

Fig. 1. The molecule of $O[(PhCH_2)_3Sn]_2$ viewed down the threefold axis, showing the atom numbering.

The positional parameters are given in Table 1, bond lengths and angles in Table 2.* No correction for thermal motion was applied to the bond lengths.

Fig. 1 shows a view of the molecule down the threefold axis, and the numbering of the atoms. In the tables, the H atoms of the phenyl rings are given the numbers of the C atoms to which they are bonded.

Discussion. The Sn—O distance, 1.919 (1) Å, is significantly shorter than that in the phenyl analogue, $O(Ph_3Sn)_2$, 1.955 (1) Å (Glidewell & Liles, 1978b), in which the SnOSn fragment is markedly non-linear. In a similar way the P—N distance in linear $[N(PPh_3)_2]^+$, 1.539 (2) Å, is significantly less than that in the non-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34339 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis[2-[(3-aminopropyl)amino]ethanolato]copper(II) Dimalonate Pentahydrate

BY AARNE PAJUNEN

Department of Inorganic Chemistry, University of Helsinki, Vuorikatu 20, SF-00100 Helsinki 10, Finland

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Abstract. $[Cu_4(C_5H_{13}N_2O)_4](C_3H_2O_4)_2 \cdot 5H_2O$, $C_{20}H_{52}Cu_4N_8O_{44} \cdot 2C_3H_2O_4^{2-} \cdot 5H_2O$, tetragonal, $I4_1/a$, $a = b = 15.749$ (16), $c = 34.407$ (19) Å, $Z = 8$, $D_c = 1.58$, $D_m = 1.60$ Mg m⁻³, $R = 0.067$ for 2075 observed reflections. The structure contains tetranuclear complex cations with a cubane-type Cu_4O_4 core.

linear forms of this cation where the range of PNP angles is 134.6–141.8° and the range of P—N distances 1.570–1.586 Å with a mean of 1.575 (2) Å (Wilson & Bau, 1974). Apart from the single linear occurrence of the cation $[N(PPh_3)_2]^+$ (Wilson & Bau, 1974), the only other *p*-block analogue of the present molecule is the linear $O(Ph_3Si)_2$ (Glidewell & Liles, 1978a); however, amongst *d*-block species, $O[(PhCH_2)_3Ti]_2$ is isomorphous and isostructural with the compound described here (Stoeckli-Evans, 1974).

It has been suggested (Glidewell, 1978a,b) that in molecules or ions of general type $O(MR_n)_2$, linearity at the O atom may be expected if *M* is of low electronegativity: when *R* is an electron donor, it will enhance the effect of the low electronegativity of *M*. The results reported here for $O[(PhCH_2)_3Sn]_2$ and those earlier reported for analogous $O(Ph_3M)_2$ (Glidewell & Liles, 1978a,b) are consistent with this suggestion.

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Table 1. Final positional parameters ($\times 10^4$)

E.s.d.'s are given in parentheses.

The positional parameters of the H atoms were not refined.

	x	y	z
Cu(1)	4049.2 (7)	3036.8 (7)	3442.8 (4)
Cu(2)	770.7 (7)	6646.1 (7)	3458.3 (4)
O(1)	4347 (4)	1832 (4)	3494 (2)
O(2)	2345 (7)	2664 (6)	3685 (3)
O(3)	1695 (6)	3279 (6)	3206 (3)
O(11)	-469 (4)	6687 (4)	3495 (2)
O(12)	915 (4)	5198 (4)	3696 (2)
O(13)	2323 (5)	5033 (5)	3676 (2)
N(1)	3885 (5)	4270 (5)	3357 (3)
N(2)	3516 (5)	2696 (5)	2932 (3)
N(11)	2008 (5)	6779 (5)	3373 (3)
N(12)	550 (6)	6092 (5)	2932 (3)
C(1)	3937 (7)	4606 (6)	2952 (3)
C(2)	3341 (7)	4155 (7)	2670 (3)
C(3)	3575 (7)	3238 (7)	2577 (3)
C(4)	3773 (6)	1805 (6)	2848 (3)
C(5)	3846 (6)	1336 (6)	3231 (3)
C(6)	1860 (7)	3205 (7)	3563 (4)
C(7)	1454 (7)	3826 (7)	3846 (4)
C(8)	1568 (7)	4751 (6)	3728 (4)
C(11)	2346 (7)	6848 (8)	2976 (4)
C(12)	2055 (8)	6156 (8)	2704 (4)
C(13)	1114 (8)	6207 (7)	2595 (4)
C(14)	-347 (7)	6205 (7)	2831 (3)
C(15)	-844 (7)	6153 (7)	3208 (4)
O(4)	251 (5)	4163 (5)	2935 (3)
O(5)	3626 (6)	3924 (5)	1593 (3)
O(6)	4432 (23)	6851 (23)	3282 (12)
H(1)	3380	4395	3444
H(2)	4265	4532	3495
H(3)	2993	2698	3010
H(4)	2159	7239	3494
H(5)	2250	6342	3480
H(6)	623	5574	3020
H(11)	3813	5195	2950
H(12)	4510	4529	2857
H(21)	2789	4163	2779
H(22)	3333	4470	2430
H(31)	3208	3023	2382
H(32)	4148	3221	2481
H(41)	3360	1538	2692
H(42)	4308	1800	2722
H(51)	3298	1247	3334
H(52)	4117	805	3186
H(71)	858	3705	3856
H(72)	1691	3743	4095
H(111)	2186	7377	2868
H(112)	2954	6818	2988
H(121)	2380	6203	2470
H(122)	2160	5630	2823
H(131)	1002	6750	2484
H(132)	996	5779	2409
H(141)	-431	6745	2715
H(142)	-530	5772	2660
H(151)	-1412	6334	3160
H(152)	-849	5583	3295

Weissenberg photographs showed the systematic absences $h + k + l \neq 2$, $hk0h \neq 2$ and $00ll \neq 4$, indicating the space group $I4_1/a$. Intensities and cell dimensions were measured on a Syntex P2₁ automatic

four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). The intensities were corrected for Lorentz and polarization effects. Of the 4225 independent reflections ($3 < 2\theta < 50^\circ$), 2075 had $I > 2\sigma(I)$.

The structure was solved by direct methods and Fourier syntheses with the XRAY system (Stewart, 1976). The atomic parameters of non-hydrogen atoms were refined by the block-diagonal least-squares method. During the refinement the thermal parameter of one water O atom became very high, probably because of the low occupancy of this water molecule in the crystal. The occupancy parameter was later fixed at 0.5. Although most of the H atoms of the ligand and malonate ion were found by difference synthesis, their positions were calculated geometrically. They were included in the subsequent refinement at fixed positions with a fixed $U = 0.06 \text{ \AA}^2$. The H atoms of the water molecules could not be located. At the final stage of refinement, anisotropic temperature factors were introduced for all non-hydrogen atoms except one water O atom. The final R and R_w were 0.067 and 0.052 with the weighting scheme $w = 4F_o^2/\sigma^2(F_o^2)$ for the 2075 observed reflections. Final positional parameters and the bond lengths of the non-hydrogen atoms are listed in Tables 1 and 2, respectively.* Table 3 lists the bond angles.

Discussion. There are two crystallographically independent tetranuclear cations $[\text{Cu}_4(\text{C}_5\text{H}_{13}\text{N}_2\text{O})_4]^{4+}$ in the asymmetric unit, each having point symmetry $\bar{4}$. Both

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Table 2. Bond lengths (\AA)

Symmetry code: (i) $\frac{1}{4} + y, \frac{3}{4} - x, \frac{3}{4} - z$; (ii) $\frac{3}{4} - y, \frac{3}{4} + x, \frac{3}{4} - z$; (iii) $1 - x, \frac{1}{2} - y, z$; (iv) $-x, \frac{1}{2} - y, z$.

Cu(1)···Cu(1) ⁱ	3.222 (2)	Cu(2)···Cu(2) ⁱⁱ	3.255 (2)
Cu(1)···Cu(1) ⁱⁱⁱ	3.439 (2)	Cu(2)···Cu(2) ^{iv}	3.623 (2)
Cu(1)—O(1)	1.963 (6)	Cu(2)—O(11)	1.957 (6)
Cu(1)—O(1) ⁱ	1.996 (7)	Cu(2)—O(11) ⁱⁱ	1.977 (7)
Cu(1)—O(1) ⁱⁱⁱ	2.541 (6)	Cu(2)—O(11) ^{iv}	2.671 (6)
Cu(1)—O(2)	2.871 (11)	Cu(2)—O(12)	2.433 (7)
Cu(1)—N(1)	1.981 (7)	Cu(2)—N(11)	1.981 (8)
Cu(1)—N(2)	2.020 (9)	Cu(2)—N(12)	2.039 (9)
C(1)—C(2)	1.528 (15)	C(11)—C(12)	1.507 (18)
C(2)—C(3)	1.523 (15)	C(12)—C(13)	1.530 (18)
C(4)—C(5)	1.516 (15)	C(14)—C(15)	1.519 (16)
C(1)—N(1)	1.494 (14)	C(11)—N(11)	1.471 (7)
C(3)—N(2)	1.495 (14)	C(13)—N(12)	1.474 (16)
C(4)—N(2)	1.489 (12)	C(14)—N(12)	1.466 (14)
C(5)—O(1)	1.431 (12)	C(15)—O(11)	1.425 (13)
C(6)—C(7)	1.521 (17)	C(7)—C(8)	1.524 (16)
C(6)—O(2)	1.219 (15)	C(8)—O(12)	1.251 (13)
C(6)—O(3)	1.261 (16)	C(8)—O(13)	1.282 (14)

Table 3. Bond angles (°)

Symmetry code: (i) $\frac{1}{2} + y, \frac{3}{2} - x, \frac{3}{2} - z$; (ii) $\frac{3}{2} - y, \frac{3}{2} + x, \frac{3}{2} - z$; (iii) $1 - x, \frac{1}{2} - y, z$; (iv) $-x, \frac{3}{2} - y, z$; (v) $\frac{3}{2} - y, -\frac{1}{2} + x, \frac{3}{2} - z$; (vi) $-\frac{1}{2} + y, \frac{3}{2} - x, \frac{3}{2} - z$.

O(1)—Cu(1)—O(1) ⁱ	87.0 (3)	O(11)—Cu(2)—O(11) ⁱⁱ	87.8 (3)
O(1)—Cu(1)—O(1) ⁱⁱⁱ	80.5 (2)	O(11)—Cu(2)—O(11) ^{iv}	77.7 (2)
O(1) ⁱ —Cu(1)—O(1) ⁱⁱⁱ	72.8 (2)	O(11) ⁱⁱ —Cu(2)—O(11) ^{iv}	70.1 (2)
O(1)—Cu(1)—N(2)	85.5 (3)	O(11)—Cu(2)—N(12)	84.3 (3)
O(1)—Cu(1)—O(2)	90.0 (3)	O(11)—Cu(2)—O(12)	95.9 (2)
O(1) ⁱ —Cu(1)—O(2)	86.9 (3)	O(11) ⁱⁱ —Cu(2)—O(12)	88.0 (3)
O(1) ⁱⁱⁱ —Cu(1)—O(2)	157.8 (3)	O(11) ^{iv} —Cu(2)—O(12)	158.2 (2)
N(1)—Cu(1)—O(1) ⁱ	94.8 (3)	N(11)—Cu(2)—O(11) ⁱⁱ	94.3 (3)
N(1)—Cu(1)—O(1) ⁱⁱⁱ	93.4 (2)	N(11)—Cu(2)—O(11) ^{iv}	94.5 (3)
N(1)—Cu(1)—N(2)	94.4 (3)	N(11)—Cu(2)—N(12)	94.7 (4)
N(1)—Cu(1)—O(2)	97.0 (3)	N(11)—Cu(2)—O(12)	93.2 (3)
N(2)—Cu(1)—O(1) ⁱ	119.7 (3)	N(12)—Cu(2)—O(11) ⁱⁱ	115.6 (3)
N(2)—Cu(1)—O(2)	79.0 (3)	N(12)—Cu(2)—O(12)	85.0 (3)
Cu(1)—O(1)—Cu(1) ⁱⁱⁱ	98.8 (2)	Cu(2)—O(11)—Cu(2) ^{iv}	101.9 (2)
Cu(1)—O(1)—Cu(1) ^v	108.9 (3)	Cu(2)—O(11)—Cu(2) ^{vi}	111.6 (3)
Cu(1) ⁱⁱⁱ —O(1)—Cu(1) ^v	89.7 (2)	Cu(2) ^{iv} —O(11)—Cu(2) ^{vi}	87.6 (2)
N(1)—Cu(1)—C(1)	118.7 (16)	Cu(2)—N(11)—C(11)	120.1 (7)
N(1)—C(1)—C(2)	113.3 (8)	N(11)—C(11)—C(12)	114.3 (10)
C(1)—C(2)—C(3)	115.2 (9)	C(11)—C(12)—C(13)	114.2 (10)
C(2)—C(3)—N(2)	110.8 (9)	C(12)—C(13)—N(12)	112.5 (10)
C(3)—N(2)—Cu(1)	122.3 (6)	C(13)—N(12)—Cu(2)	123.0 (7)
C(3)—N(2)—C(4)	111.2 (8)	C(13)—N(12)—C(14)	112.2 (9)
Cu(1)—N(2)—C(4)	107.8 (6)	Cu(2)—N(12)—C(14)	108.9 (7)
N(2)—C(4)—C(5)	108.2 (8)	N(12)—C(14)—C(15)	106.6 (9)
C(4)—C(5)—O(1)	109.0 (8)	C(14)—C(15)—O(11)	110.3 (8)
C(5)—O(1)—Cu(1)	109.9 (5)	C(15)—O(11)—Cu(2)	110.4 (6)
C(5)—O(1)—Cu(1) ^v	122.8 (6)	C(15)—O(11)—Cu(2) ^{vi}	123.5 (6)
C(7)—C(6)—O(2)	119.6 (11)	C(7)—C(8)—O(12)	117.7 (10)
C(7)—C(6)—O(3)	118.6 (10)	C(7)—C(8)—O(13)	118.6 (9)
O(2)—C(6)—O(3)	121.9 (12)	O(12)—C(8)—O(13)	123.7 (9)
C(6)—C(7)—C(8)	113.2 (10)		

(one is shown in Fig. 1) have the same cubane-type Cu₄O₄ core as found in the structures of the corresponding chloride (Pajunen & Nieminen, 1975), nitrate (Nieminen, 1977) and bromide (Nieminen & Pajunen, 1978). Most of the bond lengths and angles are closely similar in the two cations. The differences occur especially in the coordination of the Cu atom. Both Cu(1) and Cu(2) form four short bonds of about 2 Å with two N atoms of the ligands and two bridging O atoms of the Cu₄O₄ cores. The other atoms in the coordination sphere of the Cu atoms are the third core O atom and the O atom of the carboxyl group of the malonate ion which complete the distorted-octahedral coordination at longer distances. The Cu—carboxylate O distances are quite different indicating that the malonate ion is coordinated more strongly to Cu(2) than to Cu(1). This difference in the coordination has an effect on the bond lengths in the Cu₄O₄ cores. The Cu(1)—O(1)ⁱⁱⁱ and Cu(1)—Cu(1)ⁱⁱⁱ distances are 2.541 (6) and 3.439 (2) Å, respectively, while the corresponding distances in the other Cu₄O₄ core, Cu(2)—O(11)^{iv} and Cu(2)—Cu(2)^{iv}, are 2.671 (6) and 3.623 (2) Å. Within the malonate ion the bond lengths and angles are normal.

The malonate ion is coordinated to two different Cu atoms, and each complex cation is bonded to four others. The cations and malonate ions form layers parallel to the *xy* plane. Because the H atoms of the

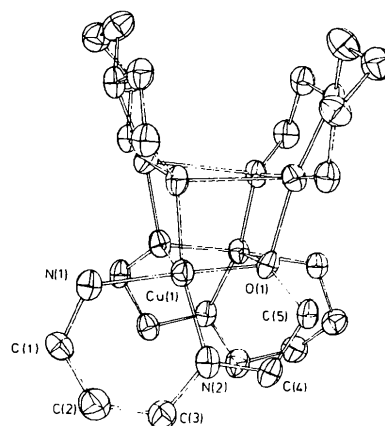


Fig. 1. Perspective view of one of the two crystallographically independent complex cations.

Table 4. Distances (Å) indicating possible hydrogen bonds

Symmetry code: (i) $\frac{1}{2} + y, \frac{3}{2} - x, \frac{3}{2} - z$; (ii) $\frac{3}{2} - y, \frac{3}{2} + x, \frac{3}{2} - z$; (iii) $-\frac{1}{2} + x, y, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$; (v) $-\frac{1}{2} + y, \frac{3}{2} - x, -\frac{1}{2} + z$.

N(1)···O(2) ⁱ	2.91 (1)	N(12)···O(4)	3.07 (1)
N(1)···O(13)	2.95 (1)	O(4)···O(3)	2.82 (1)
N(2)···O(3)	3.15 (1)	O(4)···O(5) ⁱⁱⁱ	3.05 (1)
N(11)···O(12) ⁱⁱ	3.01 (1)	O(5)···O(2) ^{iv}	3.08 (1)
N(11)···O(13)	2.98 (1)	O(5)···O(13) ^v	2.99 (1)

water molecules were not determined and the positional parameters of other H atoms were not refined, a detailed discussion of the geometry of the hydrogen bonds is not justified. N···O and O···O distances indicating possible hydrogen bonds are given in Table 4. Examination of the distances suggests that the layers are held together mainly by hydrogen bonds formed between the uncoordinated O(3) and O(13) of the malonate ion and water O(4) and O(5).

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