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The Crystal and Molecular Structure of Dichlorobis(Triphenylphosphine Oxide)Copper(II)

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The structure of dichlorobis(triphenylphosphine oxide)-copper(II) has been determined by a single-crystal x-ray diffraction study. The compound crystallizes as orthorhombic crystals (a=*31.961(4) Å,* b=*20.839(4) Å, and* c=*9.886(2) Å of space group Fdd2 with eight molecules per unit cell* ($\rho_{obs}=1.40(2)$ *g/cm*^{3}; $\rho_{calc}=1.38$ *g/cm*^{3}). *The structure was solved from Patterson and electron density maps and refined by least-squares methods to a conventional R value of 0.044 for 1386 independent, non-zero reflections. The complex has 2-fold symmetry and the coordination about copper is a slightly elongated tetrahedron with a Cu—Cl distance of 2.170(2) Å and a Cu—O—distance of 1.958(4) Å; the Cu—O—P angle is 150.9(3).*

Introduction

Although there have been numerous studies of copper(II) complexes, there have been relatively few structure studies of tetrahedral copper(II) complexes.[1-7] All of the tetrahedral complexes which have been studied have been distorted from tetrahedral toward square planar by a compression of the tetrahedron.

The complexes $Cu(TPPO)_2X_2$ (where TPPO represents triphenylphosphine oxide and X represents chloride or bromide) have been reported and, on the basis of spectral and magnetic properties, assigned tetrahedral structures.[8] Although it was suggested[8] that the tetrahedron might be flattened as in other cases, consideration of molecular models indicates that an elongated tetrahedron would be more likely for a bent Cu—O—P arrangement. Since such a distortion has not been observed for a copper(II) complex, the structure of one or both of these compounds would be of interest.

In addition to the question of the stereochemistry of the copper(II), the structure of the $Cu(TPPO)_2X_2$ complexes are of interest because of questions concerning the Cu—O—P arrangement. A linear Cu—O—P arrangement was found[9] for $Cu_4OCl_6(TPPO)_4$; on the basis of a lower P—O stretching frequency, a bent Cu—O—P arrangement was proposed for $Cu(TPPO)_2Cl_2$.

In this paper the crystal and molecular structure of dichlorobis(triphenylphosphine oxide)copper((II) is reported.

Experimental Section

Collection and Reduction of the X-ray Data. The compound was prepared by the method reported in the literature[1] and was recrystallized from absolute ethanol.

The crystal chosen for the space group determination was needle-shaped and of approximate dimensions 0.3×0.9×0.3 mm; it was mounted along the long dimension. Precession photographs, using Zr—filtered Mo Kα radiation ($\lambda=0.710$ Å), indicated an orthorhombic unit cell; the absence of *hkl* reflections for odd values of $(h+k)$, $(h+l)$, and $(k+l)$, the absence of *0kl* reflections for $(k+l)\neq 4n$, and the absence of *k0l* reflections for $(h+l)\neq 4n$, defined the space group as Fdd2, No. 43.[10]

The crystal was transferred to am automated Picker four-circle diffractometer; 12 reflections were used to refine cell parameters by a least-squares procedure. The cell parameters obtained are $a=31.961(4)$,[11] $b=20.839(4)$, $c=9.886(2)$ Å, and V=6584.0 Å^3 (25 °C, Mo radiation). The calculated density of 1.39 g/cm^3 for eight formula units per unit cell agrees well with the observed density of 1.40(2) g/cm^3 measured by the flotation method.

The x-ray intensity measurements were made on the same crystal as used for the unit cell determination and Zr—filtered MoKα radiation was again used. The intensities were measured with a scintillation counter mounted 21 cm from the crystal; the intensities were collected by the θ—2θ scan technique with a take-off angle of 1.6° and a scan rate of 1°/min. A symmetrical scan of 2° was taken about the calculated position for each reflection; stationary background counts of 20 sec. were taken at the beginning

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(11) Numbers in parentheses here and elsewhere in this paper are the estimated standard deviations in the least significant digits.

(bgd1) and at the end (bgd2) of the scan. Calibrated copper attenuators were used in the collection of data; the threshold point was set so that the counting rate would not exceed 10^4 counts/second. The pulse height analyzer was set for approximately a 90% window, centered on the MoKα peak. A recorder monitored the scan of each peak and the scans were examined for erratic background and for the inclusion of Kβ peaks. A standard reflection (800) was intermittently scanned to check for instrument of crystal variations; no significant variation in the number of counts for this reflection was observed during the entire data collection period. Corrected intensities (I) were obtained by subtracting three times the total measured background from the total integrated peak count (CT),

$$I = CT - 0.5(t_c/t_b)(bgd1 + bgd2)$$

were t_c is the scan time and t_b is the counting time of each background (either bgd1 or bgd2). The corrected intensities were assigned standard deviations according to the formula[12]

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(bgd1 + bgd2) + (pI)^2]^{1/2}$$

A total of 1386 reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.30 with $p = 0.02$. The intensities were corrected for Lorentz and polarization effects;[1] since the linear absorption coefficient, μ, was 16.3 cm^{-1} absorption corrections were not made.

Solution of the Structure. Computations were carried out on a Burroughs B-5500 computer and on a Univac 1108 computer; programs employed included modified versions of F. L. Carter's program for calculating diffractometer settings, Zalkin's FORDAP Fourier summation program, the Busing-Martin-Levy XFLS and ORFFE least-square and function and error programs, Johnson's ORTEP plotting program, and various locally written programs. In structure factor calculations, the scattering factors tabulated by Ibers[13] were employed for all atoms; the tabulation by Templeton[14] was used to correct for the real and imaginary anomalous scattering by copper, phosphorus, and chlorine.

In space group Fdd2 with eight formula units per cell, the copper ions are required to occupy special positions on the two-fold axes and all other atoms occupy general positions. Since the unit cell origin

Table I. Final Coordinates for non-Hydrogen Atoms of $CuCl_2(TPPO)_2$

Atom	x	y	z
Cu	0	0	0
Cl	—0.0164(1)	0.0771(1)	0.1377(3)
P	0.0692(1)	0.0870(1)	0.8254(2)
O	0.0358(1)	0.0405(2)	0.8638(4)
C11	0.1157(2)	0.0779(3)	0.9303(6)
C12	0.1231(2)	0.0199(3)	0.9940(9)
C13	0.1577(3)	0.0136(4)	0.0757(8)
C14	0.1850(3)	0.0632(5)	0.0941(8)
C15	0.1781(2)	0.1206(4)	0.0300(8)
C16	0.1157(2)	0.0779(3)	0.9303(6)
C21	0.0819(2)	0.0749(3)	0.6519(6)
C22	0.0554(3)	0.0381(6)	0.5759(10)
C23	0.0627(5)	0.0320(8)	0.4339(10)
C24	0.0963(5)	0.0623(3)	0.3784(10)
C25	0.1231(4)	0.0946(6)	0.4534(10)
C26	0.1162(3)	0.1028(5)	0.5907(9)
C31	0.0537(2)	0.1695(3)	0.8437(6)
C32	0.0431(2)	0.2062(3)	0.7323(8)
C33	0.0298(3)	0.2696(3)	0.7495(9)
C34	0.0292(2)	0.2955(3)	0.8757(9)
C35	0.0398(2)	0.2611(3)	0.9868(8)
C36	0.0520(2)	0.1963(3)	0.9725(7)

Table II. Anisotropic Thermal Parameters for non-Hydrogen Atoms of $CuCl_2(TPPO)_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00090(1)	0.00123(2)	0.00559(9)	0.00007(2)	0	0
Cl	0.0042(1)	0.0024(1)	0.0105(2)	0.0012(1)	0.0013(1)	—0.0013(1)
P	0.00068(2)	0.00159(3)	0.00634(1)	—0.00021(2)	—0.0005(4)	0.00004(6)
O	0.00076(4)	0.0019(1)	0.0082(5)	—0.00042(6)	0.0003(1)	0.0000(1)
C11	0.00075(7)	0.0017(1)	0.0064(6)	0.00013(8)	—0.0002(2)	—0.0004(2)
C12	0.00104(7)	0.0022(2)	0.0106(8)	0.00012(8)	0.0001(3)	0.0005(4)
C13	0.00129(9)	0.0034(2)	0.0095(8)	0.0006(1)	—0.0002(2)	0.0011(4)
C14	0.00104(9)	0.0044(3)	0.0084(8)	0.0008(1)	—0.0007(2)	—0.0010(4)
C15	0.00084(8)	0.0034(2)	0.0127(9)	0.0002(1)	—0.0010(2)	—0.0028(4)
C16	0.00092(7)	0.0019(2)	0.0112(8)	0.0001(1)	—0.0007(2)	—0.0010(3)
C21	0.00081(7)	0.0023(2)	0.0056(6)	0.00011(8)	0.0002(2)	—0.0001(3)
C22	0.0014(1)	0.0051(3)	0.0098(9)	—0.0007(2)	0.0004(3)	—0.0028(5)
C23	0.0023(2)	0.0072(5)	0.0093(9)	—0.0001(3)	—0.0003(4)	—0.0041(6)
C24	0.0022(2)	0.0072(5)	0.0076(9)	0.0016(3)	0.0010(4)	—0.0005(7)
C25	0.0014(1)	0.0054(4)	0.0123(9)	0.0008(2)	0.0014(3)	0.0015(6)
C26	0.0011(1)	0.0038(3)	0.0108(1)	0.0001(1)	0.0007(3)	0.0008(4)
C31	0.00065(6)	0.0018(1)	0.0071(6)	—0.0001(1)	—0.0000(2)	0.0002(3)
C32	0.00096(7)	0.0022(2)	0.0083(8)	—0.0001(1)	—0.0003(2)	0.0004(3)
C33	0.0014(1)	0.0021(2)	0.0116(8)	0.0002(1)	—0.0000(3)	0.0007(4)
C34	0.00099(8)	0.0019(2)	0.0148(9)	0.0000(1)	—0.0002(2)	—0.0006(4)
C35	0.00099(7)	0.0024(2)	0.0101(8)	0.0000(1)	—0.0002(2)	—0.0012(3)
C36	0.00092(8)	0.0023(2)	0.0073(8)	0.0000(1)	—0.0001(2)	—0.0004(3)

Anisotropic thermal parameters are expressed in the form: exp $-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

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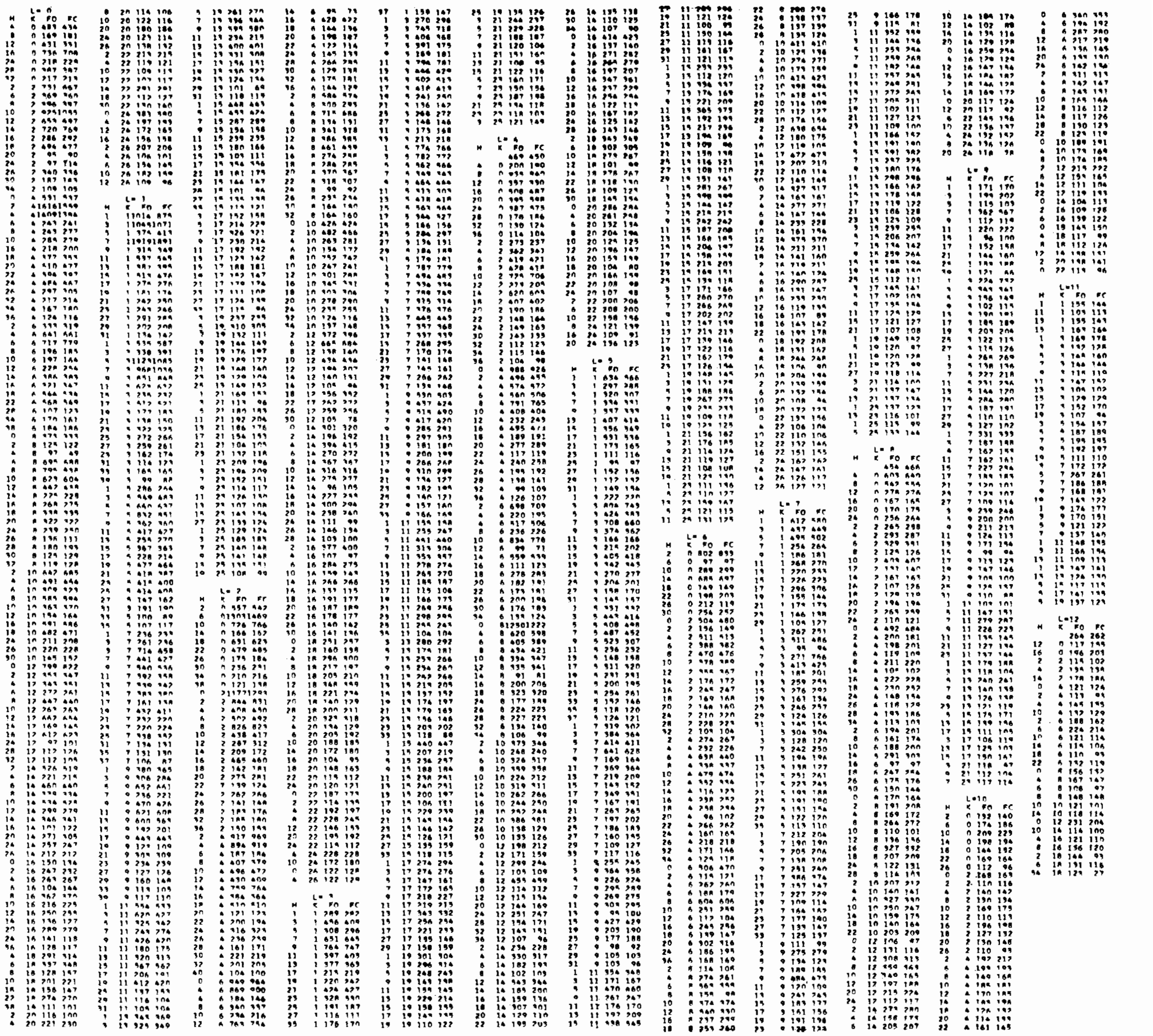
Table III. Coordinates Assigned to Hydrogen Atoms oı $CuCl_2(TPPO)_2$

Atom[a]	x	y	z
H12	0.1022	—0.0203	0.9808
H13	0.1665	—0.0320	0.1038
H14	0.2108	0.0578	0.1555
H15	0.2002	0.1560	0.0824
H16	0.1400	0.1713	0.9033
H22	0.0297	0.0144	0.6225
H23	0.0419	0.0039	0.3750
H24	0.1040	0.0640	0.2800
H25	0.1502	0.1176	0.4249
H26	0.1377	0.1344	0.6474
H32	0.0446	0.1853	0.6371
H33	0.0200	0.2990	0.6680
H34	0.0172	0.3335	0.8801
H35	0.0389	0.2837	0.0805
H36	0.0599	0.1677	0.0548

[a] The number denotes the carbon atom to which the hydrogen is attached.

in the direction of the two-fold axis (z direction) is not determined by symmetry, the origin can be chosen to coincide with a copper ion. Coordinates for the chlorides and for the phosphorus atoms were obtained from a three-dimensional Patterson synthesis; a structure factor calculation based on copper, chloride, and phosphorus positions gave an R_1 value ($R_1 = (\Sigma \,||F_o| - |F_c||) / \Sigma |F_o|$) of 0.36. Successive structure factor and electron density calculations revealed the positions of the oxygen and carbon atoms. Full-matrix least-squares refinement, using a weighting scheme based on counting statistics ($W = 4I/\sigma(I)^2$) and minimizing $W(F_o - F_c)^2$, was used to refine a scale factor, all atomic coordinates not fixed by symmetry, and isotropic temperature factors for all atoms; the refinement converged to an R_1 value of 0.12 and an R_2 value ($R_2 = [\Sigma W(|F_o| - |F_c|)^2 / \Sigma W(F_o)^2]^{1/2}$) of 0.10; further refinement with anisotropic temperature factors for all atoms led to values of 0.050 and 0.049 for R_1 and R_2, respectively. Hydrogen atoms of the

Table IV. Observed and calculated Structure Factors (Electrons) for $CuCl_2(TPPO)_2$



phenyl groups were located in a difference Fourier which was phased on the refinement with isotropic temperature factors and hydrogen coordinates were introduced, without refinement, into the structure factor calculation; final values of 0.044 and 0.043 were obtained for R_1 and R_2, respectively. Final coordinates for all non-hydrogen atoms are listed in Table I and temperature factors are listed in Table II; coordinates of the hydrogen atoms are given in Table III and the calculated and observed structure factors are compared in Table IV.

Discussion

The structure consists of discrete molecules of $Cu(TPPO)_2Cl_2$; Figure 1 is a perspective drawing of the complex and Table V summarizes the intramolecular distances and angles for the structure. The complex has two-fold symmetry and, as expected,[8] the coordination of the copper is tetrahedral. The distortion of the tetrahedron is, however, different from that predicted and different from that observed for all other tetrahedral copper(II) complexes.[1-7]

In all complexes previously studied the tetrahedron was compressed along one of the four-fold inversion axes so that two of the corodination angles were larger than the tetrahedral angle of 109°; values of these angles for previously studied complexes are given in Table VI. This type of distortion, in the limit of 180° coordination angles, would lead to a *trans*-planar complex.

In $Cu(TPPO)_2Cl_2$ these angles (93.0(1)° and 102.2 (1)°) are less than the tetrahedral angle and indicate an elongation of the tetrahedron. In addition to this distortion, there is a twist of the O–Cu–O plane with respect to the Cl–Cu–Cl plane to give a dihedral angle of 71.6° rather than 90°; in all previous studies the dihedral angle between coordination planes, Table VI, has been close to 90°. In the limit of coordination angles of 90° and dihedral angle of 0°, this type of distortion would yield a *cis*-planar complex.

In addition to the above comparisons, it is interesting to compare the structure of $Cu(TPPO)_2Cl_2$ with the structure of a similar complex of triphenylphosphine since both triphenylphosphine oxide and triphenylphosphine give tetrahedral complexes with most of the divalent metal ions of the first transitions series. Like $Cu(TPPO)_2Cl_2$, $Ni(TPP)_2Cl_2$[15] (where TPP represents triphenylphosphine) has two-fold symmetry but the tetrahedron is slightly compressed along the two-fold axis to give a P–Ni–P angle of 117° and

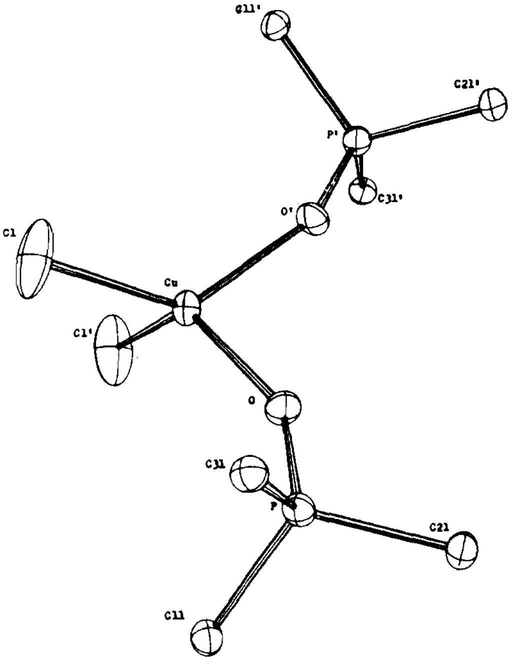


Figure 1. A perspective drawing of the complex with phenyl groups omitted. The two-fold axis through the copper is horizontal in the figure.

Table V. Intramolecular distances and angles for $CuCl_2(TPPO)_2$

Bond Distances		Bond Angles			
Atoms	Distance, Å	Atoms	Angle, Deg.	Atoms	Angle, Deg.
Cu-Cl	2.170(2)	Cl-Cu-Cl′	102.2(1)	C21-C22-C23	119.3(10)
Cu-O	1.958(4)	O-Cu-O′	93.0(1)	C22-C23-C24	118.9(11)
O-P	1.492(4)	Cl-Cu-O	104.7(2)	C23-C24-C25	121.5(9)
P-C11	1.822(6)	Cl-Cu-O′	127.5(2)	C24-C25-C26	120.8(10)
P-C21	1.781(6)	Cu-O-P	150.9(3)	C25-C26-C21	120.2(9)
P-C31	1.798(6)	O-P-C11	111.8(3)	C26-C21-C22	119.2(7)
C11-C12	1.38(1)	O-P-C21	108.4(3)	C31-C32-C33	120.5(7)
C12-C13	1.37(1)	O-P-C31	113.5(3)	C32-C33-C34	119.4(7)
C13-C14	1.37(1)	C11-P-C21	110.4(3)	C33-C34-C35	122.0(6)
C14-C15	1.37(1)	C21-P-C31	107.2(3)	C34-C35-C36	119.7(7)
C15-C16	1.38(1)	C31-P-C11	105.5(3)	C35-C36-C31	119.0(6)
C16-C11	1.39(1)	P-C11-C12	119.3(5)	C36-C31-C32	119.8(6)
C21-C22	1.37(1)	P-C11-C16	121.0(5)		
C22-C23	1.43(1)	P-C21-C22	118.0(6)		
C23-C24	1.36(2)	P-C21-C26	122.8(6)		
C24-C25	1.32(2)	P-C21-C32	121.1(5)		
C25-C26	1.39(1)	P-C31-C36	119.1(5)		
C26-C21	1.38(1)	C11-C12-C13	119.2(7)		
C31-C32	1.38(1)	C12-C13-C14	121.3(7)		
C32-C33	1.40(1)	C13-C14-C15	119.7(7)		
C33-C34	1.36(1)	C14-C15-C16	120.2(7)		
C34-C35	1.35(1)	C15-C16-C11	119.9(7)		
C35-C36	1.41(1)	C16-C11-C12	119.7(6)		
C36-C31	1.39(1)				

Table VI. Distortion in Tetrahedral Complexes

Compound	Dihedral Angle Between Coordination Planes[a]	Angle Within Coordination Plane		Reference
Cesium Tetrachlorocuprate(II)	90°	Cl-Cu-Cl	124.9°	1
			123.3	
Cesium Tetrabromocuprate(II)	90	Br-Cu-Br	126.4	2
			130.4	
Copper chromite	90	O-Cu-O	122.5	3
Bis(N-isopropylsalicylaldiminato)copper(II)	86.7	N-Cu-N	137.7	4
		O-Cu-O	137.1	
Bis(N-t-butylsalicylaldiminato)copper(II)	88.5	N-Cu-N	145.3	5
		O-Cu-O	137.4	
2,2′-Biphenylbis(2-iminomethylphenolato)copper(II)	88.3	O-Cu-N	154.6	6
			151.4	
Bis(N-ethylsalicylaldiminato)copper(II)	89.1	N-Cu-N′	156.6	7
		O-Cu-O′	151.6	
Dichlorobis(triphenylphosphine oxide)copper(II)	71.6	O-Cu-O	93.0	
		Cl-Cu-Cl	102.2	
Dichlorobis(triphenylphosphine)nickel(II)	89.1	P-Ni-P	117	14
		Cl-Ni-Cl	123	

[a] Both coordination planes include the C_2 axis of the distorted tetrahedron.

a Cl–Ni–Cl angle of 123°; the dihedral angle between these coordination planes is 89.1°. The distortion in the triphenylphosphine complex is, thus, similar to that found previously for tetrahedral copper complexes.

The Cu–O distance of 1.958(4) Å is slightly longer than the 1.89 Å found in $Cu_4OCl_6(TPPO)_4$.[9] The Cu–Cl distance of 2.170(2) Å is identical to the terminal Cu–Cl distance found for the $Cu_4OCl_{10}^{4-}$ anion[16] but is significantly shorter than the Cu–Cl distances found[17] in most other structures, 2.20-2.40 Å.

The Cu–O–P arrangement is bent as suggested[9] previously on the basis of the P–O stretching frequency; the Cu–O–P angle of 150.9(3)° is less than the 180° found for $Cu_4OCl_6(TPPO)_4$[9] or the 169° found for the $Fe(S_2C_4F_6)_2(TPPO)^{1-}$ anion.[18] Although the M–O–P arrangement is bent more than in other triphenylphosphine oxide complexes, it is not bent as much as in the trialkylphosphine oxide complexes that have been studied.[19]

The triphenylphosphine portion of the complex does not show any unusual features. The P–C distances range from 1.781(6) Å to 1.822(6) Å and the C–C bonds of the phenyl groups range from 1.32(2) Å to 1.43(1) Å with an average of 1.38 Å; the C–P–C angles vary from 105.5(3)° to 110.4(3)° and the C–C–C angles of the phenyl rings are between 119(1)° and 122(1)°.

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