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Contribution from the Department of Chemistry
University of Illinois at Chicago Circle, Chicago, Illinois 60680

Molecules with an M_4X_4 Core. VI.[1-5] Crystallographic Characterization of $Cu_4OCl_6(OPEt_3)_4$—a Product from the Aerobic Oxidation of $[PEt_3CuCl]_4$

MELVYN ROWEN CHURCHILL,* BARRY G. DeBOER, and STEPHEN J. MENDAK[6]

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The aerobic oxidation of $[PEt_3CuCl]_4$ is shown to yield the complex μ_4-oxo-hexa-μ_2-chloro-tetrakis(triethylphosphine oxide)tetracopper(II), $Cu_4OCl_6(OPEt_3)_4$. This complex has been fully characterized via a single-crystal X-ray diffraction study. It crystallizes in the noncentrosymmetric rhombohedral space group $R3c$ (C_{3v}^6; No. 161) with $a = 12.8971$ (26) Å, $\alpha = 90.55$ (2)°, $V = 2145$ (1) Å^3, and $Z = 2$. Single-crystal X-ray diffraction data, complete to $2\theta = 40°$ [Mo Kα radiation], were collected with a Picker FACS-1 automated diffractometer and the structure was solved via a combination of Patterson, Fourier, and least-squares refinement techniques. The final discrepancy indices are $R_F = 3.62\%$ and $R_{wF} = 4.28\%$ for 986 independent reflections. The molecule has precise (i.e., crystallographically dictated) C_3 symmetry with the O(3)–Cu(1)–O(1)–P(1) system lying on the threefold axis. The central μ_4-oxide ion [O(3)] is linked to all four copper atoms, with Cu(1)–O(3) = 1.896 (10) Å and Cu(2)–O(3) = 1.919 (4) Å (three times). One triethylphosphine oxide ligand is O bonded to each copper atom; however, that bonded to the apical Cu(1) participates in a linear or close-to-linear Cu–O–P linkage [Cu(1)–O(1) = 1.936 (13) Å, O(1)–P(1) = 1.392 (15) Å], whereas the remaining three (symmetry-related) Cu–O–P systems are bent significantly and have longer O–P bond lengths [Cu(2)–O(2)–P(2) = 141.02 (46)°; Cu(2)–O(2) = 1.933 (6) Å, O(2)–P(2) = 1.503 (6) Å]. The six chloride ligands define a distorted octahedron (with Cl···Cl = 3.973 (4)–4.346 (5) Å) and lie above the edges of the tetrahedron defined by the four copper atoms (Cu···Cu = 3.117 (2)–3.130 (2) Å). The chloride ligands bridging apical and basal copper atoms are in symmetrical locations (Cu(1)–Cl(12) = 2.442 (3) Å, Cl(12)–Cu(2) = 2.447 (3) Å), but those bridging pairs of basal copper atoms are slightly unsymmetrical, with Cu(2)–Cl(22) = 2.431 (3) Å and Cl(22)–Cu(2') = 2.370 (3) Å. Each of the copper(II) atoms is in trigonal-bipyramidal coordination to three equatorial chloride ligands and two apical oxygen atoms. Atom Cu(1) has precise C_3 symmetry with O(3)–Cu(1)–O(1) = 180.00°, Cl(12)–Cu(1)–Cl(12)$_3$ = 119.31 (2)°, Cl(12)–Cu(1)–O(1) = 94.81 (8)°, and Cl(12)–Cu(1)–O(3) = 85.19 (8)°. The arrangement of ligands about atom Cu(2) (and its symmetry-related counterparts) is less symmetrical—in particular the diequatorial Cl–Cu–Cl angles are nonequivalent with values of 109.07 (11), 118.78 (11), and 129.71 (16)°.

Introduction

We have recently been interested in investigating the structural chemistry of the tetrameric phosphinecopper(I) halides.[1-5] In the course of synthesizing and crystallizing $[PEt_3CuCl]_4$[5] we noticed that this material slowly decomposed unless air was rigorously excluded. Thus, solutions in air slowly changed from colorless to yellow-green, and red-brown dodecahedral crystals (later shown to be $Cu_4OCl_6(OPEt_3)_4$) could be recovered from solution.

As an experiment, we left a large (ca. 5 mm × 5 mm × 5 mm) crystal of $[PEt_3CuCl]_4$ exposed to air on a microscope slide and monitored its decomposition visually. The crystal changed slowly from colorless and transparent to yellow-green and opaque over ca. 7 days. Further exposure to air (ca. 7 days) yielded a green deliquescent mass (presumably containing copper(II) with chloride, carbonate, and hydroxide counter anions) from which a red-brown substance spontaneously crystallized, leaving behind a roughly equal volume of (apparently amorphous) dark green material.

The product of the aerobic oxidation of $[PEt_3CuCl]_4$ was shown (vide infra) to be $Cu_4OCl_6(OPEt_3)_4$. We note here that reports of a crystallographic study of $Cu_4OCl_6(OPPh_3)_4$ have appeared.[7,8] However, this previous study was based upon photographic data (241 reflections), only isotropic thermal parameters were included, the molecule was disordered, and the final discrepancy index (R_F) was an unimpressive 10%. Furthermore, our completed study shows a chemical dissimilarity between the $(OPEt_3)$ and the $(OPPh_3)$ derivatives—the Cu–O–PPh_3 systems in $Cu_4OCl_6(OPPh_3)_4$ are all precisely linear, while only one of the four Cu–O–PEt_3 systems in $Cu_4OCl_6(OPEt_3)_4$ is linear. [The remaining three are bent with Cu–O–P = 141.02 (46)°.]

Obtention of Crystalline $Cu_4OCl_6(OPEt_3)_4$

A saturated solution of $[PEt_3CuCl]_4$[5] in 1:2 CH_2Cl_2–CCl_4 was allowed to stand in an uncovered conical flask at room temperature for 4 days. The remaining solution was then decanted and red dodecahedral crystals of $Cu_4OCl_6(OPEt_3)_4$ were retrieved from the bottom of the flask and recrystallized from CH_2Cl_2–CCl_4. The complex melts with decomposition over the range 215–230°. It was first identified via elemental analysis (Galbraith Laboratories, Knoxville, Tenn.). Anal. Calcd for $C_{24}H_{60}Cl_6Cu_4O_5P_4$: C, 28.28; H, 5.93; Cl, 20.86; Cu, 24.93; P, 12.15; O, 7.85. Found: C, 28.74; H, 5.91; Cl, 21.36; Cu, 25.33; P, 12.35; O (by difference), 6.31.

Collection and Treatment of X-Ray Diffraction Data

A crystal of characteristic dodecahedral habit (i.e., well-formed {110} faces), but with one slightly chipped corner, was selected for the structural analysis. Maximum crystal dimensions, in three orthogonal directions, were 0.35 mm × 0.49 mm × 0.52 mm. The crystal was mounted (with [110] axial) on a glass fiber, which was then sealed into a brass pin on a eucentric goniometer.

Preliminary precession and cone-axis photographs yielded approximate unit cell parameters, indicated $\bar{3}m$ (D_{3d}) Laue symmetry, and exhibited the systematic absences hhl for $l = 2n + 1$; these extinctions are consistent with the noncentrosymmetric trigonal (rhombohedral) space group $R3c$ (C_{3v}^6; No. 161)[9a] or with the centrosymmetric trigonal space group $R\bar{3}c$ (D_{3d}^6; No. 167).[9b] The former, noncentrosymmetric, space group is required in the absence of disorder and was confirmed by the successful solution of the structure. The molecule thereby has crystallographically imposed C_3 symmetry.

The crystal was transferred to a Picker FACS-1 automated dif-

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* To whom correspondence should be addressed at the Department of Chemistry, State University of New York at Buffalo, Buffalo, N.Y. 14214.

Table I. Experimental Data for the X-Ray Diffraction Study of $Cu_4OCl_6(OPEt_3)_4$

(A) Crystal Parameters (at 22.0 ± 0.5°)[a]

Crystal system: rhombohedral   Space group $R3c$ (C_{3v}^6; No. 161)
$a = 12.8971$ (26) Å $Z = 2$
$\cos \alpha = -0.00954$ (20)   Mol wt 1019.52
$\alpha = 90.55$ (2)° ρ(calcd) = 1.579 g cm^{-3}
$V = 2145$ (1) Å^3 ρ(obsd)[b] = 1.60 (1) g cm^{-3}

(B) Measurement of Intensity Data

Radiation: Mo K_α[c]
Filter(s): Nb foil at counter aperature (~47% transmission of Mo K_α)
Attenuators: Cu foil; inserted if $I > 10^4$ counts/sec
Takeoff angle: 3.0°
Detector aperture: 6.3 × 6.3 mm
Crystal–detector distance: 330 mm
Crystal orientation: ϕ axis = [110]
Reflections measured: one quadrant of the reciprocal sphere
Maximum 2θ: 40°
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: 2.0°/min
Scan length: $\Delta(2\theta) = (1.60 + 0.692 \tan \theta)°$, starting 0.80° below the Mo $K\bar{\alpha}$ peak
Background measurement: stationary crystal, stationary counter; 10 sec each at beginning and end of 2θ scan for $2\theta \leqslant 35°$; 20 sec each for $35° < 2\theta \leqslant 40°$
Standard reflections: three remeasured after each batch of 47 reflections; rms deviations[d] were 1.82%, 1.39%, and 1.33% for the entire data set; for data with $2\theta \leqslant 35°$, these rms deviations were 1.28%, 0.68%, and 0.47%, respectively
Reflections collected: 2019 measurements merged to 988 point-group-independent reflections after correction for absorption ($R_{F^2} = 2.9\%$)

(C) Treatment of Intensity Data

Conversion[d] to ($|F_o|$ and $\sigma|F_o|$): as in ref 10, using an "ignorance factor" of $p = 0.03$ for data with $2\theta \leqslant 35°$ and $p = 0.06$ for data with $35° < 2\theta \leqslant 40°$
Absorption coefficient: $\mu = 25.775$ cm^{-1}
Range of transmission factors:[e] 0.521–0.449

[a] Unit cell parameters are from a least-squares fit to the setting angles of the Mo $K\bar{\alpha}$ peaks ($\bar{\lambda}$ 0.710730 Å)[c] of 12 reflections with $2\theta = 37$–40°. [b] Neutral buoyancy in CCl_4-*sym*-$C_2H_2Br_4$. [c] J. A. Bearden, *Rev. Mod. Phys.*, 39, 78 (1967). [d] Data reduction was performed using the Fortran IV program **RDUS2**, by B. G. DeBoer. [e] Transmission factors were calculated (and data corrected) using the Fortran IV program **DRABZ**, by B. G. DeBoer. The accuracy of the program **DRABZ** has recently been checked using the test data given by N. W. Alcock, *Acta Crystallogr., Sect. A*, **30**, 332 (1974). Maximum disagreements found were 0.04% in transmission factor and 0.8% in secondary extinction coefficient.

fractometer, was accurately centered, and was aligned with [110] precisely coincident with the diffractometer's ϕ axis. As a quantitative check on the severity of the absorption problem, the intensities of the axial 110, 220, and 550 reflections were measured via a θ–2θ scan at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The ϕ dependence of these three reflections, defined by [(maximum − minimum)/average], was 26.3%, 27.3%, and 20.9% (respectively). These data were corrected for absorption along with the basic data set; following corrections for absorption the ϕ dependence of these reflections was significantly reduced.

Data collection was carried out as described in ref 10; details specific to the present analysis are given in Table I. The crystal appeared to be stable in the X-ray beam; no systematic decrease in intensity of the standard reflections was observed, nor did the appearance of the crystal change.

Solution and Refinement of the Structure

The analytical scattering factors of Cromer and Mann[11a] for neutral copper, chlorine, phosphorus, oxygen, and carbon were used. Real and imaginary components of anomalous disposition for all nonhydrogen atoms were taken from the compilation of Cromer and Liberman.[11b]

The function minimized during least-squares refinement processes was $\sum w(|F_o| - |F_c|)^2$, where $w(hkl) = \sigma^{-2}[F(hkl)]$. Discrepancy indices used below are defined as

$$R_F = \left[\frac{\Sigma\,||F_o| - |F_c||}{\Sigma\,|F_o|}\right] \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2} \times 100\ (\%)$$

All calculations were carried out on the IBM 370/158 computer at the Computer Center of the University of Illinois at Chicago Circle. Programs used include FORDAP (Fourier synthesis, by A. Zalkin), LSHF (structure factor calculations with least-squares refinement, by B. G. DeBoer), STAN1 (distances and angles, with esd's, by B. G. DeBoer), PLOD (least-squares planes and lines, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

A three-dimensional Patterson synthesis provided the locations of the copper atoms (one in a general position, the other in a special position of C_3 symmetry). The origin of the unit cell was defined by assigning the coordinates (0.16, 0.16, 0.16) to atom Cu(1), on the C_3 axis.

A series of Fourier syntheses (each successive one being phased by an increasing number of atoms) led to the location of all nonhydrogen atoms. Full-matrix least-squares refinement of the scale factor, positional parameters, anisotropic thermal parameters for copper, chlorine, phosphorus, and oxygen atoms, and isotropic thermal parameters for carbon atoms led to convergence with $R_F = 4.00\%$ and $R_{wF} = 4.96\%$ for the 988 point-group-independent reflections.

At this point a difference-Fourier map was calculated, phased by all atoms other than C(11) (which had a suspiciously large thermal parameter). No evidence for multiple sites for C(11) (i.e., disorder) was detected (although the peak *was* elongated); neither were any hydrogen atoms discernible.

The refinement was continued with all hydrogen atoms included in calculated positions based on d(C–H) = 0.95 Å,[12] regular tetrahedral geometry about each carbon atom, and the assumption that the ethyl groups each had a perfectly staggered conformation. Four cycles of least-squares refinement (with the shifts of hydrogen atoms set equal to those of their associated carbon atoms, and with $B(H) = [B(C) + 1.0]$ Å^2) led to convergence ($(\Delta/\sigma)_{max} = 0.002$) with $R_F = 3.67\%$ and $R_{wF} = 4.68\%$ for all 988 reflections or $R_F = 3.62\%$ and $R_{wF} = 4.28\%$ for those 986 reflections for which $(|\Delta F|/(\sigma|F_o|)) < 10$. The final "goodness of fit", defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.756 where m (the number of reflections) was 986, n (the number of parameters varied) was 89, and the ratio of observations to parameters (m:n) was 11.08:1. The function $\sum w(|F_o| - |F_c|)^2$ was not markedly dependent upon either $|F_o|$ or $(\sin \theta)/\lambda$, thereby suggesting that the weighting scheme is acceptable. A careful survey of strong low-angle reflections revealed no systematic pattern of $|F_o| < |F_c|$; secondary extinction is thus not a significant feature in the analysis. The correctness of the analysis was confirmed by a final difference Fourier synthesis on which the highest peak (at 0.64, 0.46, 0.02) was of height 0.40 e Å^{-3}.

The space group $R3c$ is polar and there are two enantiomeric forms, even though each crystal contains an ordered racemic array of molecules. As a final test, the handedness *of the particular crystal selected for the present analysis* was tested rigorously by inverting the set of positional parameters $[(x, y, z) \rightarrow (-x, -y, -z)]$ and again refining the structure to convergence. The resulting discrepancy indices were $R_F = 4.42\%$ and $R_{wF} = 5.68\%$, with a "goodness of fit" of 2.169. Clearly our original choice of coordinates was correct, and these latter results were rejected.

A table of observed and calculated structure factor amplitudes may be obtained. [See paragraph at the end of paper regarding supplementary material.] Final atomic positions and isotropic thermal parameters are collected in Table II. Anisotropic thermal parameters are given in Table III.

The Molecular Structure

The geometry of the $Cu_4OCl_6(OPEt_3)_4$ molecule is shown in Figures 1 and 2. Interatomic distances, with their estimated standard deviations (esd's), are collected in Table IV; bond angles, with esd's, are given in Table V.

The molecule consists of a tetrahedron of copper(II) atoms at the center of which is a μ_4-oxide ion and above each of the six edges of which is a μ_2-chloride ion; the structure is

Table II. Final Atomic Positions and Isotropic Thermal Parameters for $Cu_4OCl_6(OPEt_3)_4$[a–c]

Atom	x	y	z	B, Å^2
Cu(1)[d]	0 16[e]	=x	=x	4.648
Cu(2)	0.34948 (12)	0.31350 (12)	0.16431 (13)	3.801
Cl(12)	0.25870 (22)	0.23239 (24)	0.01666 (21)	5.514
Cl(22)	0.25933 (24)	0.47065 (21)	0.21420 (26)	5.952
P(1)[d]	0.00959 (28)	=x	=x	5.818
P(2)	0.53866 (24)	0.37579 (23)	0.01262 (23)	5.133
O(1)[d]	0.07252 (60)	=x	=x	9.55
O(2)	0.45472 (50)	0.39060 (54)	0.09128 (53)	5.35
O(3)[d]	0.24568 (46)	=x	=x	3.05
C(11)	0.0060 (23)	0.0435 (22)	−0.1196 (21)	17.7 (10)
C(12)	0.0803 (17)	0.0714 (18)	−0.1858 (20)	13.8 (6)
C(21)	0.5197 (12)	0.4616 (12)	−0.0925 (11)	8.4 (3)
C(22)	0.4218 (14)	0.4452 (16)	−0.1429 (16)	13.0 (6)
C(23)	0.6629 (12)	0.4206 (11)	0.0650 (12)	8.6 (3)
C(24)	0.7018 (14)	0.3568 (14)	0.1478 (13)	11.4 (5)
C(25)	0.5453 (9)	0.2457 (9)	−0.0288 (9)	6.9 (3)
C(26)	0.6263 (12)	0.2266 (12)	−0.1155 (12)	9.5 (4)
H(11A)	−0.0394	0.1010	−0.1204	18.7
H(11B)	−0.0263	−0.0138	−0.1541	18.7
H(12A)	0.0518	0.0867	−0.2521	14.8
H(12B)	0.1150	0.1311	−0.1585	14.8
H(12C)	0.1282	0.0162	−0.1923	14.8
H(21A)	0.5252	0.5308	−0.0669	9.4
H(21B)	0.5723	0.4499	−0.1422	9.4
H(22A)	0.4147	0.4926	−0.1984	14.0
H(22B)	0.3688	0.4572	−0.0937	14.0
H(22C)	0.4159	0.3763	−0.1690	14.0
H(23A)	0.6560	0.4890	0.0918	9.6
H(23B)	0.7119	0.4207	0.0104	9.6
H(24A)	0.7670	0.3819	0.1727	12.4
H(24B)	0.6535	0.3565	0.2029	12.4
H(24C)	0.7094	0.2882	0.1215	12.4
H(25A)	0.5614	0.2035	0.0291	7.9
H(25B)	0.4794	0.2260	−0.0564	7.9
H(26A)	0.6262	0.1556	−0.1356	10.5
H(26B)	0.6928	0.2455	−0.0886	10.5
H(26C)	0.6108	0.2680	−0.1741	10.5

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the last digit of the preceding number. They are derived from the inverse of the final least-squares matrix. [b] For Cu, Cl, P, and O atoms, equivalent isotropic thermal parameters are given. For the full anisotropic thermal parameters, see Table III. [c] The molecule lies on a crystallographic C_3 axis. Coordinates for atoms of the basic crystallographic unit are given here; the other two-thirds of the molecule may be generated by using cyclic permutations of the coordinates, viz., $x', y', z' = y, z, x$ and $x'', y'', z'' = z, x, y$. [d] These atoms lie on the C_3 axis and are given an occupancy factor of $^1/_3$ in structure factor calculations. [e] This coordinate defines the origin of the unit cell.

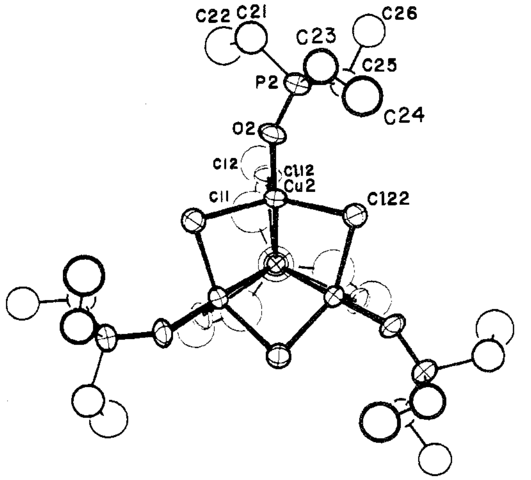


Figure 1. The $Cu_4OCl_6(OPEt_3)_4$ molecule projected on (111)–i.e., viewed down the crystallographic C_3 axis. Atoms on the molecular C_3 axis have not been labeled but are (going away from the viewer) O(3)–Cu(1)–O(1)–P(1) [ORTEP diagram, 30% probability contours, and hydrogen atoms omitted].

completed by four terminal, O-bonded triethylphosphine oxide ligands (one per copper atom).

While the central $Cu_4OCl_6(OP)_4$ portion of the molecule could, in principle, have precise T_d symmetry [and, in fact, the related $Cu_4OCl_6(OPPh_3)_4$ molecule actually lies on a site of crystallographic T_d symmetry[8]], in actuality, the observed molecular geometry has no more than the crystallographically imposed C_3 symmetry. This arises because (i) one $OPEt_3$ ligand is bonded to a copper(II) atom with a *linear* Cu–O–P arrangement, while the remaining three $OPEt_3$ ligands bind to copper with *bent* Cu–O–P frameworks, and (ii) the possible C_{3v} symmetry resulting from this perturbation is further reduced to C_3 symmetry by asymmetric Cu–Cl–Cu bridges between basal copper atoms and by systematic variations in Cl···Cl distances. Interesting features of the structure are described in detail below.

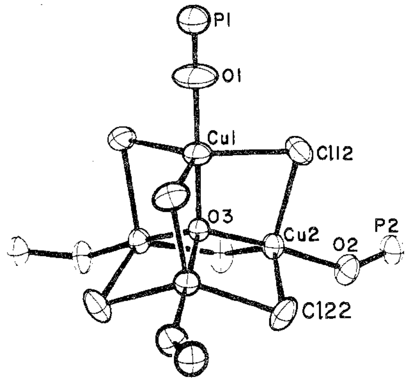


Figure 2. The $Cu_4OCl_6(OP)_4$ core of the molecule [ORTEP diagram, 30% probability ellipsoids].

Table III. Anisotropic Thermal Parameters for $Cu_4OCl_6(OPEt_3)_4$[a,b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[c]
Cu(1)	4.634 (48)	$=B_{11}$	$=B_{11}$	−0.697 (45)	$=B_{12}$	$=B_{12}$	0.201, 0.261, 0.261
Cu(2)	3.525 (57)	4.148 (60)	3.748 (57)	−0.068 (38)	0.695 (41)	0.427 (43)	0.191, 0.226, 0.238
Cl(12)	5.12 (13)	7.85 (17)	3.54 (11)	−0.95 (12)	−0.02 (10)	−0.25 (11)	0.211, 0.247, 0.322
Cl(22)	6.58 (15)	2.98 (11)	8.37 (18)	0.23 (10)	2.90 (13)	0.90 (11)	0.189, 0.240, 0.364
P(1)	5.81 (12)	$=B_{11}$	$=B_{11}$	−0.46 (14)	$=B_{12}$	$=B_{12}$	0.247, 0.283, 0.283
P(2)	4.61 (13)	5.86 (15)	4.97 (14)	0.27 (11)	1.46 (11)	0.46 (12)	0.206, 0.265, 0.287
O(1)	9.48 (48)	$=B_{11}$	$=B_{11}$	−3.33 (44)	$=B_{12}$	$=B_{12}$	0.187, 0.405, 0.405
O(2)	4.30 (33)	5.40 (35)	6.39 (38)	−0.15 (27)	2.57 (30)	0.55 (28)	0.179, 0.262, 0.320
O(3)	3.05 (20)	$=B_{11}$	$=B_{11}$	0.26 (22)	$=B_{12}$	$=B_{12}$	0.189, 0.189, 0.211

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic parameter and have units of A^2. They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)a^{*2}]$. [b] Esd's were obtained from the inverse of the final least-squares matrix. [c] These values correspond to the root-mean-square amplitudes of vibration (in A) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see the figures.

Table IV. Interatomic Distances (A) with Esd's for $Cu_4OCl_6(OPEt_3)_4$[a-c]

Atoms	Dist	Atoms	Dist
	(A) Copper–(Bridging Chlorine)		
Cu(1)–Cl(12)	2.4423 (27)	Cu(2)–Cl(22)	2.4307 (27)
Cu(2)–Cl(12)	2.4469 (29)	$Cu(2)–Cl(22)_3$	2.3697 (25)
	(B) Copper–(Central Oxygen)		
Cu(1)–O(3)	1.896 (10)	Cu(2)–O(3)	1.919 (4)
	(C) Copper–(Phosphine Oxide)		
Cu(1)–O(1)	1.936 (3)	Cu(2)–O(2)	1.933 (6)
Cu(1)...P(1)	3.328 (6)	Cu(2)...P(2)	3.242 (3)
	(D) Copper...Copper		
Cu(1)...Cu(2)	3.1300 (21)	$Cu(2)...Cu(2)_3$	3.1165 (20)
	(E) Chlorine...Chlorine		
$Cl(12)...Cl(12)_3$	4.2153 (46)	$Cl(12)...Cl(22)_3$	4.1456 (39)
Cl(12)...Cl(22)	3.9728 (42)	$Cl(22)...Cl(22)_3$	4.3457 (47)
	(F) Phosphorus–Oxygen		
P(1)–O(1)	1.392 (16)	P(2)–O(2)	1.503 (6)
	(G) Phosphorus–Carbon		
P(1)–C(11)	1.727 (26)	P(2)–C(23)	1.820 (16)
P(2)–C(21)	1.775 (14)	P(2)–C(25)	1.759 (11)
	(H) Carbon–Carbon		
C(11)–C(12)	1.339 (28)	C(23)–C(24)	1.444 (18)
C(21)–C(22)	1.428 (21)	C(25)–C(26)	1.557 (17)

[a] Esd's are calculated by considering all elements of the full positional covariance matrix of the last cycle of refinement. Esd's of cell constants were included. [b] No distances have been corrected for the effects of thermal motion. [c] Atom X_3 is related to atom X by a 120° rotation about the molecular C_3 axis.

The Central μ_4-Oxide Ion

The central μ_4-oxide ion, O(3), is in tetrahedral coordination to four copper(II) atoms. The (apical copper)–oxygen distance is Cu(1)–O(3) = 1.896 (10) Å, while the three crystallographically equivalent (basal copper)–oxygen distances are defined by Cu(2)–O(3) = 1.919 (4) Å. The average Cu–O(3) distance is 1.913 ± 0.012 Å.[13] The two independent Cu–O(3)–Cu angles are 110.30 (28) and 108.63 (29)°, with an average value of 109.47 ± 1.19°.[13]

While the oxide ion always, of course, has a full octet of electrons, examples of it forming four σ bonds to surrounding atoms are relatively rare. The classic example is basic beryllium acetate, $Be_4O(CH_3CO_2)_6$, which has been studied by such workers as Bragg, Pauling, and Tulinsky;[14] other such species upon which X-ray diffraction studies have been carried out include $Zn_4O(CH_3CO_2)_6$,[15] $Mg_4OBr_6(Et_2O)_4$,[16] $Cu_4OCl_6(OPPh_3)_4$,[7,8] $Cu_4OCl_6(py)_4$ (py = pyridine),[17] $[NMe_4]_4[Cu_4OCl_{10}]$,[18] $Cu_4OBr_6(NH_3)_4$,[19] $Cu_4OBr_6(py)_4$,[20] $Cu_4OCl_3Br_3(py)_4$,[21] and $[Pb_6O(OH)_6][ClO_4]_4 \cdot H_2O$.[22] (This last species contains a central Pb_4O grouping; the six lead atoms define a bicapped tetrahedron.)

Another less well-characterized species, which is also believed to contain a central M_4O core is $Co_4O(Me_3CCO_2)_6$.[23]

Coordination Geometry of the Copper(II) Atoms

Each of the copper(II) atoms has a coordination geometry which approximates to trigonal bipyramidal (ideally, of D_{3h} symmetry) with oxygen atoms in axial positions and chloride ligands in equatorial sites. [See Table VI.]

The detailed geometry about atom Cu(1) differs substantially from that about the other three equivalent copper atoms, in that it is considerably more regular. The Cu(1)–O distances are Cu(1)–O(1) = 1.936 (13) Å and Cu(1)–O(3) = 1.896 (10) Å. The three Cu(1)–Cl distances are crystallographically equivalent with Cu(1)–Cl(12) = 2.4423 (27) Å. The diaxial angle O(1)–Cu(1)–O(3) is precisely 180.00° and the diequatorial $Cl(12)–Cu(1)–Cl(12)_3$ angle is 119.31 (2)°. The axial–equatorial angles are O(1)–Cu(1)–Cl(12) = 94.81 (8)° and O(3)–Cu(1)–Cl(12) = 85.19 (8)°, reflecting the fact that Cu(1) lies 0.205 Å "outside" the plane defined by the three equatorial chloride ligands—i.e., is displaced toward O(1).

The arrangement of ligands about Cu(2) [and about the two other copper atoms related by C_3^1 and C_3^2 operations to Cu(2)] is far less regular than that about Cu(1). Presumably this is associated with the "bent" mode of coordination of $OPEt_3$ at these atoms, as opposed to the "linear" coordination of $OPEt_3$ at Cu(1). The axial Cu(2)–O distances are Cu(2)–O(2) = 1.933 (6) Å and Cu(2)–O(3) = 1.919 (4) Å. Each of the basal copper atoms is associated with two "long" [Cu(2)–Cl(12) = 2.4469 (29) Å and Cu(2)–Cl(22) = 2.4307 (27) Å] and one "short" [$Cu(2)–Cl(22)_3$ = 2.3697 (25) Å] copper–chlorine bonds. The diaxial angle O(2)–Cu(2)–O(3) deviates slightly but significantly from 180°, with a value of 175.22 (35)°. The axial–equatorial angles fall into two sets with O(3)–Cu(2)–Cl = 84.09 (13)–85.79 (14)° and O(2)–Cu(2)–Cl = 92.32 (20)–99.60 (24)°—again reflecting the fact that the copper atom is displaced out of the equatorial plane (toward O(2)) by 0.216 Å. The diequatorial Cl–Cu(2)–Cl angles vary widely, with individual values of 109.07 (11), 118.78 (11), and 129.71 (16)°.

The Cu_4 Tetrahedron and the Cl_6 Octahedron

The four copper atoms define a tetrahedron of C_{3v} (but not perfect T_d) symmetry; the two independent copper···copper distances are Cu(1)···Cu(2) = 3.1300 (21) Å and $Cu(2)···Cu(2)_3$ = 3.1165 (20) Å. We note here that the six equivalent Cu···Cu distances in the molecule $Cu_4OCl_6(OPPh_3)_4$ (studied by Bertrand[8]) are 3.110 (3) Å and that the author concludes, on the basis of structural and magnetic information, that "...there appears to be no interaction between the metal atoms".

The six chlorine atoms define an octahedron which is distorted so as to have only C_3 symmetry. Distances within the Cl(12) triangle are 4.2153 (46) Å while those in the opposed parallel Cl(22) triangle are 4.3457 (47) Å. The possible C_{3v} symmetry of the octahedral array of chloride ligands is destroyed by a slight rotation (away from a perfectly

Table V. Interatomic Angles (deg) for $Cu_4OCl_6(OPEt_3)_4$[a]

Atoms	Angle	Atoms	Angle
	(A) Angles about Copper Atoms		
Cl(12)-Cu(1)-Cl(12)$_3$	119.31 (2)	Cl(12)-Cu(2)-Cl(22)	109.07 (11)
O(1)-Cu(1)-O(3)	180.00 (0)	Cl(12)-Cu(2)-Cl(22)$_3$	118.78 (11)
O(1)-Cu(1)-Cl(12)	94.81 (8)	Cl(22)-Cu(2)-Cl(22)$_3$	129.71 (16)
O(3)-Cu(1)-Cl(12)	85.19 (8)	O(2)-Cu(2)-O(3)	175.22 (35)
O(3)-Cu(2)-Cl(12)	84.58 (29)	O(2)-Cu(2)-Cl(12)	99.60 (24)
O(3)-Cu(2)-Cl(22)	84.09 (13)	O(2)-Cu(2)-Cl(22)	92.32 (20)
O(3)-Cu(2)-Cl(22)$_3$	85.79 (14)	O(2)-Cu(2)-Cl(22)$_3$	94.13 (21)
	(B) Angles about Chlorine Atoms		
Cu(1)-Cl(12)-Cu(2)	79.61 (9)	Cu(2)-Cl(22)-Cu(2)$_3$	80.95 (10)
	(C) Angles about μ_4-Oxide Ion		
Cu(1)-O(3)-Cu(2)	110.30 (28)	Cu(2)-O(3)-Cu(2)$_3$	108.63 (29)
	(D) Cu-O-P Angles		
Cu(1)-O(1)-P(1)	180.00 (0)	Cu(2)-O(2)-P(2)	141.02 (46)
	(E) O-P-C Angles		
O(1)-P(1)-C(11)	115.0 (11)	O(2)-P(2)-C(23)	110.4 (6)
O(2)-P(2)-C(21)	109.9 (6)	O(2)-P(2)-C(25)	111.3 (5)
	(F) C-P-C Angles		
C(11)-P(1)-C(11)$_3$	103.4 (13)	C(23)-P(2)-C(25)	111.0 (6)
C(21)-P(2)-C(23)	101.8 (7)	C(25)-P(2)-C(21)	112.1 (7)
	(G) P-C-C Angles		
P(1)-C(11)-C(12)	132.3 (24)	P(2)-C(23)-C(24)	113.3 (12)
P(2)-C(21)-C(22)	112.1 (13)	P(2)-C(25)-C(26)	113.8 (9)

[a] See footnotes to Table IV.

Table VI. Least-Squares Planes and Deviations (Å) of Atoms Therefrom[a,b]

Atom	Dev	Atom	Dev
	Equatorial Coordination Plane of Cu(1)		
	$0.57730X + 0.51782Y + 0.58289Z = 3.7445$		
Cl(12)(*x, y, z*)	0.000	Cu(1)	−0.205
Cl(12)(*y, z, x*)	0.000	O(1)	−2.140
Cl(12)(*z, x, y*)	0.000	O(3)	1.691
	Equatorial Coordination Plane of Cu(2)		
	$0.69051X + 0.46599Y - 0.55321Z = 3.5643$		
Cl(12)(*x, y, z*)	0.000	Cu(2)	0.216
Cl(22)(*x, y, z*)	0.000	O(2)	2.142
Cl(22)(*y, z, x*)	0.000	O(3)	−1.702

[a] Planes are in orthogonal (Å) cartesian coordinates with the *X*, *Y*, and *Z* axes in the directions ($b \times c^*$, *b*, and c^* (respectively). [b] Calculations were performed using the program PLOD, by B. G. DeBoer.

staggered conformation) of the Cl(12) relative to the Cl(22) triangle. The interconnecting Cl···Cl vectors thus become nonequivalent, with Cl(12)···Cl(22) = 3.9728 (42) Å and Cl(12)···Cl(22)$_3$ = 4.1456 (39) Å. All of these chlorine···chlorine distances are, of course, substantially greater than the sum of van der Waals radii (Cl···Cl = 3.60 Å)[24] and are clearly dictated by other restraints.

The Cu-($OPEt_3$) Linkages and the $OPEt_3$ Ligands

The completed structural analysis shows that three copper atoms [Cu(2) and its symmetry-related copper atoms] are bonded to triethylphosphine oxide residues with *bent* Cu-O-P systems [Cu(2)-O(2)-P(2) = 141.02 (46)°], while the fourth copper atom is involved in *linear* coordination to a triethylphosphine oxide ligand [Cu(1)-O(1)-P(1) = 180.00 (0)°].

The "bent coordination" of R_3PO ligands (R = alkyl, aryl, halogen) is well documented and occurs in $Co(OPMe_3)_2(NO_3)_2$ [Co-O-P = 133.2 (10) and 139.6 (10)°; P-O = 1.53 (3) and 1.55 (3) Å],[26] $SbCl_5(OPMe_3)$ [Sb-O-P = 144.9 (23)°, P-O = 1.56 (4) Å],[26] $SbCl_5(OPCl_3)$ [Sb-O-P = 145.0 (16)°, P-O = 1.47 (2) Å],[26] and $NbCl_5(OPCl_3)$ [Nb-O-P = 148.8 (12)°, P-O = 1.45 (2) Å].[26]

"Linear coordination" of an R_3PO ligand appears to be less well documented, but Bertrand[8] reported that all four triphenylphosphine oxide ligands were bonded in a linear manner in $Cu_4OCl_6(OPPh_3)_4$.

We have considered the possibility that the observations of linearly coordinated R_3PO ligands in $Cu_4OCl_6(OPPh_3)_4$ and in $Cu_4OCl_6(OPEt_3)_4$ might be illusionary and be due to disorder of the oxygen atom in the Cu-O-P linkages.

In Bertrand's study of $Cu_4OCl_6(OPPh_3)_4$,[8] the thermal parameter of the O($OPPh_3$) atom is reasonable [3.8 (9) Å^2, as compared to *B*(Cu) = 2.1 (1) Å^2 and *B*(P) = 2.9 (3) Å^2]. In the event of disorder, one would expect this thermal parameter to be much higher.

The case of the $Cu_4OCl_6(OPEt_3)_4$ molecule can be analyzed in greater detail.

(i) Although the thermal parameter for O(1) is rather large [B_{equiv} = 9.55 Å^2 as opposed to values of 4.648 Å^2 for Cu(1), 5.818 Å^2 for P(1), and 5.35 Å^2 for O(2)], the final difference-Fourier map shows the region around O(1) to be relatively clean. There is a residual electron density of +0.17 e Å^{-3} at the precise position of O(1), and there are no significant peaks or troughs around this position. In the event of threefold, $3n$-fold, or cylindrical disorder of O(1) about the crystallographic C_3 axis, associated with a Cu(1)-O(1)-P(1) angle of ~140°, we would expect to observe (in the difference density map) a large negative region at the position of O(1), surrounded by a torus of residual electron density.

(ii) The thermal vibration ellipsoid associated with atom O(1) is quite sensible and defines an oblate spheroid in which the rms displacements along the principal axes are 0.187, 0.405, and 0.405 Å. [The minor axis lies along the Cu(1)···P(1) vector.]

(iii) The Cu(1)···P(1) distance of 3.328 (6) Å is 0.086 ± 0.007 Å longer than the Cu(2)···P(2) distance of 3.242 (3) Å. If the Cu(1)-O(1)-P(1) system were disordered, with the real (as opposed to apparent) Cu(1)-O(1)-P(1) angle being ~140° (i.e., equivalent to that for Cu(2)-O(2)-P(2)), these Cu···P vectors should be of equal length.

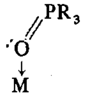
(iv) The copper-oxygen distances for "bent" and "linear" coordination of $OPEt_3$ are equivalent—Cu(1)-O(1) = 1.936 (13) Å and Cu(2)-O(2) = 1.933 (6) Å. If the refined position of O(1) were the composite of several disordered locations away from the C_3 axis (and assuming Cu-O-P = 140°), the observed

Cu(1)–O(1) distance should be ~0.08 Å *shorter* than the Cu(2)–O(2) bond length.

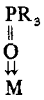
(v) The P(1)–O(1) distance of 1.392 (15) Å is significantly (i.e., 0.111 Å or 6.9σ) shorter than the P(2)–O(2) bond length of 1.503 (6) Å. However, a rational explanation for this is available (vide infra).

The above evidence is not compatible with there being disorder of O(1) about the threefold axis in conjunction with a true Cu(1)–O(1)–P(1) angle of ~140°. It is still possible, however, that there is a minor (cylindrical) disorder of O(1), engendered by a *slight* bending of the Cu(1)–O(1)–P(1) system. A *lower limit* for the Cu(1)–O(1)–P(1) angle can be estimated by assuming that the thermal ellipsoid of O(1) should be perfectly spherical and that its eccentricity results from displacement of O(1) from the crystallographic C_3 axis. The observed eccentricity of 0.218 Å, in association with the observed Cu(1)–O(1) and O(1)–P(1) distances of 1.936 and 1.392 Å leads to a predicted Cu–O–P angle of 164.67° ($= \tan^{-1}[d(\text{Cu–O})_{\text{obsd}}/\text{eccentricity}] + \tan^{-1}[d(\text{P–O})_{\text{obsd}}/\text{eccentricity}]$). Note that (i) this angle of 164.67° is assuredly a lower limit, since the vibration ellipsoids of Cu(1) and P(1) are also oblate spheroids (with eccentricities of 0.060 and 0.036 Å), and (ii) if we accept this angle as correct, the corrected Cu(1)–O(1) and O(1)–P(1) distances are 1.948 and 1.409 Å, respectively (i.e., these bond lengths change by +0.012 and +0.017 Å or by 0.92σ and 1.13σ only!).

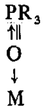
The bonding of R_3PO ligands to transition metals has been discussed previously.[8,27] The valence-bond description for "bent coordination" is shown in I. "Linear coordination" can only be accomplished by inducing sp hybridization at the oxygen atom—i.e., as in II or III. Our experimental data (which show that the Cu–O bond length does *not* change as we go from "bent" to "linear" coordination of R_3PO, whereas the P–O bond length decreases significantly) are entirely consistent with the linear coordination's being described by structure III. The triple bond in III can be envisioned as being formed from a P(sp^3)–O(sp_z) σ bond and O(p_x)–P(d_{xz}) and O(p_y)–P(d_{yz}) π bonds.



I



II



III

Finally we note that all carbon atoms have large thermal parameters and that their accurate location is rendered nigh impossible by the presence of the many heavy atoms (four coppers, four phosphorus, six chlorines). The resulting P–C distances range from 1.727 (26) to 1.820 (16) Å, while C–C distances vary from 1.339 (28) to 1.557 (17) Å.

Conclusions

The observation of one "linear" and three "bent" Cu–O–P linkages in the $Cu_4OCl_6(OPEt_3)_4$ molecule clearly indicates that the bent → linear transformation, although requiring electronic reorganization in the Cu–O–P system, is of sufficiently low energy that it can be brought about by steric effects and crystal packing forces. This is borne out by Bertrand's study on the analogous species $Cu_4OCl_6(OPPh_3)_4$ in which there are *four* linear Cu–O–P linkages.[8]

A second point which merits consideration is the mode of formation of $Cu_4OCl_6(OPEt_3)_4$ from $[PEt_3CuCl]_4$. While it clearly takes place spontaneously in the presence of air, it is not possible at present to determine whether the process occurs on a discrete molecular level with retention of the Cu_4 tetrahedron or whether the $[PEt_3CuCl]_4$ molecule breaks down into its oxidized constituents ($OPEt_3$, Cu^{2+}, Cl^-) which then reassemble with incorporation of a μ_4-oxide ion.

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Registry No. $Cu_4OCl_6(OPEt_3)_4$, 55853-46-8; $[PEt_3CuCl]_4$, 25668-59-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC502164-10-75.

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$$\text{esd of average} = \left[\sum_{i=1}^{i=N} (d_i - \bar{d})^2/(N-1)\right]^{1/2}$$

are preceded by "±"—e.g., $X.XXX \pm X.XXX$ Å. Here d_i is the ith value and $\bar{d}$ is the mean of N equivalent measurements.

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