There are no abnormally short intermolecular distances (Table IV).

It is interesting to point out that the presence of a trimethylene chain allows the $\gamma$ nitrogen atoms to reach the apical positions of the coordination octahedron, although with some difficulty, the *trans*-planar configuration being then possible for the salicylaldimine residues. In the structure of the square-pyramidal complex bis(N-$\beta$-diethylaminoethyl-5-chlorosalicylaldiminato)nickel(II)[1d] the $\beta$ nitrogen atom of the bonded en chain coordinates in the basal plane of the square pyramid with the azomethine nitrogen atom and the oxygen atom of one salicylaldimine group. The two salicylaldimines must therefore coordinate in the *cis* position, the angle between the mean planes through them being 85° 6′.

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# Five-Coordinate Complexes. III. Structure and Properties of $\mu_4$-Oxo-hexa-$\mu$-chloro-tetrakis{(triphenylphosphine oxide)copper(II)}[1]

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The preparation, structure, and properties of a cluster compound of copper(II), $Cu_4OCl_6(TPPO)_4$, are reported. The compound crystallizes as orange, cubic crystals ($a$ = 12.22 A) of space group P$\bar{4}$3m with one formula unit per unit cell. In the structure, four copper atoms tetrahedrally surround an oxygen atom; chlorine atoms bridge adjacent copper atoms, and each copper atom is, thus, bonded to three chlorine atoms. The oxygen of the phosphine oxide completes a slightly distorted trigonal bipyramid about the copper atom. The linear Cu–O–P arrangement indicates $\pi$ bonding and the high P–O stretching frequency (1194 cm$^{-1}$) indicates a higher bond order than in other phosphine oxide complexes. The spectral and magnetic properties of the complex are consistent with the formulation as trigonal-bipyramidal copper(II) and there is no indication of any interaction between the copper atoms.

## Introduction

The preparation and properties of dichlorobis(triphenylphosphine oxide)copper(II) were reported[3] several years ago; it is a yellow compound which can be recrystallized from various solvents, including lower ketones. During further investigation of the complexes between copper(II) halides and triphenylphosphine oxide (hereafter abbreviated TPPO), an attempted recrystallization of $CuCl_2(TPPO)_2$ from methyl isobutyl ketone yielded orange, cubic crystals which were analyzed as $Cu_4OCl_6(TPPO)_4$. Further investigation has provided an alternate preparation, the structure, and some of the properties of this new compound, $\mu_4$-oxo-hexa-$\mu$-chloro-tetrakis{(triphenylphosphine oxide)copper(II)}.

## Experimental Section

**Preparation.**—Stoichiometric amounts of $CuCl_2$, CuO, and TPPO were mixed in nitromethane and refluxed for several hours; the solution was filtered while hot. Orange crystals slowly deposited over a period of several days. *Anal.* Calcd for $Cu_4Cl_6O_5P_4C_{72}H_{60}$: Cu, 15.92; Cl, 13.33; P, 7.76; C, 54.17; H, 3.80. Found: Cu, 16.21; Cl, 13.55; P, 7.41; C, 53.61; H, 3.64.

**Spectral Measurements.**—Visible and near-infrared spectra were measured using a Cary Model 14 spectrophotometer; acetone was used as solvent for the solution spectrum and a KBr pellet was used for the spectrum of the solid. The spectrum of a single crystal in the 10,000-cm$^{-1}$ region was obtained with a microspectrophotometer; the crystal spectrum was identical with that obtained for the solid in a KBr pellet.

The infrared spectrum was measured using a Perkin-Elmer Model 21 spectrophotometer; a KBr pellet was used. Two peaks were found in the P–O stretching region, 1194 and 1125 cm$^{-1}$.

**Magnetic Susceptibility Measurement.**—The magnetic susceptibility (1909 × $10^{-6}$ cgs unit/g-atom of copper) was determined by the Gouy method at 25°, using $HgCo(CNS)_4$ as a calibrant. A correction for diamagnetism (221 × $10^{-6}$ cgs unit) was made, using published atomic values.[4] The value of $\mu_{eff}$ was found to be 2.2 (+0.1) BM.

**Collection and Reduction of the X-Ray Data.**—Optical examination of the crystals indicated that they were cubic; a crystal in the shape of a cube with edges of approximately 0.2 mm was mounted, and precession photographs were taken. Zero-level photographs confirmed the cubic system and a unit cell dimension, $a$, of 12.22 (±0.02) A was obtained. Assuming one formula unit of $Cu_4OCl_6(TPPO)_4$ per unit cell, the calculated density was 1.51; an experimental value of 1.49 was obtained by the flotation method. Precession photographs of the $hk0$ and $hk1$ zones showed fourfold symmetry; systematic absences were not observed on any of the diffraction photographs. Although either centric or acentric space groups were possible at this point, the acentric P$\bar{4}$3m was chosen from a consideration of the formula of the compound and the available special positions of the possible space groups.

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[1] Part II: J. A. Bertrand and J. A. Kelley, *J. Am. Chem. Soc.*, **88**, 4746 (1966).

[2] Alfred P. Sloan Research Fellow, 1966–1968.

[3] D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 2298 (1961).

[4] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., John Wiley and Sons, Inc., New York, N. Y., 1960, p 403.

Intensity data were collected using the same crystal as used for the space group photographs; Mo K$\alpha$ radiation was used with the precession camera. A total of 241 unique reflections were visually estimated from $hkx$ ($x$ = 0–3) photographs; Lorentz-polarization corrections were computed,[5] but no correction for absorption was made.

## Solution of the Structure

A three-dimensional Patterson synthesis revealed the copper atom positions; a minimum function based on vectors between copper atoms revealed positions for all atoms of the asymmetric unit except the atoms of the phenyl group. One oxygen was in the 1a (0, 0, 0) set; copper, phosphorus, and the oxygen of the phosphine oxide were in 4e $(x, x, x; x, \bar{x}, \bar{x}; \bar{x}, x, \bar{x}; \bar{x}, \bar{x}, x)$ sets, and the chlorine atoms were in a 6f $(x, 0, 0; 0, x, 0; 0, 0, x; \bar{x}, 0, 0; 0, \bar{x}, 0; 0, 0, \bar{x})$ set. Two cycles of least-squares refinement resulted in an $R$ value of 0.22; a Fourier synthesis was then computed, using phases calculated for the known part of the structure.

Peaks corresponding to four 24j (general) sets and two 12i (on mirror planes) sets were located in the Fourier; reasonable phenyl rings could be constructed by placing carbon atoms in the two 12i sets and assuming that the remaining carbon atoms were disordered in the four 24j sets; the ring consists of two carbons, one from each of the 12i sets, on the mirror plane, and four carbons, one from each of the 24j sets, located on one side of the mirror plane; the four related positions across the mirror plane were considered vacant.

Least-squares refinement of all atom coordinates not defined by symmetry, individual isotropic temperature factors, and individual scale factors for the four levels of data was continued until successive cycles gave no appreciable change in any parameter; the final $R$ value was 0.10. Table I lists the final structure parameters and Table II lists observed and calculated structure factors. To express the $F_o$ values in electrons, the values in Table II must be multiplied by scale factors; the factors for the $hk0$, $hk1$, $hk2$, and $hk3$ levels are 1.16, 1.24, 1.29, and 1.21, respectively.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $Cu_4OCl_6(TPPO)_4$

| Atom | $x$ | $y$ | $z$ | $B$, A$^2$ |
|---|---|---|---|---|
| Cu | 0.0900 (3)$^a$ | 0.0900 | 0.0900 | 2.1 (1) |
| O(1) | 0.0000 | 0.0000 | 0.0000 | 6.5 (2.9) |
| O(2) | 0.179 (2) | 0.179 | 0.179 | 3.8 (9) |
| Cl | 0.237 (1) | 0.0000 | 0.0000 | 4.6 (3) |
| P | 0.2508 (7) | 0.2508 | 0.2508 | 2.9 (3) |
| C(1) | 0.248 (3) | 0.207 (3) | 0.394 (3) | 2.5 (8) |
| C(2) | 0.165 (3) | 0.165 | 0.437 (4) | 4.8 (1.0) |
| C(3) | 0.146 (3) | 0.146 | 0.548 (4) | 6.6 (1.3) |
| C(4) | 0.236 (4) | 0.140 (4) | 0.610 (4) | 4.0 (1.0) |
| C(5) | 0.320 (7) | 0.182 (6) | 0.566 (7) | 8.0 (2.0) |
| C(6) | 0.345 (5) | 0.211 (5) | 0.459 (5) | 5.2 (1.4) |

$^a$ Values in parentheses are estimated standard deviations in the last digit or, in cases where decimal values are given in parentheses, the last two digits.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Cu_4OCl_6(TPPO)_4$

| H | K | FO | FC |
|---|---|---|---|
| L=0 | | | |
| 1 | 2 | 86 | 90 |
| 0 | 2 | 62 | 54 |
| 2 | 2 | 24 | 23 |
| 0 | 3 | 90 | 83 |
| 1 | 3 | 34 | 32 |
| 3 | 3 | 46 | 49 |
| 1 | 4 | 6 | 0 |
| 2 | 4 | 24 | 24 |
| 3 | 4 | 72 | 72 |
| 4 | 4 | 82 | 88 |
| 0 | 5 | 44 | 40 |
| 1 | 5 | 28 | 32 |
| 2 | 5 | 42 | 43 |
| 3 | 5 | 10 | 10 |
| 4 | 5 | 62 | 68 |
| 5 | 5 | 77 | 69 |
| 0 | 6 | 58 | 51 |
| 1 | 6 | 63 | 59 |
| 3 | 6 | 11 | 10 |
| 4 | 6 | 30 | 28 |
| 5 | 6 | 51 | 60 |
| 6 | 6 | 65 | 65 |
| 1 | 7 | 21 | 17 |
| 2 | 7 | 26 | 25 |
| 4 | 7 | 31 | 32 |
| 5 | 7 | 42 | 42 |
| 6 | 7 | 33 | 35 |
| 7 | 7 | 25 | 27 |
| 0 | 8 | 36 | 28 |
| 1 | 8 | 9 | 8 |
| 3 | 8 | 27 | 24 |
| 4 | 8 | 55 | 52 |
| 5 | 8 | 25 | 23 |
| 6 | 8 | 16 | 15 |
| 8 | 8 | 35 | 39 |
| 0 | 9 | 44 | 37 |
| 1 | 9 | 28 | 25 |
| 2 | 9 | 22 | 17 |
| 3 | 9 | 16 | 16 |
| 1 | 10 | 29 | 31 |
| 2 | 10 | 23 | 23 |
| 4 | 10 | 21 | 17 |
| 5 | 10 | 30 | 25 |
| 6 | 10 | 23 | 18 |
| 7 | 10 | 24 | 19 |
| 8 | 10 | 10 | 7 |
| 9 | 10 | 10 | 12 |
| 10 | 10 | 24 | 20 |
| 0 | 11 | 36 | 41 |
| 1 | 11 | 30 | 35 |
| 3 | 11 | 10 | 7 |
| 4 | 11 | 19 | 14 |
| 5 | 11 | 24 | 24 |
| 6 | 11 | 26 | 22 |
| 7 | 11 | 17 | 17 |
| 9 | 11 | 10 | 9 |
| 10 | 11 | 9 | 14 |
| 11 | 11 | 16 | 16 |
| 0 | 12 | 51 | 50 |
| 1 | 12 | 31 | 29 |
| 2 | 12 | 10 | 4 |
| 5 | 12 | 10 | 11 |
| 6 | 12 | 26 | 25 |
| 8 | 12 | 10 | 5 |
| 9 | 12 | 13 | 9 |
| 10 | 12 | 13 | 9 |
| 11 | 12 | 14 | 15 |
| 0 | 13 | 27 | 29 |
| 1 | 13 | 19 | 17 |
| 2 | 13 | 10 | 6 |
| 8 | 13 | 9 | 5 |
| 9 | 13 | 12 | 8 |
| 0 | 14 | 17 | 9 |
| 2 | 14 | 10 | 10 |
| 0 | 15 | 13 | 6 |
| 1 | 15 | 13 | 9 |
| 2 | 15 | 13 | 9 |
| 3 | 15 | 9 | 3 |
| L=1 | | | |
| 1 | 2 | 39 | 39 |
| 2 | 2 | 72 | 77 |
| 1 | 3 | 26 | 28 |
| 2 | 3 | 56 | 55 |
| 3 | 3 | 54 | 60 |
| 1 | 4 | 9 | 9 |
| 2 | 4 | 32 | 27 |
| 3 | 4 | 36 | 37 |
| 4 | 4 | 60 | 58 |
| 1 | 5 | 45 | 46 |
| 3 | 5 | 18 | 15 |
| 4 | 5 | 60 | 52 |
| 5 | 5 | 67 | 67 |
| 1 | 6 | 55 | 58 |
| 2 | 6 | 30 | 30 |
| 4 | 6 | 44 | 40 |
| 5 | 6 | 34 | 35 |
| 6 | 6 | 18 | 20 |
| 1 | 7 | 42 | 44 |
| 2 | 7 | 27 | 27 |
| 4 | 7 | 33 | 34 |
| 5 | 7 | 40 | 39 |
| 6 | 7 | 16 | 15 |
| 7 | 7 | 33 | 33 |
| 1 | 8 | 13 | 14 |
| 2 | 8 | 13 | 13 |
| 3 | 8 | 35 | 31 |
| 4 | 8 | 35 | 29 |
| 5 | 8 | 19 | 17 |
| 7 | 8 | 10 | 15 |
| 8 | 8 | 22 | 22 |
| 1 | 9 | 19 | 20 |
| 2 | 9 | 27 | 24 |
| 3 | 9 | 39 | 36 |
| 5 | 9 | 10 | 12 |
| 8 | 9 | 10 | 11 |
| 9 | 9 | 18 | 19 |
| 1 | 10 | 25 | 29 |
| 2 | 10 | 10 | 12 |
| 3 | 10 | 17 | 16 |
| 4 | 10 | 10 | 11 |
| 5 | 10 | 18 | 18 |
| 6 | 10 | 23 | 24 |
| 7 | 10 | 18 | 19 |
| 8 | 10 | 11 | 8 |
| 10 | 10 | 11 | 10 |
| 1 | 11 | 23 | 26 |
| 3 | 11 | 15 | 13 |
| 4 | 11 | 18 | 15 |
| 5 | 11 | 26 | 24 |
| 6 | 11 | 21 | 23 |
| 7 | 11 | 18 | 17 |
| 9 | 11 | 11 | 6 |
| 10 | 11 | 11 | 8 |
| 11 | 11 | 11 | 12 |
| 1 | 12 | 18 | 18 |
| 2 | 12 | 15 | 12 |
| 9 | 12 | 11 | 8 |
| 10 | 12 | 11 | 9 |
| 11 | 12 | 11 | 10 |
| 12 | 12 | 10 | 10 |
| 1 | 13 | 19 | 20 |
| 2 | 13 | 11 | 11 |
| 5 | 13 | 11 | 12 |
| 7 | 13 | 11 | 12 |
| 8 | 13 | 11 | 8 |
| 10 | 13 | 10 | 6 |
| 3 | 14 | 11 | 10 |
| 1 | 15 | 11 | 9 |
| 3 | 15 | 11 | 14 |
| L=2 | | | |
| 2 | 3 | 60 | 63 |
| 3 | 3 | 62 | 58 |
| 2 | 4 | 36 | 39 |
| 3 | 4 | 46 | 40 |
| 4 | 4 | 59 | 44 |
| 2 | 5 | 20 | 26 |
| 3 | 5 | 28 | 25 |
| 4 | 5 | 31 | 26 |
| 5 | 5 | 8 | 8 |
| 2 | 6 | 71 | 79 |
| 3 | 6 | 22 | 20 |
| 4 | 6 | 27 | 25 |
| 5 | 6 | 12 | 10 |
| 6 | 6 | 16 | 16 |
| 2 | 7 | 35 | 40 |
| 3 | 7 | 36 | 36 |
| 4 | 7 | 31 | 30 |
| 5 | 7 | 9 | 8 |
| 6 | 7 | 10 | 12 |
| 7 | 7 | 22 | 22 |
| 2 | 8 | 33 | 36 |
| 3 | 8 | 38 | 40 |
| 4 | 8 | 36 | 33 |
| 5 | 8 | 10 | 10 |
| 6 | 8 | 22 | 19 |
| 7 | 8 | 21 | 18 |
| 8 | 8 | 28 | 27 |
| 2 | 9 | 35 | 35 |
| 3 | 9 | 32 | 31 |
| 4 | 9 | 18 | 17 |
| 5 | 9 | 10 | 7 |
| 6 | 9 | 11 | 14 |
| 7 | 9 | 15 | 15 |
| 8 | 9 | 22 | 21 |
| 9 | 9 | 19 | 23 |
| 2 | 10 | 18 | 19 |
| 3 | 10 | 18 | 21 |
| 4 | 10 | 15 | 12 |
| 5 | 10 | 19 | 19 |
| 6 | 10 | 31 | 29 |
| 7 | 10 | 16 | 15 |
| 8 | 10 | 16 | 14 |
| 9 | 10 | 11 | 12 |
| 4 | 11 | 11 | 10 |
| 5 | 11 | 16 | 14 |
| 6 | 11 | 20 | 21 |
| 7 | 11 | 11 | 14 |
| 2 | 12 | 11 | 12 |
| 3 | 12 | 11 | 13 |
| 4 | 12 | 11 | 14 |
| 10 | 12 | 12 | 10 |
| 2 | 13 | 12 | 12 |
| 3 | 13 | 17 | 18 |
| 4 | 13 | 12 | 12 |
| 2 | 14 | 17 | 21 |
| 3 | 14 | 12 | 16 |
| 4 | 14 | 12 | 13 |
| L=3 | | | |
| 3 | 4 | 58 | 54 |
| 4 | 4 | 59 | 50 |
| 3 | 5 | 34 | 29 |
| 4 | 5 | 16 | 17 |
| 5 | 5 | 8 | 8 |
| 3 | 6 | 16 | 17 |
| 4 | 6 | 12 | 9 |
| 5 | 6 | 19 | 16 |
| 6 | 6 | 29 | 25 |
| 3 | 7 | 50 | 58 |
| 4 | 7 | 20 | 29 |
| 5 | 7 | 13 | 14 |
| 6 | 7 | 17 | 19 |
| 3 | 8 | 25 | 29 |
| 4 | 8 | 28 | 32 |
| 5 | 8 | 25 | 22 |
| 6 | 8 | 10 | 11 |
| 7 | 8 | 30 | 25 |
| 8 | 8 | 40 | 35 |
| 3 | 9 | 18 | 22 |
| 4 | 9 | 26 | 32 |
| 5 | 9 | 26 | 26 |
| 6 | 9 | 15 | 13 |
| 7 | 9 | 35 | 32 |
| 8 | 9 | 25 | 23 |
| 3 | 10 | 22 | 25 |
| 4 | 10 | 11 | 12 |
| 7 | 10 | 11 | 10 |
| 3 | 12 | 12 | 10 |
| 4 | 12 | 12 | 9 |
| 8 | 12 | 12 | 11 |
| 3 | 13 | 25 | 28 |
| 4 | 13 | 12 | 14 |
| 8 | 13 | 13 | 13 |
| 9 | 13 | 13 | 17 |
| 3 | 14 | 13 | 18 |

## Description of the Structure

The cluster, shown in Figure 1 with phenyl groups omitted, is analogous to that found[6] in $Mg_4OBr_6(C_4H_{10}O)_4$; interatomic distances and angles for the structure are given in Table III. The oxide ion, O(1), is at the center of a regular tetrahedron of copper ions with a Cu–O distance of 1.90 A. The six chloride ions bridge adjacent copper ions of the tetrahedron with a Cu–Cl distance of 2.38 A; each copper is on a threefold axis and the three chloride ions coordinated to each copper are related by this threefold axis. The copper ion is displaced 0.23 A from the plane of the chloride ions to give a Cl–Cu–O(1) angle of 85°. Completing a

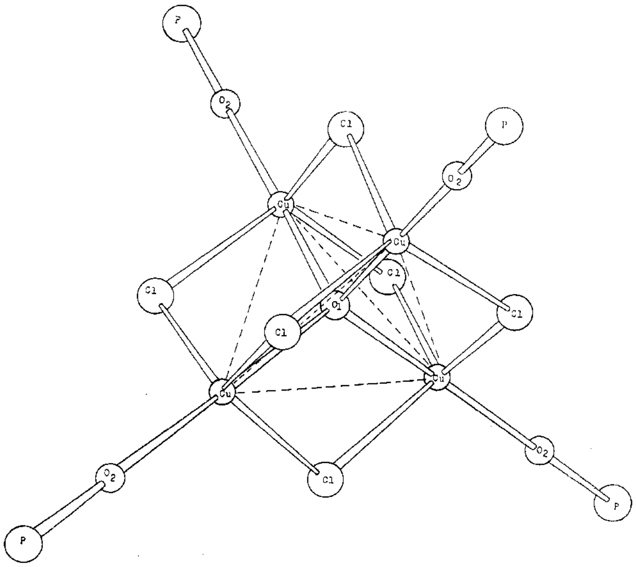

Figure 1.—Perspective drawing of the structure of $\mu_4$-oxo-hexa-$\mu$-chloro-tetrakis{(triphenylphosphine oxide)copper(II)}. The phenyl groups are omitted.

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(5) All computations were made on the Burroughs B 5500 computer. Programs for Lorentz-polarization corrections, Fourier summations, and minimum functions were written by the author; translations of the Busing, Martin, and Levy ORFLS least-squares refinement and ORFFE function and error programs were used.

(6) G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 4821 (1964).

TABLE III

INTERATOMIC DISTANCES AND ANGLES FOR $Cu_4OCl_6(TPPO)_4$

| Atoms | Interatomic distance, A | Atoms | Angle, deg |
|---|---|---|---|
| Cu-Cu′ | 3.110 (3) | Cl-Cu-O(2) | 95.6 (7) |
| Cu-O(1) | 1.905 (3) | C(1)-C(2)-C(3) | 128 (4) |
| Cu-O(2) | 1.89 (2) | C(2)-C(3)-C(4) | 115 (4) |
| Cu-Cl | 2.38 (1) | C(3)-C(4)-C(5) | 113 (5) |
| O(2)-P | 1.51 (2) | C(4)-C(5)-C(6) | 133 (8) |
| P-C(1) | 1.83 (4) | C(5)-C(6)-C(1) | 109 (6) |
| C(1)-C(2) | 1.25 (4) | C(6)-C(1)-C(2) | 117 (4) |
| C(2)-C(3) | 1.39 (5) | | |
| C(3)-C(4) | 1.34 (6) | | |
| C(4)-C(5) | 1.28 (8) | | |
| C(5)-C(6) | 1.39 (8) | | |
| C(6)-C(1) | 1.44 (7) | | |

slightly distorted trigonal bipyramid around the copper is the oxygen of the triphenylphosphine oxide, O(2), with a Cu–O distance of 1.89 A.

Since Cu, O(2), and P lie on the threefold axis (unit cell diagonal), the bond angle at the oxygen of the phosphine oxide is 180°.

The disorder of the carbon atom leads to two possible positions for each phenyl group; the plane of the phenyl group makes an angle of 27° with the P–O(2) bond direction, but the disorder makes it possible for the phenyl group to be rotated 27° in either direction. If all three phenyl groups of a triphenylphosphine oxide molecule rotated in the same direction, the threefold symmetry would be preserved. This arrangement is illustrated in Figure 2, which shows the relationship of the phenyl groups to the chlorides about the threefold axis. Two of the phenyl groups of triphenylphosphine[7] show similar orientation, making angles of about 30° with the normal to the base of the pyramid formed by the phosphorus and the three carbons bonded to phosphorus; the third phenyl group of triphenylphosphine makes an angle of about 60° with this normal.

The alternative of different phenyl groups of the same triphenylphosphine oxide molecule being rotated in opposite directions is not possible since such an arrangement would lead to too short a distance (*ca.* 2.0 A) between the C(6) atoms of the disordered rings.

## Discussion

There are few molecular compounds in which oxygen is four-coordinate; some examples of such compounds are the magnesium compound previously mentioned, the basic beryllium acetate,[8] $Be_4O(C_2H_3O_2)_6$, and the analogous basic zinc acetate.[9] The present structure is similar to the basic acetate structure, with chlorides replacing the acetates; the smaller size of the chloride necessitates a different coordination around the metal and an additional group to complete the coordination sphere.

Although four copper atoms are bonded to one oxygen

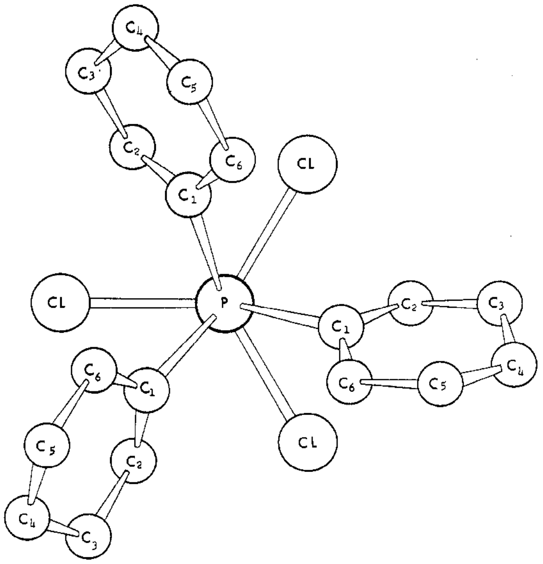

Figure 2.—The relationship between the phenyl groups of the triphenylphosphine oxide and the chloride ions, viewed down the threefold axis.

in the structure, there appears to be no interaction between the metal atoms. Since superexchange is usually found in copper complexes which contain a bridging oxygen,[10] such an interaction had been expected. However, the magnetic moment, 2.2 BM, is only slightly above the range predicted[11] for trigonal-bipyramidal copper(II) and no interaction is indicated. There have been suggestions that superexchange involves coupling of the spins through $\pi$ orbitals on oxygen,[12] and, with the outer s and p orbitals used for $\sigma$ bonding, there are no $\pi$ orbitals available on the oxygen in this cluster.

The visible and near-infrared spectrum of copper(II) in this cluster, Figure 3, is similar to the spectrum reported for the trigonal-bipyramidal $CuCl_5^{3-}$ ion.[13] The absorption bands of this complex, 9900 and 11,200 $cm^{-1}$, occur at higher energy than those of $CuCl_5^{3-}$, 8200 and 10,400 $cm^{-1}$, as would be expected from comparison of the ligand field strength of oxygen and chlorine atoms.

Comparison of the infrared spectrum of $Cu_4OCl_6(TPPO)_4$ with spectra of other phosphine oxide complexes[14] reveals that the P–O stretching frequency of this compound is at higher frequency than for any previously reported phosphine oxide complex and is essentially unshifted from the value for the free ligand. It has been pointed out[14] that, in a complex with the same bond order as the free ligand, this band would be expected to occur approximately 50–150 $cm^{-1}$ higher than in the free ligand owing to coupling of the two oscillators, P–O and O–M. Thus, $Cu_4OCl_6(TPPO)_4$ shows a decreased bond order in comparison to the free ligand, but the bond order is not decreased as much as in other complexes.

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[7] J. J. Daly, *J. Chem. Soc.*, 3799 (1964); *Z. Krist.*, **118**, 332 (1963).

[8] W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.* (London), **A104**, 437 (1923); G. T. Morgan and W. T. Astbury, *ibid.*, **A112**, 441 (1926); L. Pauling and J. Sherman, *Proc. Natl. Acad. Sci. U. S.*, **20**, 340 (1934).

[9] J. Wyart, *Bull. Soc. Franc. Mineral.*, **49**, 148 (1926); H. Koyama and Y. Saito, *Bull. Chem. Soc. Japan*, **27**, 112 (1954).

[10] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

[11] K. A. Boudreaux, *Trans. Faraday Soc.*, **59**, 1055 (1963).

[12] R. L. Martin and H. Waterman, *J. Chem. Soc.*, 1359 (1959).

[13] (a) P. Day, *Proc. Chem. Soc.*, 18 (1964); (b) W. E. Hatfield, H. D. Bedon, and S. M. Horner, *Inorg. Chem.*, **4**, 1181 (1965).

[14] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

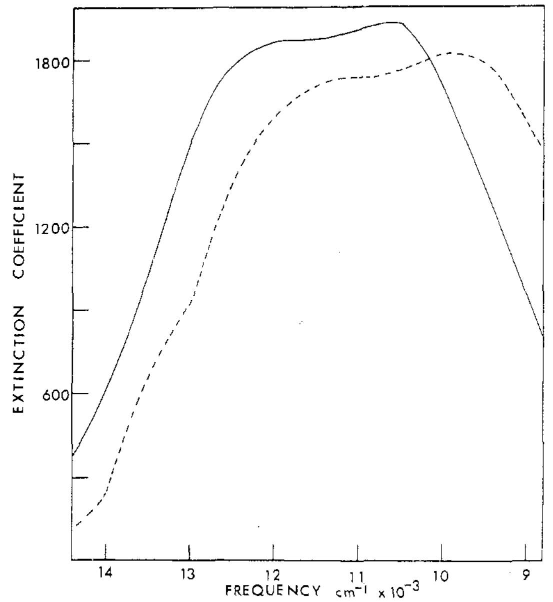

Figure 3.—Absorption spectrum of $Cu_4OCl_6(TPPO)_4$ in acetone (solid line) and as the solid in a potassium bromide pellet (broken line). The extinction coefficients refer to the solution spectrum; the solid spectrum is on an arbitrary scale.

Cotton, *et al.*,[14] list three factors which have an effect on the P–O bond order: (1) the $\sigma$ bond, P→O, is enhanced by the positively charged metal ion; (2) the $p\pi$–$d\pi$ back-bonding, P→O, is decreased by the positive charge of the metal ion; (3) the drift of metal electrons toward oxygen through $d\pi$–$p\pi$ overlap, M→O, enhances the O→P back-donation. Normally, the second of these factors is dominant and the O–P bond order is decreased. In addition to these charge effects, the hybridization of oxygen orbitals would have an effect on the bond order. If the P–O bond in phosphine oxides is considered to be a triple bond[15] involving a $\sigma$ bond and two $\pi$ bonds (the $\pi$ bonds resulting from overlap of vacant, $d_{xz}$, $d_{yz}$ orbitals on phosphorus with filled $p_x$, $p_y$ orbitals on oxygen), formation of a complex in which the P–O–M arrangement is bent would involve a change in the hybridization of oxygen from sp to $sp^2$ and, thus, decrease the $\pi$ bonding and bond order more than formation of a complex in which the P–O–M arrangement is linear. This effect would explain the smaller change in P–O frequency for $Cu_4OCl_6(TPPO)_4$, which is linear, compared to the other phosphine oxide complexes if all of the others are assumed to have a bent arrangement. The trigonal-bipyramidal arrangement around copper in $Cu_4OCl_6(TPPO)_4$ could make the third factor discussed above relatively more important since the copper $d_{xz}$ and $d_{yz}$ orbitals would be in positions to overlap with oxygen $p_x$ and $p_y$ orbitals. Although structures have not been reported for any other complexes of triphenylphosphine oxide, other phosphine oxide structures[16,17] have indicated a bent arrangement; incomplete results in our laboratories on the structure of $CuCl_2(TPPO)_2$ also indicate a bent arrangement.

## Conclusions

There are several features of this structure that are unusual: (1) It is one of the few molecular compounds in which oxygen is four-coordinate. (2) It is an example of a trigonal-bipyramidal complex of copper(II), although it is somewhat distorted, and its spectral and magnetic properties are in accord with theoretical predictions. (3) It is the first complex reported in which a phosphine oxide is complexed in a linear arrangement and the P–O bond order is higher than in any other phosphine oxide complex reported.

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