

Kovalenzradien (Pauling, 1968) beträgt dagegen 2,21 Å, die beobachtete Aufweitung der Tl—O-Bindung entspricht damit den Donoreigenschaften des Liganden Pyridin-*N*-oxid. In der vorausgehenden Strukturbestimmung (Ruiz-Valero *et al.*, 1984) berichten die Autoren von Tl—O-Abständen von 2,22 (4) und 2,50 (4) Å, diese Werte sind jedoch die Folge fehlender Absorptionskorrektur und der Wahl der falschen Raumgruppe.

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Structure of *catena*-Bis[μ -(aminomethyl)methylphosphinato-*N,O'*]- μ -chloro-copper(II)]

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Abstract. $[\text{Cu}_2(\text{C}_2\text{H}_7\text{NO}_2\text{P})_2\text{Cl}_2]$, $M_r = 414.1$, monoclinic, $P2_1/c$, $a = 8.122(3)$, $b = 6.341(3)$, $c = 13.231(5)$ Å, $\beta = 110.04(5)^\circ$, $U = 640.2$ Å³, $Z = 2$, $D_m = 2.15(1)$, $D_x = 2.148$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.10$ mm⁻¹, $F(000) = 412$, room temperature, final $R = 0.030$ for 910 reflexions. The coordination around Cu is a distorted tetragonal pyramid, consisting of two O atoms from different phosphinato groups, N and two Cl atoms. The five-membered chelate ring has an envelope-like conformation. The Cu atoms are bridged by two Cl atoms and linked into infinite chains by the phosphinato bridges. The Cu...Cu distances are 3.282(1) and 4.806(1) Å. The ligand occurs in anionic form.

Introduction. The structure of the title compound has been determined as one of a series of studies of complexes of aminophosphonic and aminophosphinic acids with divalent metal ions. So far only the crystal structures of the seven compounds listed by Sawka-Dobrowolska & Głowiak (1983) have been investigated. A typical feature of these complexes is their polymeric nature. Of the seven complexes investigated, only one is monomeric (Głowiak & Sawka-Dobrowolska, 1977*b*) and one is dimeric (Sawka-Dobrowolska & Głowiak, 1983). In this group of compounds the metal ions are linked by single or double phosphate bridges.

Our recent studies of the $\text{Cu}(\text{NH}_3^+\text{CH}_2\text{PO}_3^{2-})_2$ (Głowiak, Sawka-Dobrowolska, Jeżowska-

Trzebiatowska & Antonów, 1980) and $[\text{Cu}\{\text{NH}_3^+\text{CH}_2\text{P}(\text{CH}_3)\text{O}_2^-\}\text{Cl}_2(\text{H}_2\text{O})_2]$ (Sawka-Dobrowolska & Głowiak, 1983) complexes have shown that the amino N atom does not participate in the direct binding of the metal ion.

The present structure is the first metal complex with aminomethylphosphinic acid where amino N and phosphinic O bond to the metal ion forming a five-membered ring.

Experimental. Prepared by reaction between cupric chloride and (aminomethyl)methylphosphinic acid in stoichiometric ratio 1:1. Blue crystals from aqueous solution at pH = 7 at room temperature, dimensions 0.18 × 0.10 × 0.25 mm; D_m by flotation in $\text{CHBr}_3/\text{CHCl}_3$; monoclinic from Weissenberg photographs, $P2_1/c$; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflexions with $20 \leq 2\theta \leq 32^\circ$ measured on the diffractometer; 1132 independent reflexions; $2\theta_{\text{max}} = 50.0^\circ$; variable θ - 2θ scans, scan rate 2.0–29.3° min⁻¹, depending on intensity; two standards (225, 423) measured every 50 reflexions, intensity variation $\pm 2.5\%$; Lorentz and polarization corrections; no correction for absorption; 910 reflexions with $I > 4.0\sigma(I)$ used for structure determination; index range h 0 to 9, k 0 to 7, l -15 to 14; calculations performed on a Nova 1200 computer with programs supplied by Syntex (1976); neutral-atom scattering

factors from *International Tables for X-ray Crystallography* (1974); structure determined by heavy-atom method; full-matrix least-squares refinement; $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1/\sigma^2(F)$; H atoms of CH_3 group from difference synthesis, other H atoms in calculated positions; non-H atoms refined with anisotropic thermal parameters and H atoms with fixed coordinates and thermal parameters $B = 3.0 \text{ \AA}^2$; in final least-squares cycle $(\Delta/\sigma)_{\text{max}} = 0.01$; $(\Delta\rho)_{\text{max}} = 0.5$, $(\Delta\rho)_{\text{min}} = -0.4 \text{ e \AA}^{-3}$; $R = 0.030$, $wR = 0.035$, $S = 2.943$.

Discussion. Final positional parameters are given in Table 1.* Fig. 1 shows part of the crystal structure and indicates the numbering system used.

In this structure the coordination around Cu is a distorted tetragonal pyramid. The tridentate (amino-methyl)methylphosphinic acid ligand coordinates to the Cu atom through O(1) and N forming a five-membered ring and O(2) is bonded to another Cu atom. The equatorial plane is defined by two O atoms, O(1) and O(2), from different phosphinato groups, and by one N

* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42115 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent isotropic thermal factors (\AA^2) with e.s.d.'s in parentheses*

	x	y	z	B_{eq}
Cu	0.0445 (1)	0.0749 (1)	0.1253 (1)	1.67 (4)
P	-0.2123 (2)	0.1807 (2)	0.2339 (1)	1.55 (8)
Cl	0.1999 (2)	0.1807 (2)	0.0173 (1)	2.09 (8)
O(1)	-0.0418 (4)	0.0655 (6)	0.2461 (3)	2.2 (3)
O(2)	-0.2034 (4)	0.3392 (5)	0.3207 (3)	2.0 (2)
N	-0.1283 (5)	0.3051 (6)	0.0624 (3)	2.0 (3)
C(1)	-0.2792 (7)	0.2992 (9)	0.1012 (4)	2.4 (4)
C(2)	-0.3773 (7)	-0.0057 (9)	0.2311 (4)	2.7 (4)

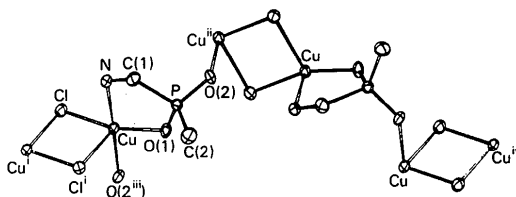


Fig. 1. Part of the crystal structure of the title compound. The H atoms are not shown.

Table 2. *Bond distances (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses*

Cu—Cu ⁱ	3.282 (1)	Cu—Cl—Cu ⁱ	80.43 (5)
Cu—Cu ⁱⁱ	4.806 (1)	Cl—Cu—Cl ⁱ	99.57 (5)
Cu—Cl	2.307 (1)	O(1)—Cu—Cl	160.3 (1)
Cu—Cl ⁱ	2.749 (1)	O(1)—Cu—Cl ⁱ	99.6 (1)
Cu—O(1)	1.954 (3)	O(2 ⁱⁱⁱ)—Cu—Cl	90.9 (1)
Cu—O(2 ⁱⁱⁱ)	1.943 (3)	O(2 ⁱⁱⁱ)—Cu—Cl ⁱ	91.8 (1)
Cu—N	1.998 (4)	O(2 ⁱⁱⁱ)—Cu—O(1)	93.2 (1)
P—O(1)	1.524 (4)	N—Cu—Cl	89.1 (1)
P—O(2)	1.510 (3)	N—Cu—Cl ⁱ	84.6 (1)
P—C(1)	1.813 (5)	N—Cu—O(1)	88.0 (2)
P—C(2)	1.778 (6)	N—Cu—O(2 ⁱⁱⁱ)	176.4 (2)
C(1)—N	1.482 (7)	O(1)—P—O(2)	115.7 (2)
		O(1)—P—C(1)	105.2 (2)
		O(1)—P—C(2)	109.5 (2)
		O(2)—P—C(1)	112.4 (2)
		O(2)—P—C(2)	107.3 (2)
		C(1)—P—C(2)	106.4 (3)
		P—C(1)—N	109.7 (4)

Symmetry code

- (i) $-x, -y, -z$
 (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$
 (iii) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$

and one Cl atom. The coordination sphere is completed by a loosely bound axial Cl atom (related by a symmetry centre), Cu—Clⁱ distance 2.749 (1) \AA . The distribution of atoms around Cu is summarized in Fig. 1 and Table 2. The four closest ligand atoms are not truly coplanar (see angles in Table 2). The molecular geometry of the complex found here is as expected for square-pyramidal Cu complexes (Fischer & Bau, 1978).

The Cu atoms related by a symmetry centre are linked by double Cl bridges forming a dimeric Cu—Cl₂—Cu unit, where the Cu...Cu distance is 3.282 (1) \AA . These dimers are held together by the phosphinato groups O(1)—P—O(2) in polymeric —Cu—Cl₂—Cu—O—P—O—Cu—Cl₂—Cu— chains. The Cu...Cuⁱⁱ separation of adjacent pyramids (related by the 2₁ axis) is 4.806 (1) \AA .

The ligand in this complex occurs in anionic form. The most noticeable difference between it and the free acid is in the C(2)—P—C(1) angle whose value of 106.4 (3)° in the Cu complex is greater than that in free (aminomethyl)methylphosphinic acid (Głowiak & Sawka-Dobrowolska, 1977*a*), 101.7 (2)°. Further, angle O(1)—P—C(1), 105.2 (2)°, is slightly decreased and O(2)—P—C(1), 112.4 (2)°, is slightly increased compared with the corresponding angles in the free acid [107.5 (2) and 109.1 (2)°, respectively]. Other valence angles and interatomic distances of the ligand are similar to those in the free acid and in the dimeric Cu complex (Sawka-Dobrowolska & Głowiak, 1983).

It is interesting to note that in the title complex the torsion angle C(2)—P—C(1)—N of $-133.5 (4)^\circ$ is different from that of the free acid, where the methyl group is *trans* to the amino group and this angle is $-179.8 (5)^\circ$. In the dimeric Cu complex [C(2)—P—C(1)—N $-76.5 (7)^\circ$] the methyl group is twisted by about 45° around the P—C(1) bond, relative to the situation in the title complex.

The five-membered chelate ring shows an envelope-like conformation with N deviating $-0.439(4)$ Å from the plane through Cu, O(1), P, C(1).

The crystal structure of the Cu complex contains a network of weak hydrogen bonds. The amino group and O(1), O(2) of the phosphinato group are coordinated to Cu and also form hydrogen bonds. All H atoms attached to N are involved [H(2)⋯O(1)($-\frac{1}{2}x, \frac{1}{2}+y, \frac{1}{2}-z$) 2.27 , N⋯O(1) $2.942(5)$ Å, \angle N—H(2)⋯O(1) 124° ; and H(1)⋯O(2)($x, \frac{1}{2}-y, -\frac{1}{2}+z$) 2.22 , N(1)⋯O(2) $3.177(6)$ Å, \angle N—H(1)⋯O(2) 160°].

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On the SiOSi Angle in 1,2-Di-*tert*-butyl-1,1,2,2-tetraphenyldisiloxane

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Abstract. C₃₂H₃₈OSi₂, $M_r = 494.83$, monoclinic, $P2_1/n$, $a = 11.783(2)$, $b = 14.259(2)$, $c = 17.358(2)$ Å, $\beta = 90.90(1)^\circ$, $V = 2916.0$ Å³, $Z = 4$, $D_x = 1.127$ g cm⁻³, Cu $K\alpha$, $\lambda = 1.54178$ Å, $\mu = 12.5$ cm⁻¹, $F(000) = 1063.9$, room temperature, final $R = 4.54\%$ for 3981 reflections with $|F_o| > 3\sigma$. The principal geometric parameters are: $r(\text{Si—O})_{\text{av}} = 1.635(3)$ Å; $\angle\text{SiOSi} = 152.4(1)^\circ$; $r(\text{Si}\cdots\text{Si}) = 3.177(1)$ Å; $r(\text{Si—C})_{\text{av}} = 1.879(5)$ Å. The *tert*-butyl groups are *gauche* to each other when considered with respect to the virtual Si⋯Si bond. The six Si—C bonds are staggered about the Si⋯Si direction with approximate $\bar{3}$ symmetry. One Si—C(butyl) bond is near the plane formed by the SiOSi moiety.

Introduction. Organodisiloxanes appear to adopt either a bent configuration with an SiOSi angle of 140 – 160° or a linear configuration with SiOSi equal to 180° . The value of the SiOSi angle has been determined by gas-phase electron diffraction for O(SiH₃)₂ (Almenningen, Bastiansen, Ewing, Hedberg & Trøtteberg, 1963), for O(SiF₃)₂ (Airey, Glidewell, Rankin, Robiette, Sheldrick & Cruickshank, 1970) and for O(SiCH₃)₂ (Airey, Glidewell, Robiette & Sheldrick, 1971) to be 144.1 , 155.7 and 146° , respectively. From low-temperature X-ray diffraction analyses of single

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crystals, the SiOSi angle has been found to have a value of 142.2° for O(SiH₃)₂ and 148.8° for O[Si(CH₃)₃]₂ (Barrow, Ebsworth & Harding, 1979). At room temperature, methylpentaphenyldisiloxane has an SiOSi angle of 158.9° (Voronkov, Nesterov, Gusev, Alexeev & Lotarev, 1981). The unexpected linear arrangement of SiOSi was observed for the first time in the crystal of O[Si(C₆H₅)₃]₂, where the O atom lies on a center of symmetry in a $P\bar{1}$ cell (Glidewell & Liles, 1978b). Subsequently, linear SiOSi angles were found in O[Si(CH₂C₆H₅)₃]₂ (Glidewell & Liles, 1981), O[Si(CH=CH₂)₃]₂ (Gusev, Antipin, Yufit, Struchkov, Sheludyakov, Zhun & Vlasenko, 1983) and possibly O[Si(CH₂CH₂CF₃)₃]₂, although a very high R factor precludes a definitive statement (Gusev, Nesterov, Alexeev, Rodzevich, Zverev, Ivanova & Sobolevskii, 1976).

The crystal structures of a number of hexaphenyl ethers of Group IVa elements (Ph₃MOM'Ph₃) were determined for comparison with the hexaphenyl ether of Si. For ethers of Ge and Sn where $M=M'$ (Glidewell & Liles, 1978a,c) and for mixed ethers of (Si,Ge), (Ge,Sn), and (Si,Sn) where $M\neq M'$ (Morosin & Harrah, 1981) the values for the MOM' angles were confined to the range of 135 – 144° , in sharp contrast to the value of 180° for the SiOSi angle in Ph₃SiOSiPh₃. However, for the