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# Metal–Phenoxyalkanoic Acid Interactions. Part 8*. Crystal and Molecular Structure of Aquabis(4-chloro-2-methylphenoxyacetato)bis(pyridine)copper(II)

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As part of a study of the interaction of metal ions with phenoxyalkanoic acids, metal(II) complexes of the commercial herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA) are currently being investigated. The crystal structure of tetraaquabis(4-chloro-2-methylphenoxyacetato) magnesium(II) dihydrate has already been reported [2] and is monomeric six-coordinate with *trans*-related MCPA ligands. Interaction of MCPA with copper(II) results in a pale blue complex for which analysis gives an indeterminate stoichiometry, unlike the $[Cu(MCPA)_2(H_2O)_2]$ reported by Heath and Clark [3]. This complex forms a blue crystalline product of basic formula $Cu(MCPA)_2(py)_2(H_2O)$ when reacted with pyridine in ethanol. The crystal structure of the pyridine adduct was determined to ascertain the nature of the coordination and to compare the conformation of the MCPA ligand with that of the free acid [4].

## Experimental

The title compound was prepared by digesting an ethanolic solution of the Cu(II)–MCPA complex with an excess of pyridine. Crystals obtained from the resultant solution were pale blue flat needles elongated along *b*. A cleaved section (0.25 X 0.15 X 0.05 mm) mounted about the prism axis was used for preliminary X-ray examination and for data collection.

### *Crystal Data*

$C_{28}H_{28}Cl_2CuN_2O_7$, $M_r$ = 639.0, monoclinic, space group *C*2 ($C_2^3$, No. 5), $a$ = 15.828(9), $b$ = 5.815(2), $c$ = 16.591(4) Å, $\beta$ = 110.83(3)°, $V$ = 1427 Å$^3$, $Z$ = 2, $D_c$ = 1.49 g cm$^{-3}$, $F(000)$ = 658, $\mu$(Mo-K$\alpha$) = 10.3 cm$^{-1}$.

### *Collection of X-ray Data and Structure Solution*

Data were collected on a Nicolet R3 four-circle diffractometer using graphite monochromatized Mo-K$\alpha$ radiation ($\lambda$ = 0.71069 Å). 1608 unique reflections were collected up to $2\theta$ = 52°. The intensity data were processed with the learnt profile fitting procedure of Diamond [5], and 771 observed reflections with $I > 1.5\ \sigma(I)$ were used in structure analysis. Intensity statistics [mean$|E^2 - 1|$= 0.79] and the presence of two molecules in the unit cell were consistent with either of the non-centrosymmetric space groups *C*2 or *Cm*. The space group *C*2 places fewer symmetry constraints on the stereochemistry of the complex and the structure was subsequently solved in *C*2 using the heavy atom method by placing copper at the origin, with the remainder of the non-hydrogen atoms located from several difference-Fourier syntheses. Full-matrix least-squares refinement with isotropic thermal parameters for all atoms except Cu, Cl and the coordinated atoms [Ow, N(1p) and O(11)] reduced $R$ [= $\Sigma|Fo - Fc\|/\Sigma|Fo|$] to 0.113 and $Rw$ [=$\Sigma w(\|Fo - Fc\|^2/\Sigma|Fo|^2)^{1/2}$] to 0.104. A value $w$ = $1.29/[\sigma^2(Fo) + 0.00257\ (Fo)^2]$ was used. Hydrogens were not included in the refinement. The maximum peak in the final difference-Fourier was 0.26 eÅ$^{-3}$. No correction was made for absorption as 360° $\psi$ scans of several selected reflections showed that it had a negligible effect. The high residual $R$ is considered to be due to poor crystal quality, also found to be a problem in the Mg(II) complex [2] and in MCPA itself [4]. All computations were carried out using SHELX 76 [6]. Final atomic positional parameters are listed in Table I while bond distances and angles are given in Table II.

## Discussion

The molecules of $[Cu(MCPA)_2(py)_2(H_2O)]$ are monomeric five-coordinate with square pyramidal stereochemistry (Fig. 1). The coordination sphere around each copper(II) ion consists of two oxygens from the carboxyl groups of unidentate MCPA ligands [Cu–O, 1.95(1) Å] and two nitrogens from

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*Part 7: $[Mn(2,4,5\text{-}T)(H_2O)_5]^+[2,4,5\text{-}T]^-$ and its $Mg^{II}$ polymorph [1].

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TABLE I. Atomic Coordinates ($\times 10^4$).

| | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Cu | 0 | 0 | 0 |
| Ow | 0 | 3897(51) | 0 |
| C(1) | 1124(19) | −3836(53) | 3360(18) |
| C(2) | 1285(17) | −5832(46) | 3845(17) |
| C(21) | 570(15) | −6796(48) | 4133(15) |
| C(3) | 2154(16) | −6873(52) | 4155(15) |
| C(4) | 2806(17) | −5880(50) | 3876(16) |
| Cl(4) | 3883(5) | −7126(20) | 4226(6) |
| C(5) | 2660(20) | −3939(58) | 3399(20) |
| C(6) | 1808(17) | −2757(59) | 3102(16) |
| O(7) | 283(11) | −3015(38) | 3058(10) |
| C(8) | 41(17) | −1179(56) | 2532(17) |
| C(9) | −33(19) | −1643(68) | 1535(20) |
| O(10) | 88(13) | −3708(39) | 1385(13) |
| O(11) | −213(9) | 102(52) | 1087(11) |
| N(1p) | −1367(11) | −375(45) | −675(12) |
| C(2p) | −1830(18) | −2068(57) | −480(18) |
| C(3p) | −2807(16) | −2176(51) | −940(16) |
| C(4p) | −3183(17) | −637(49) | −1602(16) |
| C(5p) | −2692(21) | 1163(56) | −1774(19) |
| C(6p) | −1714(18) | 1320(53) | −1312(17) |

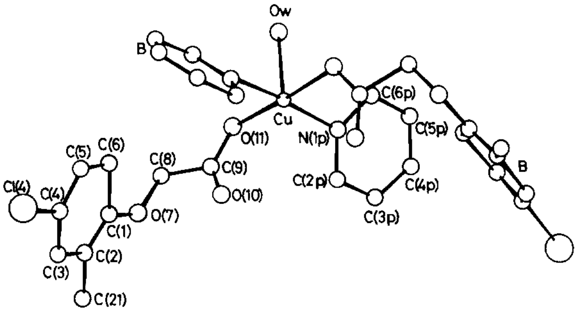

Fig 1 Complex stereochemistry and atom naming scheme for [Cu(MCPA)$_2$(py)$_2$(H$_2$O)]. The primed section of the molecule is generated by the two-fold symmetry operation (−x, y − z).

pyridines [Cu–N, 2.06(1) Å] forming the basal plane. The fifth coordination position is provided by a water oxygen [Cu–Ow, 2.27(2) Å] giving the molecule two-fold rotational symmetry coincident with a crystallographic *C*2 axis. In this respect the complex differs from the square pyramidal aquabis-

TABLE II. Bond Distances (Å) and Angles (degrees)

a. *Distances*

| | | | |
|---|---|---|---|
| Cu–Ow | 2.27(2) | C(1)–O(7) | 1.33(2) |
| Cu–O(11) | 1.95(1) | O(7)–C(8) | 1.35(2) |
| Cu–N(1p) | 2.06(1) | C(8)–C(9) | 1.64(3) |
| C(1)–C(2) | 1.38(2) | C(9)–O(10) | 1.25(2) |
| C(2)–C(3) | 1.42(2) | C(9)–O(11) | 1.23(3) |
| C(2)–C(21) | 1.49(2) | N(1p)–C(2p) | 1.33(2) |
| C(3)–C(4) | 1.40(2) | C(2p)–C(3p) | 1.46(2) |
| C(4)–C(5) | 1.35(3) | C(3p)–C(4p) | 1.38(3) |
| C(4)–Cl(4) | 1.75(2) | C(4p)–C(5p) | 1.39(3) |
| C(5)–C(6) | 1.44(3) | C(5p)–C(6p) | 1.46(3) |
| C(6)–C(1) | 1.44(3) | C(6p)–C(1p) | 1.41(2) |

b. *Angles*

| | | | |
|---|---|---|---|
| Ow–Cu–O(11) | 88.3(7) | C(3)–C(4)–C(5) | 123(2) |
| Ow–Cu–N(1p) | 96.1(6) | C(3)–C(4)–Cl(4) | 118(2) |
| O(11)–Cu–N(1p) | 90.7(5) | C(5)–C(4)–Cl(4) | 119(2) |
| O(11)–Cu–O(11)′ | 176.5(8) | C(4)–C(5)–C(6) | 123(2) |
| O(11)–Cu–N(1p)′ | 89.7(8) | C(5)–C(6)–C(1) | 114(2) |
| N(1p)–Cu–N(1p)′ | 167.9(7) | C(1)–O(7)–C(8) | 123(2) |
| Cu–O(11)–C(9) | 117(2) | O(7)–C(8)–C(9) | 115(2) |
| Cu–N(1p)–C(2p) | 120(1) | C(8)–C(9)–O(10) | 113(2) |
| Cu–N(1p)–C(6p) | 113(1) | C(8)–C(9)–O(11) | 113(2) |
| C(2)–C(1)–C(6) | 122(2) | O(10)–C(9)–O(11) | 133(3) |
| C(2)–C(1)–O(7) | 118(2) | C(2p)–N(1p)–C(6p) | 127(2) |
| C(6)–C(1)–O(7) | 119(2) | N(1p)–C(2p)–C(3p) | 118(2) |
| C(1)–C(2)–C(3) | 122(2) | C(2p)–C(3p)–C(4p) | 118(2) |
| C(1)–C(2)–C(21) | 120(2) | C(3p)–C(4p)–C(5p) | 122(2) |
| C(3)–C(2)–C(21) | 118(2) | C(4p)–C(5p)–C(6p) | 120(2) |
| C(2)–C(3)–C(4) | 116(2) | C(5p)–C(6p)–C(1p) | 114(2) |

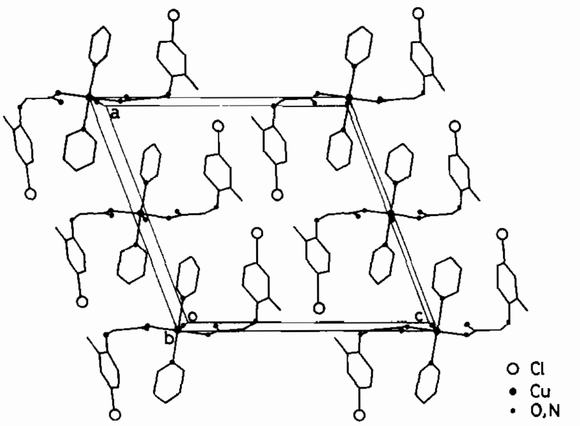

Fig. 2. Perspective view of the packing in the cell (hydrogens omitted).

(phenoxyacetato)bis(pyridine)copper(II), [7] which has no rotational symmetry, the two phenoxy ligands being conformationally dissimilar. However, bond distances and angles within the coordination sphere are similar [1.98(1), 2.04(1), 2.24(1) Å for Cu–O, Cu–N and Cu–Ow respectively]. Triaquabis(phenoxyacetato) copper(II) is another example of a metal–phenoxy complex with square pyramidal stereochemistry [8].

In the present example, the conformation of the phenoxy ligand is considerably changed from that of the planar MCPA acid molecule [torsion angles: C(6)–C(1)–O(7)–C(8), −1.4°; C(1)–O(7)–C(8)–C(9), +74.1°; O(7)–C(8)–C(9)–O(11), −176.7°, compared with +8.3°, +173.5°, +176.3° respectively for the equivalent angles in MCPA]. The torsion angle C(8)–C(9)–O(11)–Cu is +163.8°. However, the gross *syn–syn* (carbonyl) conformation of MCPA is retained, the assignment of the carboxylate oxygens as having 'carbonyl' [O(10)] or 'hydroxyl' [O(11)] origin being possible on the basis of the difference between the C–C–O angles [9] ['carbonyl', 119(3)°; 'hydroxyl', 109(3)°]. The dihedral angle between the benzene ring and the acid group [C(9), O(10), O(11)] is 108.8°.

Packing of the molecules in the unit cell results in stacks down the *b* direction at $x = 0$ and $x = \frac{1}{2}$ (Fig. 2). The distance between Cu and the coordinated water molecule of the next complex unit along the two-fold axis is 3.54 Å. In the phenoxyacetato complex, the equivalent distance is 3.63 Å [7]. Apart from symmetrical intermolecular contacts between the water and the un-coordinated carboxylate oxygens (2.65 Å), there are no other hydrogen bonding interactions between the stacks of molecules. The intramolecular O(7)[ether]–O(10)[carboxylate] distance is 2.71 Å which compares with 2.62 Å in the free acid and the mean of 2.71 Å for a series of 17 phenoxyalkanoic acids [10].

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## References

1 G. Smith, E. J. O'Reilly and C. H. L. Kennard, *Inorg Chim. Acta, 62,* 241 (1982) (accepted for publication).
2 G. Smith, E. J. O'Reilly and C. H. L. Kennard, *Cryst. Struct. Comm., 10,* 1397 (1981).
3 O. V. S Heath and J. E. Clark, *Nature, 183,* 1176 (1959).
4 G. Smith and C. H. L. Kennard, *Cryst. Struct. Comm., 10,* 295 (1981).
5 R. Diamond, *Acta Cryst., A25,* 43 (1969).
6 G M. Sheldrick, SHELX 76. Programme for crystal structure determination, University of Cambridge, England
7 C. K. Prout, M. J. Barrow and F. J. C. Rossotti, *J Chem. Soc. A,* 3326 (1971).
8 C. V. Goebel and R. J. Doedens, *Inorg. Chem., 10,* 2607 (1971).
9 G. Smith, E J. O'Reilly, C. H. L. Kennard, K. Stadnika and B. Oleksyn, *Inorg. Chim. Acta, 47,* 111 (1981).
10 G. Smith and C. H. L Kennard, *J Agr. Food Chem., 27,* 779 (1979)