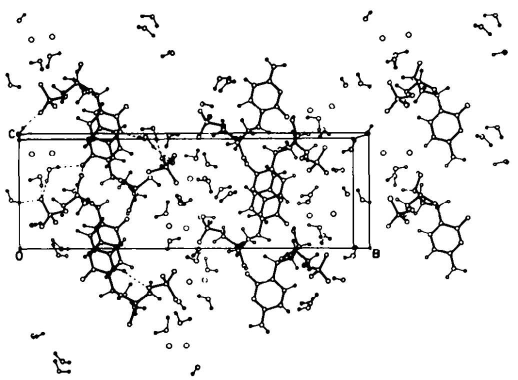

Fig. 5. The molecular packing viewed down **a**. Hydrogen bonds are indicated by broken lines.

The two cations are completely surrounded by water molecules (Fig. 6).* Na(1) has six neighbours in a nearly octahedral environment. Na(2) is pentacoordinated, sharing four of the water molecules with Na(1). The coordination polyhedra extend in infinite chains along **a**. Coordination distances are given in Table 2, angles have been deposited.*

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* See deposition footnote.

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Bis[μ-ammoniomethyl(methyl)phosphinato-*O*,*O*′]-diaquatetrachlorodicopper(II), $Cu_2(C_2H_8NO_2P)_2Cl_4(H_2O)_2$

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Abstract. $C_4H_{20}Cl_4Cu_2N_2O_6P_2$, $M_r = 523{\cdot}05$ triclinic, $P\bar{1}$, $a = 8{\cdot}975\,(2)$, $b = 8{\cdot}658\,(2)$, $c = 6{\cdot}326\,(2)$ Å, $\alpha = 90{\cdot}32\,(1)$, $\beta = 117{\cdot}34\,(1)$, $\gamma = 94{\cdot}37\,(1)°$, $V = 434{\cdot}9$ Å^3, $Z = 1$, $D_m = 1{\cdot}99\,(1)$ (by flotation), $D_x = 2{\cdot}00$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 10{\cdot}65$ mm^{-1}, $F(000) = 262$, $R = 0{\cdot}058$ for 1139 observed counter reflexions. The coordination sphere of the Cu atom is square pyramidal, consisting of two O atoms from different phosphinato groups, two Cl atoms and one water molecule. The Cu atoms are bridged by two phosphinato groups, giving rise to an eight-membered ring. The Cu—Cu distance is 5·081 (2) Å. The ligand exists as a zwitterion.

Introduction. The structure of the title compound has been determined as one of a series of complexes of aminomethylphosphonic and aminomethyl(methyl)phosphinic acids (AMPh and AMMPh, respectively) with divalent metal ions. So far only the crystal structures of the six compounds $[Mn(AMMPh)_2(H_2O)_2]Br_2.2H_2O$ (Głowiak & Sawka-Dobrowolska, 1977*a*), $[MnCl_2(AMMPh)_2(H_2O)_2]$ (Głowiak & Sawka-Dobrowolska, 1977*b*), $[Cu(AMPh)_2]$ (Głowiak, Sawka-Dobrowolska, Jeżowska-Trzebiatowska & Antonów, 1980*a*), $[Zn(AMMPh)_2Cl_2]$ (Žák, Kožíšek & Głowiak, 1981), $[Zn(AMPh)_2].4H_2O$ (Fenot, Darriet & Garrigou-Lagrange, 1978), $[Co(AMPh)_2(H_2O)_2].H_2O$ (Głowiak, Sawka-Dobrowolska, Jeżowska-Trzebiatowska & Antonów, 1980*b*) have been investigated. A typical feature of these complexes is their polymeric nature. Of the six complexes investigated, only one is monomeric. In this group of compounds the

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metal ions are linked by single or double phosphate bridges.

In this paper we report the structure of the new dimeric Cu complex formed during the reaction between cupric chloride and aminomethyl(methyl)-phosphinic acid (AMMPh) in stoichiometric ratio.

Experimental. Blue-green crystals from aqueous solution, triclinic space group from Weissenberg photographs, $P\bar{1}$ assumed, refinement confirmed this choice; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter,. graphite monochromator, cell parameters by least squares from setting angles of 15 reflexions, 1175 independent reflexions, $2\theta_{max} = 110{\cdot}0°$, variable θ–2θ scans, scan rate 2·0—20·0° min^{-1} depending on intensity; standard measured every 15 reflexions, no significant change; intensities corrected for Lorentz and polarization but not for absorption, 1139 with $I > 1{\cdot}96\sigma(I)$ used for structure determination, calculations performed on Syntex (1976) *XTL* system with neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); heavy-atom method, full-matrix least squares in $P\bar{1}$, H atoms from difference synthesis; inclusion of non-H atoms with anisotropic thermal parameters and H atoms with fixed coordinates and thermal parameters $B = 2{\cdot}5$ Å^2 gave $R = 0{\cdot}058$, $R_w = 0{\cdot}079$, where $w = 1/\sigma^2(F)$.*

Discussion. Final positional parameters are given in Table 1, bond lengths and angles in Table 2. Fig. 1 shows the projection of the crystal structure on (001) and indicates the numbering system.

The crystal structure contains discrete units of the dimeric molecule $[Cu(AMMPh)Cl_2(H_2O)]_2$ in which the Cu atom has approximately square-pyramidal coordination. The equatorial plane is defined by two oxygen atoms, O(1) and O(2), from different phosphinato groups, Cl(2) and a water molecule, O(*W*). The coordination sphere is completed by a loosely bound axial chlorine atom, Cu—Cl(1) distance 2·637 (2) Å. The distribution of atoms around Cu is summarized in Fig. 1 and Table 2. The Cu atom lies slightly [−0·17 (2) Å] out of the base plane of the pyramid, in the direction of the chlorine atom. The four closest ligand atoms are not truly coplanar.

The equation of the least-squares plane through atoms O(1), O(2), Cl(2) and O(*W*) is $0{\cdot}3243\,X - 0{\cdot}4470\,Y - 0{\cdot}8337\,Z + 0{\cdot}5882 = 0$, and the deviations of the atoms from this plane are: O(1) −0·053 (6), O(2) 0·060 (6), Cl(2) 0·050 (2), and O(*W*)

Table 1. *Positional parameters* (×10⁴) *with e.s.d.'s in parentheses*

$B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	x	*y*	*z*	B_{eq}(Å^2)
Cu	1724 (2)	2554 (1)	407 (2)	2·2 (1)
Cl(1)	2051 (3)	4121 (3)	4204 (4)	1·6 (2)
Cl(2)	4481 (3)	2807 (3)	1269 (4)	2·3 (2)
P	1903 (3)	−1068 (2)	860 (4)	1·1 (2)
O(1)	1891 (8)	543 (7)	1762 (11)	1·8 (5)
O(2)	−725 (8)	2316 (6)	−1137 (11)	1·9 (5)
O(*W*)	1453 (8)	4510 (7)	−1396 (11)	1·8 (5)
N	4120 (9)	−3331 (8)	2597 (13)	1·6 (6)
C(1)	1605 (12)	−1069 (12)	−2109 (16)	2·2 (8)
C(2)	3993 (10)	−1639 (10)	2763 (16)	1·2 (6)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Cu—Cu^{i}	5·081 (2)	P—O(1)	1·506 (6)
Cu—Cu^{ii}	5·323 (2)	P—O(2^{i})	1·521 (7)
Cu—Cl(1)	2·637 (2)	P—C(1)	1·771 (7)
Cu—Cl(2)	2·268 (3)	P—C(2)	1·813 (10)
Cu—O(1)	1·931 (6)	C(2)—N	1·485 (11)
Cu—O(2)	1·945 (7)		
Cu—O(*W*)	2·014 (6)		
Cl(1)—Cu—Cl(2)	97·1 (1)	Cu—O(1)—P	133·3 (4)
Cl(1)—Cu—O(1)	95·6 (2)	Cu—O(2)—P^{i}	129·3 (4)
Cl(1)—Cu—O(2)	95·3 (2)	O(1)—P—O(2^{i})	116·0 (4)
Cl(1)—Cu—O(*W*)	91·3 (2)	O(1)—P—C(1)	111·2 (4)
Cl(2)—Cu—O(1)	92·9 (2)	O(2^{i})—P—C(1)	111·1 (4)
O(1)—Cu—O(2)	92·7 (3)	O(1)—P—C(2)	105·2 (4)
Cl(2)—Cu—O(*W*)	87·7 (2)	O(2^{i})—P—C(2)	104·3 (4)
O(*W*)—Cu—O(2^{i})	85·2 (3)	C(1)—P—C(2)	108·4 (4)
O(1)—Cu—O(*W*)	172·9 (3)	P—C(2)—N	113·2 (6)
Cl(2)—Cu—O(2)	165·9 (3)		

Symmetry code (i) $-x,-y,-z$ (ii) $1-x,-y,1-z$

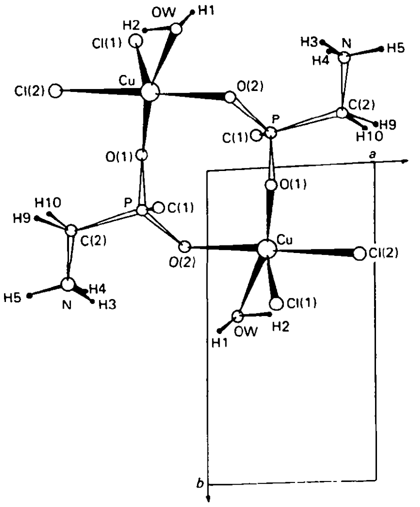

Fig. 1. Projection of the structure $[Cu(AMMPh)Cl_2H_2O]_2$ along **c**.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38248 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

−0·057 (6) Å (see also angles in Table 2). The molecular geometry of the complex found here is as expected in a square-pyramidal Cu complex (Fischer & Bau, 1978).

The two Cu atoms of one dimeric unit are held together by two bridging phosphinato groups. The Cu atoms and the phosphinato groups form a puckered eight-membered ring where the Cu···Cu distance is 5·081 (2) Å. The torsion angles Cu—O(1)—P—C(2) and Cu—O(2)—P^{i}—C(2^{i}) are 113·8 (5) and −141·4 (6)°, respectively.

Like the molecule in the crystal of free aminomethyl(methyl)phosphinic acid, the AMMPh ligand in the Cu complex occurs in zwitterionic form. The most noticeable difference appears in the C(1)—P—C(2) angle whose value 108·4 (5)° in the Cu complex is greater than that found in AMMPh acid, 101·7 (2)°. On the other hand, the O(2)—P—C(2) 104·3 (4) and O(1)—P—C(2) 105·2 (4)° angles are slightly decreased compared with those in AMMPh acid 109·1 (2) and 107·5 (2)°, respectively. However, other valence angles and interatomic distances of the ligand are similar to those observed in AMMPh acid (Głowiak & Sawka-Dobrowolska, 1977*c*). In the present structure the phosphinato group is negatively charged, the charge being distributed between O(1) and O(2); P—O lengths 1·506 (6) and 1·521 (7) Å. The conformations of free AMMPh acid and AMMPh ligand in the Cu complex are described by the torsion angles in Fig. 2.

The Cu complex contains a network of hydrogen bonds which plays an important role in stabilization. the hydrogen-bond lengths and angles are given in Table 3. All H atoms available for hydrogen-bond formation are used. Cl(1) is the acceptor in four of the five bonds, two from the amino group and two from the O(*W*) molecule. The NH_3^+ group, which is not involved in metal coordination, forms H bonds with Cl(1) and O(*W*) of neighboring molecules. O(*W*) is coordinated to Cu and also forms hydrogen bonds with Cl(1).

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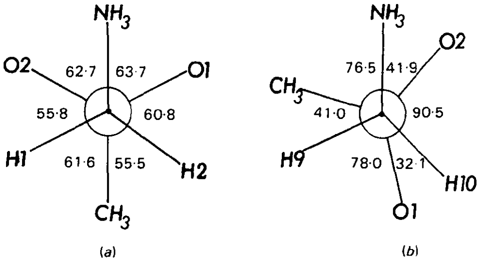

Fig. 2. Newman projections along P—C. (*a*) AMMPh; (*b*) AMMPh in the Cu complex. E.s.d.'s are 0·5 and 0·7°, respectively, for angles not involving H atoms.

Table 3. *Hydrogen-bond lengths* (Å) *and angles* (°)

D—H···*A*	*D*···*A*	*D*—H	H···*A*	∠*D*—H···*A*
N—H(3)···Cl(1^{i})	3·237 (7)	0·99	2·29	161
N—H(4)···O(W^{i})	3·052 (10)	0·97	2·33	131
N—H(5)···Cl(1^{ii})	3·204 (7)	0·98	2·24	179
O(*W*)—H(2)···Cl(1^{iii})	3·088 (7)	1·03	2·09	165
O(*W*)—H(1)···Cl(1^{iv})	3·148 (7)	0·97	2·18	176

Symmetry code (i) $x,y-1,z$ (iii) $x,y,z-1$
(ii) $1-x,-y,1-z$ (iv) $-x,1-y,-z$

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