# $\mu$-{1,4-Bis[(2-pyridyl)amino]phthalazine-$N^1,N^3,N^4,N^6$}-$\mu$-chloro-dichloro-$\mu$-hydroxo-dicopper(II) Sesquihydrate

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**Abstract.** [Cu$_2$(C$_{18}$H$_{14}$N$_6$)Cl$_3$(OH)] . 1·5H$_2$O, $M_r$ = 591·93, monoclinic, $P2_1/c$, $a$ = 12·950 (1), $b$ = 14·262 (1), $c$ = 22·773 (2) Å, $\beta$ = 96·07 (1)°, $Z$ = 8, $D_m$ = 1·85, $D_x$ = 1·88 g cm$^{-3}$. The structure refined to $R$ = 0·036 for 7271 independent reflections (Mo $K\alpha$). Each Cu$^{2+}$ ion in each binuclear complex is five-coordinate (tetragonal pyramid), coordinated by two N atoms, two Cl$^-$ ions (one bridging), and a bridging hydroxide ion.

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**Introduction.** Thompson, Chacko, Elvidge, Lever & Parish (1969) have reported the preparation of the ligand 1,4-bis[(2-pyridyl)amino]phthalazine (*L*) and a number of its copper complexes. Crystals were provided by Professor Lever and we have determined the structure in order to ascertain the details of the coordination and some structural details of the ligand.

Data were collected by $\theta$–$2\theta$ diffractometer scans at 2° ($2\theta$) min$^{-1}$ and 20 s background counts with Nb-filtered Mo $K\alpha$ radiation on a dark-green prismatic crystal with dimensions 0·20 × 0·20 × 0·16 mm. Cell parameters were calculated by least squares from $2\theta$
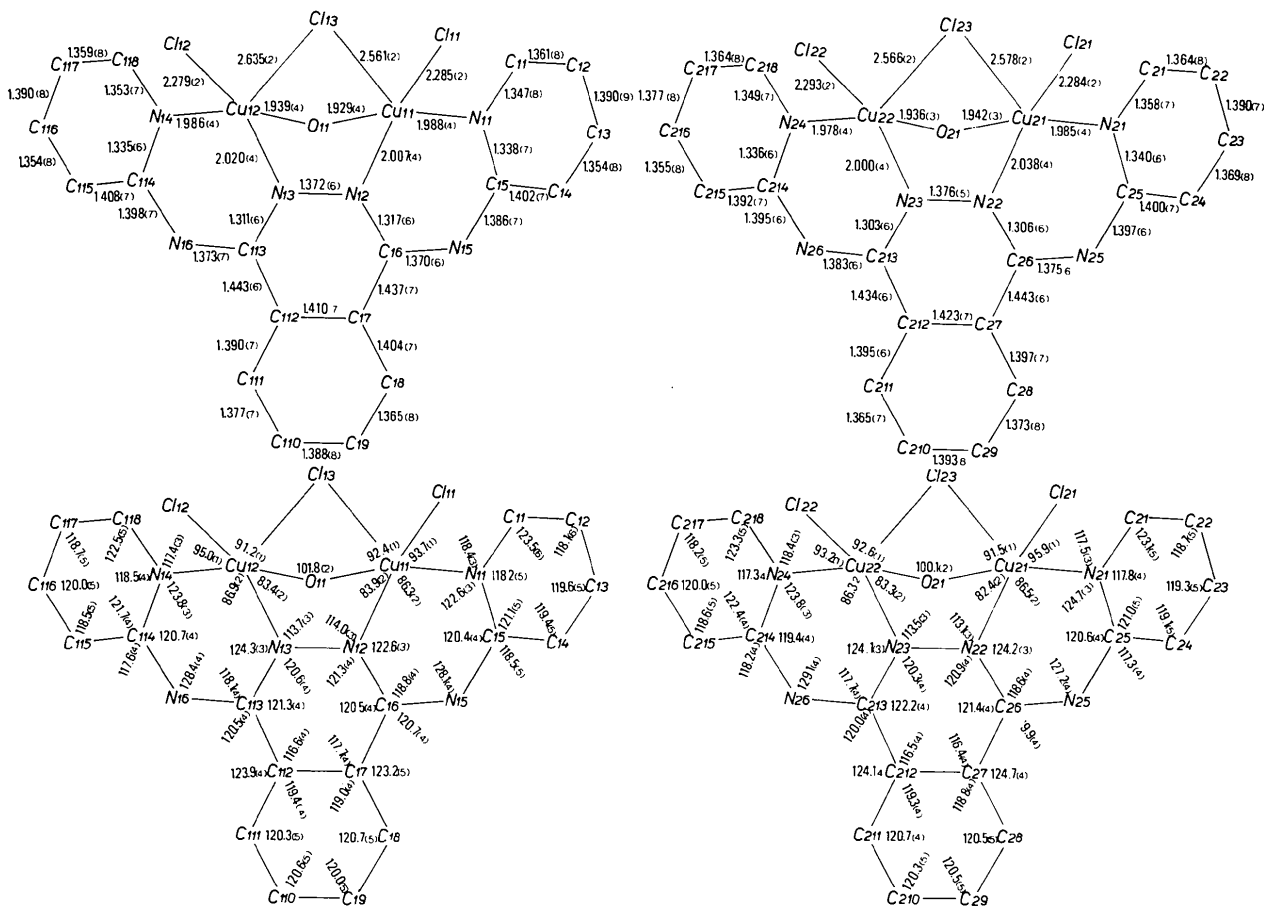


Fig. 1. Interatomic distances (Å) and angles (°).

## Table 1. Fractional atomic coordinates (×10⁴; ×10⁵ for Cu and ×10³ for H) and equivalent isotropic thermal parameters (×10⁴; ×10³ for H)

$$U_{eq} = \tfrac{1}{3}(\text{trace } \tilde{U}).$$

| | $x$ | $y$ | $z$ | $U_{eq}$ (Å²) |
|---|---|---|---|---|
| Cu(11) | 23454 (5) | 32369 (4) | 51173 (3) | 237 (2) |
| Cu(12) | 23565 (5) | 11889 (4) | 48157 (3) | 243 (2) |
| Cu(21) | 73177 (5) | 28857 (4) | 74171 (3) | 242 (2) |
| Cu(22) | 74127 (5) | 8523 (4) | 77034 (3) | 234 (2) |
| Cl(11) | 1080 (1) | 4241 (1) | 4726 (1) | 281 (4) |
| Cl(12) | 1123 (1) | 618 (1) | 4119 (1) | 369 (4) |
| Cl(13) | 3319 (1) | 2537 (1) | 4299 (1) | 352 (5) |
| Cl(21) | 6069 (1) | 3371 (1) | 6697 (1) | 418 (5) |
| Cl(22) | 6202 (1) | −175 (1) | 7269 (1) | 316 (4) |
| Cl(23) | 8349 (1) | 1646 (1) | 6898 (1) | 294 (4) |
| O(11) | 1426 (3) | 2171 (3) | 5025 (2) | 318 (50) |
| O(12) | 837 (4) | 750 (3) | 5764 (2) | 492 (17) |
| O(21) | 6433 (2) | 1882 (2) | 7650 (1) | 335 (12) |
| O(22) | 5673 (5) | 3332 (4) | 8368 (2) | 540 (19) |
| O(33) | 737 (4) | 2405 (3) | 8599 (2) | 1036 (25) |
| N(11) | 3312 (3) | 4265 (3) | 5396 (2) | 298 (15) |
| N(12) | 3132 (3) | 2442 (3) | 5740 (2) | 264 (15) |
| N(13) | 3137 (3) | 1504 (3) | 5606 (2) | 252 (15) |
| N(14) | 3295 (3) | 91 (3) | 4796 (2) | 273 (14) |
| N(15) | 3512 (3) | 3689 (3) | 6375 (2) | 282 (14) |
| N(16) | 3578 (3) | −23 (3) | 5841 (2) | 274 (16) |
| N(21) | 8184 (3) | 4033 (3) | 7411 (2) | 256 (14) |
| N(22) | 8130 (3) | 2586 (3) | 8211 (2) | 254 (14) |
| N(23) | 8163 (3) | 1642 (3) | 8337 (2) | 258 (14) |
| N(24) | 8387 (3) | −159 (3) | 7982 (2) | 276 (14) |
| N(25) | 8491 (3) | 4128 (3) | 8458 (2) | 274 (13) |
| N(26) | 8590 (3) | 402 (3) | 8961 (2) | 278 (15) |
| C(11) | 3500 (5) | 4947 (4) | 5012 (3) | 381 (23) |
| C(12) | 4002 (4) | 5760 (4) | 5176 (3) | 451 (22) |
| C(13) | 4342 (5) | 5888 (4) | 5770 (3) | 477 (23) |
| C(14) | 4181 (4) | 5204 (3) | 6163 (2) | 357 (19) |
| C(15) | 3664 (4) | 4381 (4) | 5966 (2) | 268 (18) |
| C(16) | 3395 (3) | 2744 (3) | 6281 (2) | 239 (16) |
| C(17) | 3527 (3) | 2096 (3) | 6767 (2) | 246 (16) |
| C(18) | 3559 (4) | 2372 (4) | 7360 (2) | 336 (20) |
| C(19) | 3626 (4) | 1721 (4) | 7802 (2) | 357 (19) |
| C(110) | 3679 (4) | 774 (4) | 7667 (2) | 321 (18) |
| C(111) | 3650 (4) | 481 (4) | 7089 (2) | 279 (18) |
| C(112) | 3555 (3) | 1132 (3) | 6632 (2) | 224 (15) |
| C(113) | 3432 (3) | 883 (3) | 6015 (2) | 231 (16) |
| C(114) | 3714 (3) | −358 (3) | 5277 (2) | 244 (15) |
| C(115) | 4284 (4) | −1192 (3) | 5239 (2) | 305 (17) |
| C(116) | 4400 (4) | −1541 (4) | 4697 (3) | 366 (21) |
| C(117) | 3973 (4) | −1072 (4) | 4194 (2) | 400 (19) |
| C(118) | 3447 (4) | −260 (4) | 4260 (2) | 331 (20) |
| C(21) | 8324 (4) | 4411 (4) | 6878 (2) | 327 (19) |
| C(22) | 8864 (4) | 5219 (4) | 6816 (2) | 366 (20) |
| C(23) | 9310 (4) | 5673 (4) | 7320 (2) | 359 (19) |
| C(24) | 9197 (4) | 5296 (3) | 7863 (2) | 320 (18) |
| C(25) | 8625 (4) | 4469 (3) | 7895 (2) | 240 (16) |
| C(26) | 8389 (3) | 3207 (3) | 8621 (2) | 221 (15) |
| C(27) | 8504 (3) | 2956 (3) | 9238 (2) | 222 (14) |
| C(28) | 8542 (4) | 3596 (3) | 9704 (2) | 270 (17) |
| C(29) | 8536 (4) | 3288 (3) | 10275 (2) | 284 (16) |
| C(210) | 8534 (4) | 2332 (3) | 10400 (2) | 312 (17) |
| C(211) | 8549 (4) | 1691 (3) | 9956 (2) | 290 (16) |
| C(212) | 8521 (3) | 1980 (3) | 9369 (2) | 202 (13) |
| C(213) | 8433 (3) | 1353 (3) | 8874 (2) | 228 (14) |
| C(214) | 8738 (3) | −294 (3) | 8549 (2) | 238 (14) |
| C(215) | 9242 (4) | −1114 (3) | 8748 (2) | 309 (17) |
| C(216) | 9404 (4) | −1788 (4) | 8348 (3) | 414 (21) |
| C(217) | 9115 (4) | −1638 (4) | 7757 (3) | 397 (20) |

## Table 1 (cont.)

| | $x$ | $y$ | $z$ | $U_{eq}$ (Å²) |
|---|---|---|---|---|
| C(218) | 8608 (4) | −825 (4) | 7594 (2) | 350 (18) |
| H(011) | 108 (4) | 227 (4) | 480 (3) | 49 (24) |
| H(021) | 616 (5) | 182 (5) | 744 (3) | 30 (14) |
| H(012) | 96 (5) | 115 (5) | 553 (3) | 84 (24) |
| H(120) | 27 (4) | 55 (4) | 570 (3) | 60 (23) |
| H(022) | 602 (5) | 289 (5) | 811 (3) | 167 (28) |
| H(220) | 526 (5) | 346 (5) | 828 (3) | 41 (29) |
| H(11) | 333 (5) | 478 (4) | 464 (3) | 57 (13) |
| H(12) | 416 (3) | 621 (3) | 490 (2) | 37 (13) |
| H(13) | 467 (4) | 642 (4) | 590 (2) | 43 (15) |
| H(14) | 435 (3) | 523 (3) | 661 (2) | 33 (11) |
| H(15) | 370 (3) | 386 (3) | 673 (2) | 20 (11) |
| H(16) | 374 (4) | −40 (3) | 609 (2) | 20 (15) |
| H(18) | 353 (4) | 303 (4) | 744 (2) | 44 (18) |
| H(19) | 363 (3) | 197 (3) | 825 (2) | 41 (13) |
| H(110) | 375 (3) | 34 (3) | 797 (2) | 20 (13) |
| H(111) | 370 (3) | −14 (3) | 699 (2) | 24 (14) |
| H(115) | 459 (3) | −147 (3) | 562 (2) | 19 (11) |
| H(116) | 483 (4) | −207 (3) | 461 (2) | 35 (15) |
| H(117) | 411 (3) | −125 (3) | 384 (2) | 34 (13) |
| H(118) | 314 (4) | 14 (3) | 394 (2) | 35 (16) |
| H(21) | 799 (3) | 401 (3) | 654 (2) | 13 (11) |
| H(22) | 896 (4) | 551 (3) | 642 (2) | 38 (14) |
| H(23) | 977 (3) | 615 (3) | 726 (2) | 29 (14) |
| H(24) | 947 (3) | 561 (3) | 823 (2) | 34 (14) |
| H(25) | 872 (4) | 449 (4) | 875 (2) | 48 (16) |
| H(26) | 868 (3) | 25 (3) | 928 (2) | 11 (14) |
| H(28) | 857 (3) | 424 (3) | 961 (2) | 28 (13) |
| H(29) | 846 (3) | 371 (3) | 1059 (2) | 34 (13) |
| H(210) | 838 (3) | 214 (3) | 1082 (2) | 23 (11) |
| H(211) | 849 (4) | 105 (3) | 1003 (2) | 29 (15) |
| H(215) | 935 (4) | −119 (3) | 916 (2) | 32 (14) |
| H(216) | 968 (4) | −229 (4) | 847 (2) | 58 (19) |
| H(217) | 927 (3) | −203 (3) | 747 (2) | 33 (14) |
| H(218) | 836 (4) | −68 (3) | 722 (2) | 24 (14) |

values for 19 reflections in the range $29° \leq 2\theta \leq 41°$ (Mo $K\alpha$, $\lambda = 0.71069$ Å). Laue symmetry $2/m$ and systematic absences of $h0l$ for $l = 2n + 1$ and of $0k0$ for $k = 2n + 1$ indicated the space group $P2_1/c$. All reflections (7271) in one quadrant of the reciprocal lattice out to $2\theta = 55°$ were measured. Of these, 1661 were found to have $I < 2\sigma(I)$ and were specially coded so that they were included in a least-squares refinement cycle only when $|F_c| > |F_o|$. Four reference reflections were recorded every 4 h as a check on the stability of the instrument and the crystal, and showed no significant variation. The intensity of each reflection and its estimated standard deviation were calculated as previously described (Marongiu, Lingafelter & Paoletti, 1969). No corrections were made for absorption ($\mu = 2.53$ mm⁻¹).

The Patterson synthesis could not be interpreted, but a set of phases derived by the application of Sayre's equation using the program of Long (1965) on the 198 reflections with $|E| \geq 2.20$ gave a Fourier synthesis from which positions of the Cu and Cl atoms could be determined. The remaining non-hydrogen atoms were located by a series of Fourier and difference-Fourier syntheses. Scattering factors were interpolated from the values given by Cromer & Waber (1965) for $Cu^{2+}$, $Cl^-$,

O, N, and C and by Stewart, Davidson & Simpson (1965) for H. Refinement was carried out by least squares using the XRAY 63 system (Stewart, 1963), minimizing $\sum w(|F_o| - |F_c|)^2$, with unit weights. After reduction of $R$ $(\sum||F_o| - |F_c||/\sum|F_o|)$ to 0·06, all H atoms except those on O(33) were located on a difference Fourier synthesis. A final series of least-squares cycles reduced $R$ to 0·036. In the final cycle the maximum shift was 0·7$\sigma$. The final atomic positional parameters and their estimated standard deviations are given in Table 1.* Bond distances and angles in the two independent molecules are given in Fig. 1.

**Discussion.** The crystal structure contains two independent $Cu_2LCl_3(OH)$ molecules. The two independent molecules are quite similar in shape, although there are small but significant differences in their details. The two molecules are oriented such that, with mean deviations of 0·0071 in $x$, 0·0025 in $y$, and 0·0014 in $z$, the atoms of molecule 2 may be derived from those of molecule 1 by the operation of a pseudo-glide plane, $x_2 = 0\cdot4991 + x_1, y_2 = 0\cdot4094 - y_1, z_2 = 0\cdot2599 + z_1$.

The two Cu atoms, Cu($J1$) and Cu($J2$), in each molecule are bridged by a Cl atom, Cl($J3$), a hydroxyl group, O($J1$), and the pair of N atoms, N($J2$) and N($J3$), of the ligand. The coordination of each Cu atom is distorted tetragonal pyramidal, with the bridging Cl atom at the apex. The base of each pyramid is slightly distorted from planar toward tetrahedral (average atomic displacements about 0·1 Å). The Cu atom is displaced from the basal plane (by about 0·3 Å) toward the apex.

The ligand is markedly non-planar. The main distortions from planarity may be described as follows. The phthalazine moiety is folded on the C($J7$)—C($J12$) bond by about 10°. The diazine ring has a boat conformation, with C($J6$) and C($J13$) about 0·12 Å

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36383 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

out of the plane of the other four atoms. The pyridine rings are rotated about the exocyclic C—N bond by about 30°.

A comparison of bond distances and angles in the four independent but chemically identical 'half-ligand' moieties shows excellent agreement. No distance or angle has a range greater than 4$\sigma$. Further, the differences between the several C—C distances and the several C—N distances are quite reasonable. There are nine chemically different C—C bonds and five different C—N bonds in the structure. For each bond type the average distance was calculated and the bond order was calculated from a simple Hückel molecular-orbital treatment of the $\pi$-electron system in the ligand. The correlation coefficient between bond distance and bond order is $-0\cdot96$ for the nine C—C bonds and $-0\cdot87$ for the five C—N bonds.

The water molecules are involved in hydrogen bonding. O(12) donates a hydrogen bond to O(11) at 2·792 (6) Å and accepts a hydrogen bond from N(25) at 2·987 (16) Å, while O(22) donates to O(21) at 2·874 (6) Å and accepts from N(16) at 3·053 (7) Å. O(33) forms a hydrogen bond to Cl(12).

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