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Structure of Dimeric Dibromo(di-2-pyridylmethane)copper(II)

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Abstract. $[\text{CuBr}_2(\text{C}_{11}\text{H}_{10}\text{N}_2)]_2$, $M_r = 787.14$, monoclinic, $P2_1/n$, $a = 8.988$ (8), $b = 13.933$ (8), $c = 9.795$ (6) Å, $\beta = 98.54$ (4)°, $V = 1213$ (3) Å³, $Z = 2$, $D_x = 2.16$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 8.332$ mm⁻¹, $F(000) = 756$, $T = 291$ K, $R = 0.053$ for 1621 unique observed reflections. The crystal consists of well defined dimeric units linked by two Cu–Br bonds. The coordination polyhedron around the Cu atom can be described as a distorted square pyramid. The basal plane is formed by the two N atoms of the di-2-pyridylmethane ligand and two Br atoms. The axial site is occupied by a Br atom from the other monomeric unit. Cu–N(1) = 2.027 (5), Cu–N(2) = 2.016 (5), Cu–Br(1) = 2.488 (1) and Cu–Br(2) = 2.391 (1) Å compared to the axial bond Cu–Br(1') = 2.804 (1) Å; Cu...Cu' = 3.869 (1) Å.

Introduction. The present work continues investigations on the structure of dimeric complexes of copper(II) (Garland, Le Marouille & Spodine, 1985). The recent interest in binuclear copper complexes is due to their potential as models for metalloproteins. A considerable number of complexes have been prepared with two metal ions at a separation of 2.5–6.0 Å. The variation of the metal–metal distance and the nature of the donor atoms allow the study of spectroscopic and magnetic properties that depend on the binuclearity of the system (Karlin & Zubieta, 1983). The structures of a number

of halogen-bridged compounds have been investigated in the hope of correlating their structural and magnetic properties (Marsh, Bowman, Hatfield & Hodgson, 1982; Wilson, Hatfield & Hodgson, 1976).

Experimental. The complex was prepared by addition of 1 mmol of anhydrous CuBr₂ to a degassed solution containing 1 mmol of ligand in freshly distilled methanol. The resultant solution was refluxed under N₂. Dark-green crystals formed when the reaction mixture was cooled.

Crystal dimensions: 0.12 × 0.20 × 0.33 mm, Nonius CAD-4 κ -geometry diffractometer, cell dimensions calculated by least-squares refinement on setting angles of 25 reflections with $12.2 \leq 2\theta \leq 20.6^\circ$; 2262 integrated reflections collected up to $(\sin\theta)/\lambda = 0.595$ Å⁻¹; ω -2 θ -scan technique, scan width $(1.0 + 0.35 \tan\theta)^\circ$; $0 < h < 10$, $0 < k < 16$, $-11 < l < 11$; 0.6% decay in intensities of three standard reflections during 31 h of irradiation; no absorption correction and no time-decay corrections applied; 2004 unique reflections after averaging ($R_{\text{int}} = 0.025$); 1621 with $F^2 > 3\sigma(F^2)$; structure solution by MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refined by full-matrix least squares based on F_o , weights based on counting statistics: $1/w = \sigma^2(F) = \frac{1}{4}\{[\sigma^2(I) + (0.08I)^2]/I\}$ (Stout & Jensen, 1968); atomic scattering factors for neutral atoms from *International*

Tables for X-ray Crystallography (1974); H atoms placed at idealized positions with C—H distances of 0.95 Å and with fixed thermal parameters (4.5 Å²) and not refined; anisotropic thermal parameters for all other atoms; refinement converged to $R = 0.053$ and $wR = 0.067$ and goodness-of-fit $S = 1.52$ for 146 refined parameters; largest shift-to-e.s.d. in the last cycle 0.01; final difference map included several peaks in the vicinity of the Br atoms, which presumably are indicative of uncorrected absorption; largest residual peak in final difference Fourier map $1.33\text{e}\text{Å}^{-3}$. All computer programs from the Enraf-Nonius SDP described by Frenz (1978).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{4}{3} \sum_i \beta_{ij} a_i a_j$$

	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
Br(1)	0.58978 (8)	0.07968 (5)	0.89038 (7)	2.61 (1)
Br(2)	0.6815 (1)	0.16268 (5)	1.23814 (8)	3.42 (2)
Cu	0.68963 (9)	0.01239 (5)	1.12156 (8)	2.15 (2)
N(1)	0.7914 (6)	-0.0955 (5)	1.0314 (6)	2.0 (1)
N(2)	0.7792 (6)	-0.0470 (4)	1.3032 (6)	2.3 (1)
C(1)	0.7205 (8)	-0.1492 (5)	0.9262 (8)	2.6 (1)
C(2)	0.7935 (9)	-0.2183 (5)	0.8616 (7)	2.7 (1)
C(3)	0.9456 (9)	-0.2330 (5)	0.9036 (9)	2.7 (1)
C(4)	1.0186 (8)	-0.1797 (5)	1.0124 (7)	2.5 (1)
C(5)	0.9399 (7)	-0.1123 (5)	1.0768 (7)	2.1 (1)
C(6)	0.9267 (8)	-0.0749 (5)	1.3220 (7)	2.1 (1)
C(7)	0.9895 (8)	-0.1162 (7)	1.4440 (7)	2.5 (1)
C(8)	0.907 (1)	-0.1309 (6)	1.5485 (8)	3.3 (2)
C(9)	0.759 (1)	-0.0997 (6)	1.5322 (8)	3.3 (2)
C(10)	0.6991 (9)	-0.0580 (6)	1.4072 (8)	2.8 (1)
C(11)	1.0084 (8)	-0.0562 (5)	1.2015 (7)	2.3 (1)

Table 2. Bond lengths (Å) and bond angles (°) of the monomeric molecule with e.s.d.'s in parentheses

Cu...Cu'	3.869 (1)	C(1)—C(2)	1.370 (9)
Cu—Br(1')	2.804 (1)	C(2)—C(3)	1.382 (9)
Cu—Br(1)	2.488 (1)	C(3)—C(4)	1.382 (9)
Cu—Br(2)	2.391 (1)	C(4)—C(5)	1.381 (8)
Cu—N(1)	2.027 (5)	C(5)—C(11)	1.501 (8)
Cu—N(2)	2.016 (5)	C(6)—C(7)	1.368 (8)
N(1)—C(1)	1.353 (8)	C(6)—C(11)	1.499 (8)
N(1)—C(5)	1.361 (7)	C(7)—C(8)	1.361 (10)
N(2)—C(6)	1.361 (7)	C(8)—C(9)	1.389 (10)
N(2)—C(10)	1.337 (8)	C(9)—C(10)	1.387 (9)
Br(1)—Cu—Br(2)	94.02 (3)	C(6)—N(2)—C(10)	118.9 (5)
Br(1)—Cu—N(1)	90.6 (1)	N(1)—C(1)—C(2)	122.4 (6)
Br(1)—Cu—N(2)	176.5 (1)	C(1)—C(2)—C(3)	119.1 (6)
Br(2)—Cu—N(1)	154.8 (1)	C(2)—C(3)—C(4)	119.0 (6)
Br(2)—Cu—N(2)	88.7 (1)	C(3)—C(4)—C(5)	120.0 (5)
N(1)—Cu—N(2)	86.0 (2)	N(1)—C(5)—C(4)	120.7 (5)
Br(1')—Cu—Br(1)	86.2 (2)	N(1)—C(5)—C(11)	116.1 (5)
Br(1')—Cu—Br(2)	109.3 (1)	C(4)—C(5)—C(11)	123.2 (5)
Br(1')—Cu—N(1)	95.7 (1)	N(2)—C(6)—C(7)	120.3 (6)
Br(1')—Cu—N(2)	95.0 (1)	N(2)—C(6)—C(11)	114.9 (5)
Cu—N(1)—C(1)	123.3 (4)	C(7)—C(6)—C(11)	124.8 (6)
Cu—N(1)—C(5)	117.9 (4)	C(6)—C(7)—C(8)	121.2 (6)
C(1)—N(1)—C(5)	118.8 (4)	C(7)—C(8)—C(9)	119.0 (6)
Cu—N(1)—C(6)	119.3 (5)	C(8)—C(9)—C(10)	118.1 (6)
Cu—N(2)—C(10)	121.8 (4)	N(2)—C(10)—C(9)	122.5 (6)
		C(5)—C(11)—C(6)	111.0 (5)

Symmetry operation: (') $1-x, -y, 2-z$.

Discussion. Table 1 lists the fractional atomic coordinates of non-H atoms, Table 2 the bond lengths and angles.*

The crystal can be described as consisting of dimeric units linked by two Cu—Br bonds. The structure of the dimeric unit is illustrated in Fig. 1 which also shows the atomic-numbering scheme. The coordination polyhedron is defined by two N atoms provided by the di-2-pyridylmethane and by three Br atoms, one of which links two monomeric units.

The bridging $\text{Cu}_2\text{Br}(1)_2$ unit is constrained to be planar by the presence of the crystallographic inversion center in the middle of the dimer. The coordination around each Cu center can be described as a distorted square pyramid with two *cis* N atoms from the di-2-pyridylmethane and two *cis* Br atoms, while the apical site is occupied by a Br atom from the other monomeric unit [$\text{Cu—N}(1) = 2.027(5)$, $\text{Cu—N}(2) = 2.016(5)$, $\text{Cu—Br}(1) = 2.488(1)$, $\text{Cu—Br}(2) = 2.391(1)$ and $\text{Cu—Br}(1') = 2.804(1)$ Å].

This structure could alternatively be described as a distorted trigonal bipyramid, the basal plane being formed by the N(1) atom of the di-2-pyridylmethane, the Br(1) atom that bridges the two monomers and the Br(2) atom. The two axial sites are occupied by the N(2) atom and the Br(1) atom, respectively. This model is severely distorted with the dihedral angle formed by the planes $\text{Br}(1)\text{—Cu—N}(1)\text{—N}(2)$ and $\text{Br}(1)\text{—Cu—Br}(2)\text{—N}(2)$ being 23.8° , instead of the 60° characteristic of an idealized trigonal bipyramid.

* Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43546 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

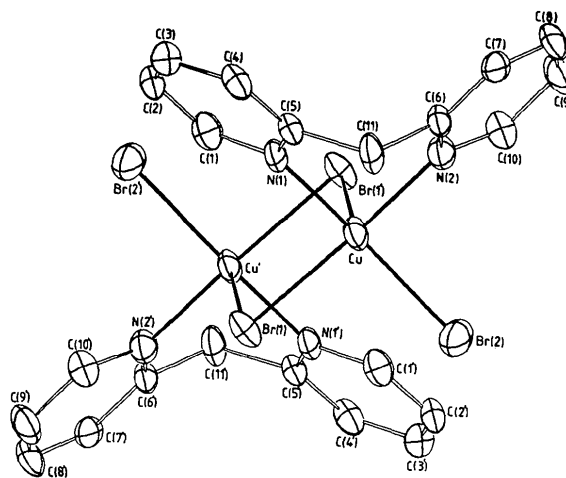


Fig. 1. A perspective view of the dimeric unit with atom numbering; H excluded for clarity.

The distortion of the square pyramid is also important, but less severe than that of the trigonal bipyramid. The four basal atoms N(1), N(2), Br(1) and Br(2) deviate strongly from coplanarity by 0.240, -0.247, -0.183 and 0.190 Å, respectively, while the Cu atom deviates from this plane by 0.252 Å in the direction of the apical Br atom. The dihedral angle between the unweighted mean planes N(1)-Cu-N(2) and Br(1)-Cu-Br(2) is 24.9°, thus indicating a distortion towards tetrahedrality, which is quite common in '4 + 1' complexes. The distances and angles of the di-2-pyridylmethane ligand are comparable with those found by us for chloro(di-2-pyridylmethane)-(di-2-pyridylmethanol)copper(II) perchlorate (Garland, Le Marouille, Spodine & Manzur, 1986).

The structure of the dibromo(di-2-pyridylmethane)-copper(II) complex is similar to that found in the bis[dibromo(4-methyloxazole)copper(II)] complex (Marsh *et al.*, 1982), in the sense that all metal-ligand distances are comparable. However, in their case the Cu atom deviates from the basal plane of the pyramid by 0.309 Å, and the in-plane Br(1)-Cu-Br(2) angle is 157.15 (4)°.

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Structure of *catena*-Bis[4-(2-aminoethyl)imidazole-*N*³,*N*⁸]- μ -chloro-copper(II) Chloride Dihydrate*

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Abstract. [CuCl(C₅H₉N₃)₂]Cl.2H₂O, $M_r = 392.77$, monoclinic, $P2_1/c$, $a = 9.727$ (2), $b = 10.463$ (2), $c = 18.022$ (3) Å, $\beta = 114.83$ (1)°, $V = 1664.6$ (6) Å³,

$Z = 4$, $D_m = 1.570$ (1), $D_x = 1.567$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 1.680$ mm⁻¹, $F(000) = 812$, room temperature, $R = 0.0424$ for 1936 observed reflections. The Cu²⁺ ions are located at two independent centers of symmetry (000 and 0½0). Two bidentate histamine ligands form a square-planar environment around the Cu²⁺ ions. The coordination sphere is

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