)₂]
M_r = 789.44
 Monoclinic, *C*2/*c*
a = 17.924 (5) Å
b = 11.702 (3) Å
c = 14.339 (4) Å
 β = 112.249 (6)°
V = 2783.6 (13) Å³
Z = 4

D_x = 1.884 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5625 reflections
 θ = 3.1–27.5°
 μ = 3.77 mm⁻¹
T = 193 (2) K
 Platelet, colorless
 0.30 × 0.12 × 0.03 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (Jacobson, 1998)
 T_{\min} = 0.397, T_{\max} = 0.895
 15 314 measured reflections

3187 independent reflections
 2742 reflections with $I > 2\sigma(I)$
 R_{int} = 0.041
 θ_{max} = 27.5°
 h = -23 → 23
 k = -13 → 15
 l = -18 → 15

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.042
 $wR(F^2)$ = 0.082
 S = 1.11
 3187 reflections
 155 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 13.432P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.05 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.68 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

I1—Cu1	2.5719 (10)	N2—C4	1.355 (6)
I1—Cu1 ⁱ	2.6933 (10)	N2—C6	1.444 (6)
Cu1—N1	2.092 (4)	N3—N4	1.365 (6)
Cu1—N4	2.102 (4)	N3—C6	1.448 (6)
N1—N2	1.374 (6)	N3—C8	1.358 (7)
N1—C2	1.338 (6)	N4—C10	1.334 (7)
Cu1—I1—Cu1 ⁱ	62.69 (2)	N4—N3—C8	112.1 (4)
I1—Cu1—N1	116.88 (10)	C6—N3—C8	130.0 (4)
I1—Cu1—N4	117.89 (11)	Cu1—N4—N3	117.7 (3)
I1—Cu1—I1 ⁱ	117.31 (2)	Cu1—N4—C10	137.2 (4)
N1—Cu1—N4	91.12 (15)	N3—N4—C10	105.0 (4)
I1 ⁱ —Cu1—N1	105.32 (11)	N1—C2—C1	119.8 (5)
I1 ⁱ —Cu1—N4	104.60 (10)	N1—C2—C3	111.0 (4)
Cu1—N1—N2	114.6 (3)	N2—C4—C3	106.6 (5)
Cu1—N1—C2	133.8 (3)	N2—C4—C5	122.3 (4)
N2—N1—C2	104.5 (4)	N2—C6—N3	111.8 (3)
N1—N2—C4	111.8 (4)	N3—C8—C7	123.5 (5)
N1—N2—C6	118.6 (3)	N3—C8—C9	105.6 (5)
C4—N2—C6	129.6 (4)	N4—C10—C9	110.1 (5)
N4—N3—C6	117.9 (4)	N4—C10—C11	120.2 (5)

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C6—H6 <i>B</i> ...I1 ⁱ	0.99	3.02	3.877 (4)	145

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

The final difference Fourier map had a peak at about 1.17 Å from atom C1. With the exception of the methyl H atoms, which were located from ΔF syntheses, all H atoms were placed in idealized positions (C—H = 0.98 Å for methyl groups, 0.99 Å for methylene groups and 0.95 Å for ring CH groups). H atoms were refined as part of a rigid rotating group (methyl H atoms) or using a riding model (other H atoms) and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H})$ values of 1.2 $U_{\text{eq}}(\text{C})$.

Data collection: *CrystalClear* (Rigaku/MS, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1589). Services for accessing these data are described at the back of the journal.

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