

Table 3. *Characteristic Berry ligand displacement motions*

|                 | Value (°)<br>observed | Value (°)<br>expected |
|-----------------|-----------------------|-----------------------|
| N(1)-Cu-N(2)    | 168.2                 | <180                  |
| O(2)-Cu-O(1)    | 140.2                 | >120                  |
| O(2)-Cu-O(5)    | 113.7                 | <120                  |
| O(5)-Cu-O(1)    | 106.0                 | <120                  |
| $\delta_{24}^*$ | 26.0                  | $0 < \delta < 53.0$   |

\*  $\delta_{24}$  is the dihedral angle between the two faces of the t.b.p. that convert to the basal plane of the r.p.

The author wishes to acknowledge the receipt of a grant from the University of New Hampshire Research Office that made possible the collection of intensity data by Dr Cynthia Day, Crystalytics Company, Lincoln, Nebraska, and the use of the computational services of the University Computation Center. He is grateful for the assistance of N. H. Alter Jr of the Center.

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*Acta Cryst.* (1986). **C42**, 149-150

## Di- $\mu$ -chloro-bis[bis(2-methylpyridine)copper(I)]

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(Received 20 May 1985; accepted 2 October 1985)

**Abstract.**  $[\text{CuCl}(\text{C}_6\text{H}_7\text{N})_2]_2$ ,  $M_r = 570.50$ , triclinic,  $P\bar{1}$ ,  $a = 8.908$  (3),  $b = 9.038$  (4),  $c = 9.532$  (3) Å,  $\alpha = 95.06$  (3),  $\beta = 117.42$  (3),  $\gamma = 109.06$  (3)°,  $V = 617.2$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.535$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 19.65$  cm<sup>-1</sup>,  $F(000) = 292$ ,  $T = 193$  K,  $R = 0.038$  for 1171 observed reflections. The Cu atoms are pseudo-tetrahedrally coordinated by two bridging Cl atoms and two N atoms from the nitrogen bases. The geometry of the  $\text{N}_4\text{Cu}_2\text{Cl}_2$  core is very similar to that of the  $\text{N}_4\text{Cu}_2\text{Br}_2$  core of the isotypic complex  $[\text{CuBr}(\text{2-methylpyridine})_2]_2$ .

**Introduction.** Copper(I) complexes are of current interest because of the metal-metal interaction in systems with  $d^{10}$  electronic configuration. Dimeric adducts of general formula  $(L_2\text{Cu}X)_2$  with  $L =$  nitrogen base have been structurally characterized for a considerable number of copper-iodine complexes (Healy, Pakawatchai & White, 1983; Hiller, 1984). Only one

similar structure is known for  $X = \text{Br}$ ,  $[\text{CuBr}(\text{2-methylpyridine})_2]_2$  (Schramm, Pierre & Hiller, 1984). The title compound is the first example of the formula  $(L_2\text{Cu}X)_2$  with  $X = \text{Cl}$ . Further examples with  $L = 2,4$ -dimethylpyridine are in preparation (Healy, 1985).

**Experimental.** Compound prepared by the reaction of CuCl in acetonitrile with 2-methylpyridine in acetone; crystallization on cooling to 250 K. Compared with the adducts of CuI and CuBr, the complex is more sensitive in the presence of oxygen. Needles with yellow-luminescence properties,  $0.10 \times 0.10 \times 0.5$  mm, Enraf-Nonius CAD-4 diffractometer (graphite monochromator), all investigations at 193 K to avoid decomposition. Unit-cell parameters from  $2\theta$  values of 25 reflections ( $10 < 2\theta < 21^\circ$ ); triclinic,  $P\bar{1}$  confirmed by structure solution. 3128 reflections ( $\theta \leq 22^\circ$ ) measured,  $h \pm 9$ ,  $k \pm 10$ ,  $l \pm 9$ . No significant intensity variation for three standard reflections. Empirical

absorption corrections ( $\psi$  scan), transmission 0.774–0.997, 1501 unique reflections ( $R_{\text{int}} = 0.017$ ), 1171 reflections with  $I > 3\sigma(I)$  used for refinement. Cu and Cl atoms from Patterson synthesis, others from difference Fourier syntheses. All H atomic positions found; methyl H positions refined with fixed isotropic temperature factors ( $B = 5 \text{ \AA}^2$ ), other H atoms used only for structure-factor calculation. Cu, Cl, N and C refined with anisotropic temperature parameters. Scattering factors from *International Tables for X-ray Crystallography* (1974). Secondary-extinction correction applied (Zachariasen, 1963); final coefficient,

refined in least squares,  $1.93 \times 10^{-8}$ .  $R = 0.038$ ,  $wR = 0.044$ , 170 parameters refined by least squares on  $F$ ,  $w = 1/\sigma_F^2$ ,  $S = 1.179$ , max.  $\Delta/\sigma = 0.01$ , largest peak in final difference Fourier map  $10.583 \text{ e \AA}^{-3}$ . All calculations performed on a Digital PDP 11/60 computer with the *SDP* system of programs (Frenz, 1978).

**Discussion.** Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.\* The structure of the dimer is shown in Fig. 1. In the title compound the asymmetric unit consists of the (2-methylpyridine)<sub>2</sub>-CuCl unit; the dimer is centrosymmetric about a crystallographic inversion centre. The  $N_4Cu_2X_2$  core geometry is very similar to that of the isotypic complex  $[\text{CuBr}(2\text{-methylpyridine})_2]_2$  (Schramm *et al.*, 1984). It is evident that the substitution of Br by Cl has no significant influence on the angles Cu–X–Cu and X–Cu–X. In the chlorine compound these angles are  $79.93(5)$  and  $100.07(5)^\circ$ , in the bromine compound  $80.4(1)$  and  $99.6(1)^\circ$ . A larger effect can be observed in the isotypic iodine compound with the angles  $69.95(6)$  and  $110.05(6)^\circ$  (Healy *et al.*, 1983). Unexpectedly, the Cu...Cu distance decreases on passing from Br to Cl. The distances are  $3.3491(6)$  and  $3.150(2) \text{ \AA}$  respectively. The shortest distance is  $3.083(3) \text{ \AA}$  in the iodine compound. We note the remarkably short distance of  $2.699(5) \text{ \AA}$  in the analogous compound  $[\text{CuI}(\text{pyridine})_2]_2$  (Dyason, Engelhardt, Healy & White, 1984). Further structural studies are necessary to interpret these effects.

I thank Professor Dr J. Strähle for helpful discussions. I am also grateful to the Deutsche Forschungsgemeinschaft for financial support.

\* Lists of structure factors, anisotropic thermal parameters, H atomic positions and further bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42558 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = 1/24\pi^2 \sum_i \sum_k B_{ik} a_i^* a_k^* (\mathbf{a}_i \cdot \mathbf{a}_k).$$

|       | x           | y          | z           | $U_{\text{eq}}$ |
|-------|-------------|------------|-------------|-----------------|
| Cu    | 0.3120 (1)  | 0.8605 (1) | 0.3556 (1)  | 0.053           |
| Cl    | 0.5366 (2)  | 0.8478 (2) | 0.6199 (2)  | 0.049           |
| N(11) | 0.0836 (5)  | 0.8139 (5) | 0.3732 (5)  | 0.042           |
| C(12) | -0.0527 (7) | 0.8608 (7) | 0.2863 (7)  | 0.040           |
| C(13) | -0.1976 (7) | 0.8385 (8) | 0.3148 (7)  | 0.044           |
| C(14) | -0.2043 (8) | 0.7624 (9) | 0.4320 (8)  | 0.059           |
| C(15) | -0.0696 (8) | 0.7086 (9) | 0.5166 (7)  | 0.075           |
| C(16) | 0.0731 (7)  | 0.7368 (7) | 0.4851 (7)  | 0.069           |
| C(17) | -0.0421 (9) | 0.9399 (8) | 0.1591 (8)  | 0.051           |
| N(21) | 0.3086 (5)  | 0.7467 (6) | 0.1615 (5)  | 0.075           |
| C(22) | 0.2885 (7)  | 0.5910 (7) | 0.1301 (7)  | 0.048           |
| C(23) | 0.3010 (8)  | 0.5241 (8) | -0.0007 (8) | 0.067           |
| C(24) | 0.3261 (8)  | 0.6150 (8) | -0.1013 (7) | 0.068           |
| C(25) | 0.3412 (8)  | 0.7728 (8) | -0.0715 (7) | 0.059           |
| C(26) | 0.3329 (7)  | 0.8341 (7) | 0.0612 (7)  | 0.048           |
| C(27) | 0.254 (1)   | 0.4933 (8) | 0.2371 (8)  | 0.084           |

Table 2. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

Symmetry operator: (i)  $1 - x, 2 - y, 1 - z$ .

|                      |           |                           |            |
|----------------------|-----------|---------------------------|------------|
| Cu–Cl                | 2.434 (2) | Cu–Cl–Cu <sup>i</sup>     | 79.93 (5)  |
| Cu–Cl <sup>i</sup>   | 2.470 (2) | Cl–Cu–Cl <sup>i</sup>     | 100.07 (5) |
| Cu–N(11)             | 2.028 (5) | Cl–Cu–N(11)               | 102.9 (1)  |
| Cu–N(21)             | 2.020 (5) | Cl–Cu–N(21)               | 113.8 (1)  |
|                      |           | Cl <sup>i</sup> –Cu–N(11) | 111.0 (1)  |
| Cu...Cu <sup>i</sup> | 3.150 (2) | Cl <sup>i</sup> –Cu–N(21) | 102.7 (1)  |
| Cl...Cl <sup>i</sup> | 3.759 (3) | N(11)–Cu–N(21)            | 124.0 (2)  |

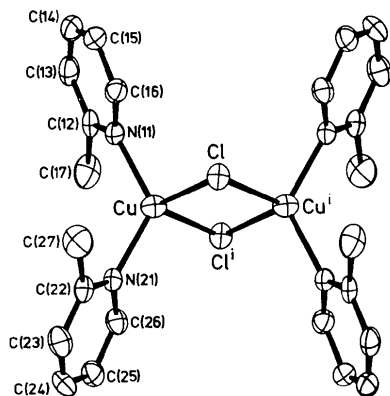


Fig. 1. Perspective view of the molecule with 80% probability ellipsoids.

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