Synthesis and Molecular Structure of An Inorganic Zwitterion: Trichloro-{[2-(diphenylphosphinyl)ethyl]dimethylammonium}copper(II)[1]

By **M. Gary Newton, H. Dan Caughman,** and **R. Craig Taylor,***† Department of Chemistry, University of Georgia, Athens, Georgia 30601, U.S.A.

The solid-state structure of the title compound has been determined by *X*-ray crystallographic methods (Patterson and Fourier) from both film and automated diffractometer data. Crystals are monoclinic, and diffractometer results indicate space group *Cc* with $Z = 8$, cell dimensions: $a = 12·713(1)$, $b = 12·633(1)$, $c = 24·474(2)$ Å, and $\beta = 91·05(1)°$. The structure was refined to R 0·071 for 2709 independent reflections.

The results clearly show the zwitterionic nature of the complex. The co-ordination polyhedron around each copper(II) atom is a distorted tetrahedron. The co-ordination sphere is comprised of the three anionic chloride ligands and the oxygen atom of the phosphinyl group. The overall solid-state packing of the individual molecules reflects the intermolecular hydrogen bonding between the proton on the nitrogen and the chlorine atoms. As a result, the molecules form hydrogen-bonded chains which run parallel to the *c* axis. Important bonds and angles are: Cu–O 2·00, P–O 1·50 Å; Cu–O–P 145·5°.

In an earlier paper[2] we reported the results of a study involving the reaction of [2-(diphenylphosphino)ethyl]-diethylamines with copper(II) chloride. Only compounds containing the Cu^I ion were isolated, presumably because of the ease with which copper(II) was reduced to copper(I) by tertiary phosphines; the tertiary phosphines were in turn oxidized to phosphine oxides. Surprisingly, the amine function was protonated during the reaction resulting in a compound which was formulated as [2-(diphenylphosphinyl)ethyl]diethylammonium dichlorocuprate(I), $[Ph_2P(O)C_2H_4\overset{+}{N}(H)Et_2][CuCl_2^-]$. This compound was the subject of an *X*-ray diffraction study which revealed the existence of a discrete linear $CuCl_2^-$ anion with the organic portion functioning only as a cation, *i.e.* no interaction between the phosphinyl oxygen and the copper(I) atom.

Because of the well known ability of phosphine oxides to function as ligands towards transition-metal ions and our recent interest in metal complexes of 'mixed' nitrogen–phosphorus cationic ligands,[3,4] we were interested in investigating the co-ordinating ability of the phosphine oxide portion of [2-diphenylphosphinyl)ethyl]-dialkylammonium halides, $[Ph_2P(O)C_2H_4\overset{+}{N}(H)R_2]X^-$, with the aim of preparing a copper(II) zwitterionic complex analogous to those found for the Co^{II} ion. We now describe the preparation, properties, and molecular structure of one such zwitterion (I), trichloro{[2-diphenylphosphinyl)ethyl]dimethylammonium}copper(II), $[Me_2\overset{+}{N}(H)C_2H_4P(O)Ph_2](CuCl_3^-)$. Because of the similarity in the P–O stretching frequency in this complex and in the dichlorocuprate(I) salt,[2] it was of interest to determine whether or not the phosphoryl oxygen was actually bonded to the Cu^{II} ion in the zwitterion. Also, there have been relatively few structural studies of inorganic zwitterions.[5-7]

EXPERIMENTAL

Reagents and Chemicals.—[2-(Diphenylphosphinyl)ethyl]-dimethylamine and [2-(diphenylphosphinyl)ethyl]dimethylammonium chloride, were prepared as described previously.[2] All other chemicals were reagent grade and were used without further purification. Carbon, hydrogen, and nitrogen analyses were performed by use of a Perkin-Elmer 240 elemental analyser. Copper analysis was by *X*-ray fluorescence techniques.[8]

Synthesis.—Compound (I) was prepared by two slightly different methods, both giving crystals with the same morphology. (*a*) Anhydrous copper(II) chloride (1·35 g, 10 mmol) in ethanol (25 ml) was added to [2-(diphenylphosphinyl)ethyl]dimethylamine, (II) (2·57 g, 10 mmol). When concentrated hydrochloric acid (*ca.* 1 ml) was added to this dark solution, it quickly became bright yellow-green. Within 1 h well formed golden-orange crystals were deposited, and were washed with cold ethanol (×3), and air dried (1·91 g, 43%).

(*b*) Concentrated hydrochloric acid (1 ml) was added to a solution of anhydrous copper(II) chloride (1·35 g, 10 mmol) dissolved in ethanol (25 ml). The yellow-green solution, which presumably contains $CuCl_4^{2-}$ as the major copper-containing species, was added to an ethanolic solution (25 ml) containing (2·57 g, 10 mmol) of (II). This was set aside for 24 h, when large orange crystals had formed and were washed and dried as before (1·36 g, 36%); m.p. (decomp.) 170 °C (Found: C, 43·4; H, 4·60; Cl, 23·9; Cu, 14·1; N, 2·85; O, 3·65. $C_{16}H_{21}Cl_3CuNOP$ requires C, 43·25; H, 4·55; Cl, 23·95; Cu, 14·3; N, 3·15; O, 3·60%).

Conductivity, Magnetic Susceptibility, and Spectral Data.—The instruments used to obtain these data are described in ref. 2.

Crystal Data.—$C_{16}H_{21}Cl_3CuNOP$, $M = 444·22$, Monoclinic, $a = 12·70(1)$, $b = 12·60(1)$, $c = 24·45(2)$ Å, $\beta = 91·0(1)°$, $U = 3911·89$ Å^3, $D_m = 1·50$, $Z = 8$, $D_c = 1·52$. Space group *Cc* or *C*2/*c* (*vide infra*). λ(Mo-K_α) = 0·7107 Å, μ(Mo-K_α) = 14·75 cm^{-1}.

Data Collection.—A single orange crystal of (I) *ca.*

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† *Present address:* Department of Chemistry, Oakland University, Rochester, Michigan 48063, U.S.A.

[1] Presented, in part, at the Southeast-Southwest Regional Amer. Chem. Society Meeting, New Orleans, La., December, 1970, and the Amer. Cryst. Assocn., Iowa State University, Ames, Iowa, August 1971. This paper is based, in part, on a Ph.D. Thesis, June 1971, by H. Dan Caughman, Graduate School, University of Georgia.

[2] M. G. Newton, H. D. Caughman, and R. C. Taylor, *J.C.S. Dalton*, 1974, 258.

[3] R. C. Taylor and R. A. Kolodny, *Chem. Comm.*, 1970, 813.

[4] R. A. Kolodny, T. L. Morris, and R. C. Taylor, *J.C.S. Dalton*, 1973, 328.

[5] J. Trotter and S. H. Whitlow, *J. Chem. Soc.* (*A*), 1970, 455.

[6] C. K. Prout and H. M. Powell, *J. Chem. Soc.*, 1961, 4177.

[7] D. F. Gaines, J. W. Lott, and J. C. Calabrese, *J.C.S. Chem. Comm.*, 1973, 295.

[8] J. M. McCall, D. E. Leyden, and C. W. Blount, *Analyt. Chem.*, 1971, **43**, 1324.

0·2 × 0·4 × 0·6 mm, was mounted inside a glass capillary and sealed from the atmosphere. Precession photographs, recorded for the *h*0*l*, *h*1*l*, and *hk*0 levels by use of a 60 mm radius Buerger precession camera with zirconium-filtered molybdenum-K_α radiation, indicated a monoclinic crystal system with the cell dimensions listed. Systematic extinctions (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) indicated space group *C*2/*c* or *Cc*.[9]

Three-dimensional intensity data were recorded on a multiple-film equi-inclination Weissenberg camera for the layers 0—10*kl* by use of nickel-filtered copper-K_α radiation ($\lambda = 1{\cdot}5418$ Å), and were estimated visually with the aid of a calibrated strip. The eleven levels of data were then correlated and corrected for Lorentz and polarization effects.[10] A total of 2536 unique non-zero reflections were used in the structural analysis.

Structure Determination.—(*a*) The statistically more likely *C*2/*c* centric space group was assumed initially. The first attempt to solve the structure by use of the symbolic-addition procedure for centric space groups[11] was unsuccessful, as was a second attempt *via* the heavy-atom method.[12] The structure was eventually solved in the acentric space group *Cc*. Examination of the three-dimensional Patterson map of one quarter of the unit cell revealed five high-intensity peaks, which were assigned to the vectors of two copper and three chlorine atoms. A structure-factor calculation[13] using these five positions gave R 0·506. The subsequent Fourier synthesis map[14] for half of the unit cell revealed the positions of three more chlorine and two copper atoms. A structure-factor calculation based on these ten positions gave an R of 0·401. The next Fourier revealed all 46 non-hydrogen atomic positions, and a structure-factor calculation for all these gave R 0·326. Least-squares refinement[15] of all atomic positions, isotropic temperature factors for carbon, nitrogen, and oxygen, and anisotropic temperature factors for copper, chlorine, and phosphorus using all 2536 reflections gave R 0·12. Because the calculation involved a large number of atoms the least-squares refinement had to be done piecemeal (by refining sections of the complete structure in separate least-squares calculations). Atomic scattering curves were taken from ref. 16.*

After the structure was solved in the acentric space group it was discovered that the unit cell possessed a pseudocentre of symmetry. To ascertain that the crystal symmetry was truly *Cc* and not *C*2/*c*, atomic positions were transformed and refined under *C*2/*c* operations. After least-squares refinement of all atomic positions and isotropic temperature factors of all atoms a minimum R of 0·380 was obtained. During the estimation of the three-dimensional intensity data for each *hkl* reflection it was observed that *hkl* reflections with all even parity (*e,e,e*) or all odd parity (*o,o,o*) were much greater in intensity than those reflections with (*e,e,o*) or (*o,o,e*). This phenomenon was later attributed to the fact that much of the scattering matter is located near the (x,1/4,z) plane. This concentration of electron density on (x,1/4,z) involves the dense copper atoms and 2/3 of the chlorine atoms, and is in agreement with the structure-factor equation for *Cc* symmetry,[17] which contains a real and imaginary part, both of which depend on the common factor $\cos 2\pi(ky - 1/4)$. If the y co-ordinate for the scattering matter (assuming all atoms located in the same plane) is 0·25, then the expression becomes $\cos \pi/2(k + l)$. If $k + l = 2n + 1$, which occurs for the case in which hkl = (*e,e,o*) or (*o,o,e*), then this factor vanishes; therefore the real and imaginary parts vanish and the intensity goes to zero. Of course in the present study not all of the matter was located at $y = 1/4$ therefore some finite but small intensity occurs for reflections with indices of (*e,e,o*) and (*o,o,e*).

(*b*) In order additionally to refine several important bonding parameters and to prove conclusively that the true space group of (I) is *Cc* and not *C*2/*c* it was decided that the diffraction data should be collected on an automated diffractometer.

A second crystal with dimensions closely similar to those of the first was mounted atop a glass fibre and manually aligned on an Enraf-Nonius computer automated three-circle diffractometer (CAD 3). Automation was performed by a Digital Corporation PDP/8I computer. Unit-cell dimensions, determined by use of nickel-filtered copper-K_α radiation by least-squares refinement (program RAM) based on accurately measured angular settings of at least ten reflections, were as follows: $a = 12{\cdot}713$, $b = 12{\cdot}633$, $c = 24{\cdot}474$ Å, and $\beta = 91{\cdot}05°$. These values agree very closely with those obtained from the precession data (*vide supra*).

Intensities from *hk*0—25 were measured by a scintillation counter using nickel-filtered copper-K_α radiation with a take-off angle of 4°. A pulse-height discriminator was used and a θ—2θ scan was employed, scan rate of 20° min^{-1}. The rate of scan varied, *i.e.*, $k > k > l$. The indices were generated from an input-orientation matrix[18] in a zig-zag sequence. Angular width of scans varied as a function of θ; $s = 0{\cdot}70 + 0{\cdot}10 \tan \theta$, where s = scan range (°). The number of scans per reflection was five with $I_{\max}$ set at 5000 (if 5000 counts were obtained before 5 cycles of scan were completed, the remaining scans were terminated). Backgrounds were estimated by counting for a time equal to 1/2 the scan time for each cycle at each end of the scan range. The diameter of the receiving aperture also varied as a function of θ; $d = 0{\cdot}8 + 1{\cdot}4 \tan \theta$, where d is diameter (mm). The balance filter system was not used.

Low-intensity reflections were rejected if the intensity was $< 1{\cdot}5\sigma$ where $\sigma = (N + N_{\mathrm{L}} + N_{\mathrm{R}})^{1/2}$ in which N = the total integrated intensity, N_{L} = background counts left, and N_{R} = background counts right. In this manner 2709 reflections within the range $2\theta = 3{\cdot}50$ to $68{\cdot}00°$ were recorded on a seven-track magnetic tape and teletype. No absorption corrections were made. One of three control reflections (0,8,0; 6,0,0; 0,0,10) was monitored every 60th reflection throughout data collection. An abort signal

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* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20957 (39 pp., 1 microfiche). See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[9] 'International Tables for *X*-Ray Crystallography,' vol. I, Kynoch Press, Birmingham, 1952.

[10] Program LPCOR, M. G. Newton, University of Georgia.

[11] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[12] J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1937, 219.

[13] Program STRFAC, for structure-factor calculations abstracted from U.C.L.A. Least-Squares Structure-Factor Program, I. E. Paul, modified by M. G. Newton.

[14] Program FOURR, A. Zalkin, modified by M. G. Newton.

[15] Program LSSF, P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, modified by M. G. Newton.

[16] Ref. 10, vol. III, 1962.

[17] Ref. 9, p. 380.

[18] J. C. Schoone and A. J. M. Duisenberg, Laboratorium voor Kristallchemie, Rijksuniversitat, Utrecht, The Netherlands, modified by S. Swager; available from the Enraf-Nonius Company.

would have stopped data collection if the intensity of a control reflection had fallen below 500 counts with no filters. Intensity data were corrected for Lorentz and polarization effects.[19] A structure-factor calculation carried out by use of the 46 non-hydrogen atomic positions, the isotropic and anisotropic temperature factors obtained in the first structure determination, and the intensity data obtained from the automated diffractometer, gave R 0·144. At this point in the structure determination, refinement was begun anew in the centric space group $C2/c$. The positions of the copper atom and the two chlorine atoms were calculated from the Patterson map. These positions were fed into a structure-factor calculation resulting in an initial R of 0·582. A Fourier map based on the last structure factor revealed five more atom positions: chlorine, phosphorus, oxygen, nitrogen, and carbon. A structure-factor calculation based on these 8 positions gave R 0·482. The following Fourier E map revealed all but four of the remaining non-hydrogen atoms and gave R 0·477. The subsequent Fourier showed the position of all non-hydrogen atoms. Five-cycle full-matrix least-squares refinement of the positional and isotropic temperature factors for all non-hydrogen atoms in the space group $C2/c$ yielded a minimum R of 0·438, thus dispelling any idea that the complex belongs to the $C2/c$ space group.

After several least-squares refinements of all positional, isotropic, and anisotropic temperature factors for copper, phosphorus, chlorine, oxygen, and nitrogen, and the carbon atoms attached to the nitrogen in the space group Cc, initially with parameters obtained from the Weissenberg determination (a), R was 0·082. A Fourier-difference map calculated from these refined positions, revealed 38 peaks which were attributed to 38 of the total 42 hydrogen atoms present. These positions together with the 46 non-hydrogen atoms were used in the structure-factor calculation and gave R 0·077. After least-squares refinement of hydrogen positional parameters alone, a final R of 0·071 was obtained.

Since the structure proved to be ' almost centric ' in many features it was decided to compare experimental and theoretical values of several functions of normalized structure factors (E values) from the diffractometer data.[20] The statistical distribution and averages are listed in Table 1. It is obvious that the statistical data is in close agreement with the centric group $C2/c$; however, as demonstrated by the results of the structure-factor calculations this choice is incorrect.

TABLE 1

Statistical distributions and averages, experimental and theoretical, for (I)

Quantity	Calc.	Found	
		Centric	Acentric
$\langle\lvert E\rvert\rangle$	0·842	0·798	0·886
$\langle\lvert E\rvert^2\rangle$	1·000	1·000	1·000
$\langle\lvert\lvert E\rvert^2 - 1\rvert\rangle$	0·899	0·968	0·736
$\lvert E\rvert > 1{\cdot}0$	30·42	32·00	37·00
$\lvert E\rvert > 2{\cdot}0$	4·17	5·00	1·80
$\lvert E\rvert > 3{\cdot}0$	0·22	0·30	0·01

RESULTS

Magnetic Susceptibility, Conductivity, and Electronic and I.r. Spectral Data.—A magnetic susceptibility study by the Faraday method confirmed the presence of copper(II). Pascal constants [21] were used to correct for the diamagnetism of the sample (253×10^{-6} c.g.s.u.). The corrected room-temperature molar susceptibility, χ_M', was 1613×10^{-6} c.g.s.u. which gave an effective magnetic moment, μ_{eff}, 1·98, a typical value for copper(II) in a tetrahedral or pseudotetrahedral environment.

Concentration-dependent conductivity studies (10^{-3}—10^{-4}M) in nitromethane gave data which were indicative of a weak electrolyte. This electrolytic behaviour is typical of inorganic zwitterions and has been observed by us [3,4] and others [22] for all such systems. Apparently a solvation equilibrium (1) is established in co-ordinating solvents, such

$$[MX_3^-(L\text{–}L^+)] + \text{Solvent} \rightleftharpoons [MX_3^-(\text{Solvent})] + L\text{–}L^+ \quad (1)$$

as nitromethane, which accounts for the weak electrolytic behaviour as well as the increase in conductivity as the nitromethane solutions ' age.' This phenomenon has been studied in more detail for similar systems by Furlani *et al.*[23]

The electronic spectrum of (I) in freshly prepared solutions of nitromethane exhibits a broad asymmetric absorption with a band maximum at 396 nm and a shoulder on the low-energy side at *ca.* 455 nm. The molar extinction coefficient for the main absorption is *ca.* 1000 l mol^{-1} cm^{-1}. This spectrum is typical for Cu^{II} in a pseudotetrahedral ligand field,[24] and closely resembles the spectrum of dichlorobis(triphenylphosphine oxide)copper(II), in both band position and intensity. Absorption bands occur for the latter at 380 and 470 nm respectively. Further studies by Cotton *et al.*[25] led them to conclude that the ligand-field strength of a phosphine oxide towards copper(II) is greater than that of the chloride ion, and the present results confirm this. In our zwitterionic complex copper(II) has a co-ordination sphere comprised of a phosphine oxide and three chloride ions. The main component of the absorption band occurs at lower energies than for the copper(II) complex prepared by Cotton and Goodgame,[24] in which the co-ordination sphere around copper(II) is comprised of two phosphine oxide groups and two chloride ions.

The presence of the phosphinyl group is clearly demonstrated at higher energies by the appearance of the diagnostic ^1L_a and ^1L_b absorption bands due to the benzenoid portion of the molecule.[2]

The solid-state (Nujol mull, Polyethylene plates) far-i.r. spectrum of (I) exhibited two distinct absorptions which were absent in that of the free ligand. Only two i.r.-active Cu–Cl stretching modes are expected for the complex assuming local C_{3v} symmetry around the copper(II) ion. Therefore, the bands at 312s and 263m,br cm^{-1} have been assigned to the antisymmetric (e) and symmetric (a_1) Cu–Cl stretching modes, respectively. In the zwitterionic complex of the monoprotonated 1,4-diazabicyclo[2.2.2]octanium cation co-ordinated to CuCl$_3^-$ the Cu–Cl stretching

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[19] Program DIFCOR, Lorentz and polarization corrections, M. G. Newton.

[20] Program FAME, R. A. Dewar and A. Stone, University of Chicago.

[21] J. Lewis and R. G. Wilkins, ' Modern Co-ordination Chemistry,' Interscience, New York, 1960, p. 403.

[22] C. Ercolani, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chim. Acta*, 1969, **3**, 421.

[23] L. Sestilli, C. Furlani, and G. Festuccia, *Inorg. Chim. Acta*, 1970, **4**, 542.

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

[25] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4691.

frequencies (cm^{-1}) were observed **between 350 and 310s** and 260—280m,br.[26]

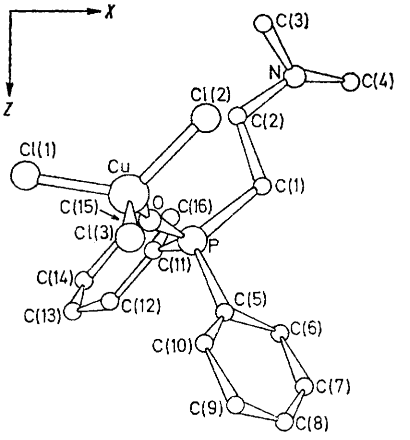

FIGURE 1 Stick drawing of one molecule of (I)

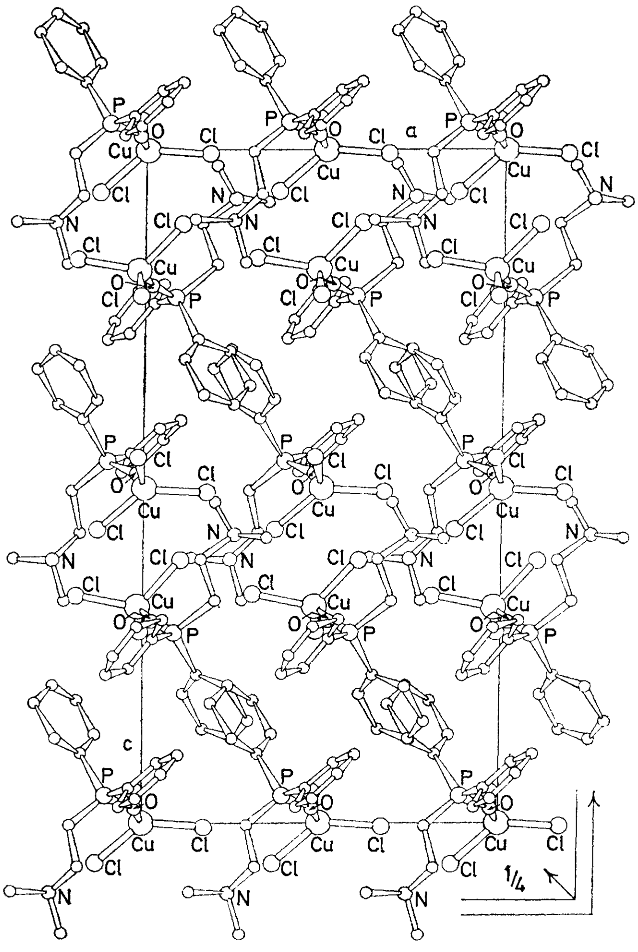

FIGURE 2 The unit cell of (I)

The absorption band due to the Cu–O stretching vibration was not observed; it probably lies hidden under the vibrations due to the ligand.

The i.r. spectrum of (I) in the P–O stretching region (1000—1250 cm^{-1}) was particularly interesting, since in ref. 2 it was shown that the phosphinyl group was too far removed from the copper(I) ion for any interaction to take place. A strong absorption at 1165 cm^{-1} in the solid-state spectrum (Nujol mull) of this compound was assigned to the P–O stretching vibration. This stretching mode occurs at 1154 cm^{-1} (Nujol mull) for (I), a difference for the two compounds of only 11 cm^{-1}. This small decrease made it difficult to state definitively that the phosphinyl oxygen was co-ordinated to the copper(II) ion. Co-ordination of a phosphine oxide to a *d* transition-metal ion usually leads to a decrease in P–O stretching frequency of anywhere from 40 to 100 cm^{-1}.[27] However the *X*-ray diffraction study enabled clarification (see later).

DISCUSSION

Description of the Structure.—A drawing of one of the molecules of (I) in the asymmetric unit of the unit cell shows that the original formulation of this complex as an inorganic zwitterion is correct (Figure 1, which shows the numbering scheme used). Atom positions in the two independent molecules are distinguished by (A) or (B), unless a mean value is used. The unit cell is shown in

TABLE 2

Positional and thermal parameters for all non-hydrogen atoms in molecule (A), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	$B/Å^2$
Cu	1·0000(0)	0·2480(3)	0·0000(0)	*
Cl(1)	1·1729(6)	0·2580(5)	0·0101(4)	*
Cl(2)	0·8748(8)	0·2446(5)	0·0629(5)	*
Cl(3)	0·9857(7)	0·0942(6)	−0·0423(4)	*
P	0·8950(5)	0·4781(5)	−0·0403(3)	*
O	0·9773(13)	0·4007(14)	−0·0202(7)	*
N	0·7396(18)	0·4677(13)	0·1049(9)	*
C(2)	0·8248(21)	0·5107(21)	0·0665(11)	*
C(3)	0·7811(17)	0·4584(19)	0·1632(11)	*
C(4)	0·6445(23)	0·5268(21)	0·1001(13)	*
C(1)	0·7917(18)	0·4836(18)	0·0068(10)	4·7(5)
C(5)	0·8263(17)	0·4491(17)	−0·1013(9)	2·0(4)
C(6)	0·7511(33)	0·5055(32)	−0·1221(16)	5·3(8)
C(7)	0·7051(21)	0·4639(22)	−0·1780(11)	4·5(5)
C(8)	0·7475(20)	0·3743(19)	−0·2017(10)	4·1(5)
C(9)	0·8035(15)	0·3318(14)	−0·1804(8)	3·1(3)
C(10)	0·8737(22)	0·3461(23)	−0·1275(12)	4·6(6)
C(11)	0·9564(19)	0·6097(18)	−0·0492(10)	4·9(5)
C(12)	1·0441(14)	0·5955(14)	−0·0873(7)	2·9(3)
C(13)	1·0936(25)	0·6970(26)	−0·1013(14)	4·3(6)
C(14)	1·0575(21)	0·7950(22)	−0·0718(11)	3·2(5)
C(15)	0·9799(13)	0·7877(12)	−0·0329(7)	1·4(3)
C(16)	0·9328(26)	0·6894(26)	−0·0176(13)	4·2(7)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	39(2)	43(2)	16(1)	00(0)	−4(2)	3(2)
Cl(1)	36(4)	36(4)	28(2)	11(6)	−12(5)	7(4)
Cl(2)	101(7)	26(4)	36(3)	−11(7)	74(7)	−7(4)
Cl(3)	81(6)	48(5)	18(2)	12(8)	00(5)	22(5)
P	31(4)	24(4)	8(1)	−2(6)	−2(3)	−3(3)
O	39(10)	44(10)	13(3)	−3(16)	8(9)	−12(8)
N	56(14)	17(10)	10(4)	14(19)	2(12)	−8(10)
C(2)	46(17)	53(17)	10(5)	−12(26)	8(13)	−13(14)
C(3)	22(11)	45(14)	12(4)	30(19)	−6(11)	20(12)
C(4)	41(16)	54(16)	15(6)	−21(25)	00(15)	−18(14)

* Anisotropic temperature factors were employed for these atoms in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; all parameters $\times 10^4$.

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[26] J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Amer. Chem. Soc.*, 1970, **93**, 482.

[27] N. M. Karayannis, C. M. Mikulski, M. J. Strocko, C. L. Pytliwski, and M. M. Labes, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2629.

Figure 2. Final atomic positional and thermal parameters are listed in Tables 2—4. Intramolecular bonding distances for both molecules in the asymmetric unit are listed in Table 5, which includes mean bond lengths. Bond angles for both molecules, and their means, are listed in Table 6.

TABLE 3

Positional and thermal parameters for all non-hydrogen atoms in molecule (B), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	B/Å^2
Cu	0·4844(2)	0·2532(2)	0·17753(9)	*
Cl(1)	0·3115(6)	0·2409(5)	0·1678(4)	*
Cl(2)	0·6088(7)	0·2578(5)	0·1125(4)	*
Cl(3)	0·4969(7)	0·4072(6)	0·2189(4)	*
P	0·5905(5)	0·0226(4)	0·2180(3)	*
O	0·5118(13)	0·1061(13)	0·2037(8)	*
N	0·7415(15)	0·0374(14)	0·0735(8)	*
C(2)	0·6591(18)	−0·0006(16)	0·1098(11)	*
C(3)	0·6925(24)	0·0542(24)	0·0158(12)	*
C(4)	0·8399(21)	−0·0380(21)	0·0731(11)	*
C(1)	0·6992(22)	0·0083(21)	0·1715(13)	2·9(5)
C(5)	0·6516(20)	0·0635(19)	0·2837(11)	2·9(5)
C(6)	0·7340(23)	−0·0102(23)	0·3031(12)	3·0(5)
C(7)	0·7927(20)	0·0018(20)	0·3507(11)	4·1(5)
C(8)	0·7626(19)	0·0951(19)	0·3798(10)	3·8(5)
C(9)	0·6549(24)	0·1843(24)	0·3586(13)	5·1(7)
C(10)	0·6294(18)	0·1423(17)	0·3115(9)	2·7(4)
C(11)	0·5259(8)	−0·1008(8)	0·2307(4)	0·7(2)
C(12)	0·4657(18)	−0·1125(17)	0·2712(9)	4·4(4)
C(13)	0·4022(29)	−0·1009(29)	0·2824(16)	5·6(8)
C(14)	0·4128(28)	−0·2870(30)	0·2534(16)	5·7(8)
C(15)	0·4934(32)	−0·2934(31)	0·2052(16)	4·9(9)
C(16)	0·5530(20)	−0·1976(20)	0·2036(11)	2·7(5)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{12}	β_{23}
Cu	54(3)	30(2)	16(1)	2(3)	2(2)	−2(2)
Cl(1)	40(4)	43(4)	26(2)	8(6)	−15(5)	13(4)
Cl(2)	82(6)	52(5)	20(2)	−50(8)	42(5)	−8(4)
Cl(3)	76(6)	40(4)	19(2)	−22(8)	3(5)	−19(4)
P	23(4)	21(4)	9(1)	8(5)	−2(3)	7(3)
O	39(10)	23(8)	20(4)	46(15)	−1(10)	12(9)
N	24(10)	45(12)	8(4)	−28(18)	−5(10)	11(10)
C(2)	29(14)	17(10)	11(5)	−9(19)	−8(12)	3(11)
C(3)	95(24)	89(22)	9(5)	−74(37)	−5(17)	−9(16)
C(4)	49(15)	61(17)	9(4)	43(26)	7(12)	20(13)

* Anisotropic temperature factors were employed for these atoms as defined in Table 2; parameters $\times 10^4$.

The mean aromatic C–C bond distance for 24 aromatic carbon–carbon interactions in the asymmetric unit is 1·42(4) Å. This value is close to that found in triphenylphosphine oxide [28] [1·40(2) Å], although both values are somewhat larger than the accepted value for an aromatic C–C bond. The P–$C_{(arom)}$ bond length in the complex is 1·80(3) Å, quite close to that found in $Ph_3P{:}O$ [1·77(1)].[28] The bond angles about phosphorus are similar to those found in triphenylphosphine oxide.

Selected dihedral angles are listed in Table 7. Large differences between several dihedral angle systems for the two molecules dramatically point out the non-equivalence of the two molecular units and provide further justification for the choice of space group symmetry as *Cc* and not *C*2/*c*.

The mean Cu–Cl(1) and Cu–Cl(3) bond distances in (A) and (B) are 2·205 Å whereas the Cu–Cl(2) bond lengths are significantly longer (2·250 Å). These longer bond lengths may be attributed to the fact that the Cl(2) atoms in each molecule are directed towards the cationic nitrogen atom. Trotter and Whitlow [5] have recently published the results of a structural determination of the copper(II) zwitterion, trichloro(octamethylcyclotetraphosphonitrilium)copper(II), in which two sets of Cu–Cl distances were found: 2·22 for two of the Cu–Cl bonds, and 2·26 Å in the $CuCl_3^-$ moiety. These values are in close agreement with the present results. The longer Cu–Cl distance is probably involved in an intermolecular hydrogen bond. In fact it appears that the over-riding force which causes (I) to adopt the crystal packing pattern shown in Figure 2 is the attractive interaction between the cationic nitrogen atom and the negatively charged chlorine atom, Cl(2). Intermolecular hydrogen bonding between the proton on the nitrogen atom and Cl(2) is very likely. Projected H · · · Cl(2) distances calculated from the hydrogen atom positional

TABLE 4

Positional parameters of hydrogen atoms in molecules (A) and (B), with estimated standard deviation in parentheses

	Molecule (A)			Molecule (B)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
HN	0·739(14)	0·378(14)	0·108(8)	0·760(15)	0·176(14)	0·082(8)
H(1)C(1)	0·844(15)	0·105(15)	−0·027(8)	0·582(15)	0·043(14)	0·214(7)
H(2)C(1)	0·727(15)	0·392(14)	0·002(8)	0·711(14)	−0·040(14)	0·181(7)
H(1)C(2)	0·870(15)	0·575(17)	0·094(9)	0·593(15)	0·055(16)	0·105(8)
H(2)C(2)	0·889(15)	0·451(15)	0·087(8)	0·653(15)	−0·059(17)	0·118(9)
H(1)C(3)	0·856(15)	0·562(15)	0·164(8)	0·738(16)	0·043(17)	0·007(9)
H(2)C(3)	0·825(16)	0·468(16)	0·156(8)	0·737(16)	0·075(17)	−0·029(9)
H(3)C(3)	0·810(16)	0·525(16)	0·171(8)	0·642(15)	0·093(15)	0·030(8)
H(1)C(4)	0·671(17)	0·614(15)	0·095(8)	0·887(15)	−0·032(15)	0·133(8)
H(2)C(4)	0·619(13)	0·525(16)	0·073(9)	0·895(17)	0·008(16)	0·067(10)
H(3)C(4)	0·592(17)	0·521(16)	0·126(10)	0·346(17)	0·393(16)	0·068(8)
HC(6)	0·752(15)	1·120(15)	−0·068(8)	0·728(15)	−0·040(14)	0·268(8)
HC(7)	0·578(14)	1·034(15)	−0·173(8)	0·863(15)	−0·038(15)	0·366(8)
HC(8)	0·723(15)	0·838(15)	−0·252(8)	0·797(15)	0·103(15)	0·417(8)
HC(9)	0·829(14)	0·803(14)	−0·197(7)	0·706(14)	0·272(14)	0·399(8)
HC(10)	0·919(15)	0·811(14)	−0·121(8)	0·542(14)	0·130(14)	0·310(7)
HC(12)	1·057(15)	0·046(14)	−0·112(8)	0·457(15)	−0·127(15)	0·278(8)
HC(13)	1·205(14)	0·758(14)	−0·106(7)	0·357(14)	−0·193(14)	0·323(8)
HC(14)	1·104(15)	0·876(14)	−0·028(8)	0·375(15)	−0·374(14)	0·260(8)
HC(15)	0·953(14)	0·874(14)	−0·035(7)	0·453(15)	−0·358(14)	0·156(8)
HC(16)	0·856(15)	0·653(14)	0·005(8)	0·641(15)	−0·221(14)	0·187(8)

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[28] G. Bandoli, G. Bortolozzo, D. A. Clemente, U. Croatto, C. Panattoni, *J. Chem. Soc.* (*A*), 1970, 2778.

parameters (Tables 4 and 5) are shown in Figure 3, and are well within the sum of the van der Waals radii (3·0 Å).[29] The results of these calculations are given in Table 8. Even in the absence of projected hydrogen-atom positions, the intermolecular distance between N(A) and Cl(2B) or N(B) and Cl(2A) is **3·13** Å, well within the sum of the van der Waals radii (3·30 Å) and well within the expected range for a N–H · · · Cl hydrogen

TABLE 5

Bond lengths (Å) in molecules (A) and (B), with estimated standard deviations in parentheses

Atom	Molecule (A)	Molecule (B)	Mean
Cu–Cl(1)	2·212(7)	2·213(8)	2·212(8)
Cu–Cl(2)	2·236(10)	2·264(9)	2·250(10)
Cu–Cl(3)	2·205(9)	2·196(8)	2·200(9)
Cu–O	2·01(2)	1·99(2)	2·00(2)
O–P	1·51(2)	1·49(2)	1·50(2)
P–C(1)	1·76(2)	1·82(3)	1·79(3)
P–C(5)	1·76(2)	1·85(3)	1·80(3)
P–C(11)	1·85(2)	1·78(1)	1·82(2)
C(1)–C(2)	1·55(4)	1·59(4)	1·57(4)
N–C(2)	1·55(3)	1·47(3)	1·51(3)
N–C(3)	1·51(3)	1·55(4)	1·53(4)
N–C(4)	1·42(4)	1·57(3)	1·50(4)
C(5)–C(6)	1·29(5)	1·47(4)	1·38(5)
C(6)–C(7)	1·57(5)	1·38(4)	1·46(5)
C(7)–C(8)	1·38(4)	1·43(4)	1·40(4)
C(8)–C(9)	1·02(3)	1·84(4)	1·44(4)
C(9)–C(10)	1·57(4)	1·30(4)	1·44(4)
C(10)–C(5)	1·57(4)	1·24(3)	1·40(4)
C(11)–C(12)	1·48(3)	1·28(2)	1·38(3)
C(12)–C(13)	1·47(4)	1·41(4)	1·44(4)
C(13)–C(14)	1·51(4)	1·32(5)	1·42(5)
C(14)–C(15)	1·38(3)	1·58(5)	1·48(4)
C(15)–C(16)	1·43(4)	1·43(5)	1·43(5)
C(16)–C(11)	1·31(4)	1·43(3)	1·37(3)

TABLE 6

Bond angles (°) in molecules (A) and (B), with estimated standard deviations in parentheses

Angle	Molecule (A)	Molecule (B)	Mean
Cl(1)–Cu–Cl(2)	130·0(4)	129·2(4)	129·6(5)
Cl(1)–Cu–Cl(3)	100·3(3)	100·1(3)	100·2(3)
Cl(1)–Cu–O	96·4(5)	97·8(5)	97·1(5)
Cl(2)–Cu–Cl(3)	104·6(3)	104·9(3)	104·8(3)
Cl(2)–Cu–O	95·0(5)	97·4(6)	96·2(6)
Cl(3)–Cu–O	136·0(6)	131·8(6)	133·9(6)
Cu–O–P	143(1)	148(1)	146(1)
O–P–C(1)	109(1)	116(1)	112(1)
O–P–C(5)	118(1)	106(1)	112(1)
O–P–C(11)	109(1)	111(1)	110(1)
C(1)–P–C(5)	102(1)	105(1)	104(1)
C(1)–P–C(11)	111(1)	112(1)	112(1)
C(5)–P–C(11)	107(1)	106(1)	107(1)
P–C(1)–C(2)	116(2)	112(2)	114(2)
N–C(2)–C(1)	108(2)	109(2)	108(2)
C(2)–N–C(3)	111(2)	112(2)	112(2)
C(2)–N–C(4)	112(2)	109(2)	110(2)
C(3)–N–C(4)	114(2)	113(2)	114(2)
P–C(5)–C(6)	125(2)	113(2)	119(2)
P–C(5)–C(10)	109(2)	127(2)	118(2)
C(10)–C(5)–C(6)	126(3)	120(2)	123(3)
C(5)–C(6)–C(7)	115(3)	125(3)	120(3)
C(6)–C(7)–C(8)	120(3)	111(2)	116(3)
C(7)–C(8)–C(9)	119(3)	125(2)	122(3)
C(8)–C(9)–C(10)	138(2)	100(2)	119(2)
C(9)–C(10)–C(5)	102(2)	139(3)	120(3)
P–C(11)–C(12)	107(1)	121(1)	114(1)
P–C(11)–C(16)	121(2)	124(1)	122(2)
C(16)–C(11)–C(12)	131(2)	114(2)	122(2)
C(11)–C(12)–C(13)	112(2)	127(2)	120(2)
C(12)–C(13)–C(14)	118(3)	119(3)	118(3)
C(13)–C(14)–C(15)	120(2)	121(3)	120(3)
C(14)–C(15)–C(16)	123(2)	110(3)	116(3)
C(15)–C(16)–C(11)	114(3)	126(2)	120(3)

TABLE 7

Dihedral angles (°) in molecules (A) and (B)

Dihedral angle system	Molecule (A)	Molecule (B)
Cl(1)–Cu–O–P	174·0	171·3
Cl(2)–Cu–O–P	53·4	34·5
Cl(3)–Cu–O–P	48·8	95·8
Cl(1)–Cu–P–C(1)	144·4	132·4
Cl(2)–Cu–P–C(1)	0·8	1·0
Cl(3)–Cu–P–C(1)	75·6	123·9
Cu–O–P–C(1)	42·2	42·8
Cu–O–P–C(5)	51·7	94·7
Cu–O–P–C(11)	178·6	168·7
O–P–C(1)–C(2)	47·7	28·3
O–P–C(5)–C(6)	173·3	179·3
O–P–C(11)–C(16)	93·7	143·9
P–C(1)–C(2)–N	169·5	163·0
C(1)–C(2)–N–C(3)	169·8	169·3
C(1)–C(2)–N–C(4)	56·2	42·4
C(1)–P–C(5)–C(6)	65·0	25·3
C(1)–P–C(11)–C(12)	177·5	165·5
C(5)–P–C(1)–C(2)	179·3	170·9
C(11)–P–C(1)–C(2)	41·3	101·0
C(5)A–C(8)A–C(5)B–C(8)B	5·4	
C(6)A–C(10)A–C(6)B–C(10)B	26·0	

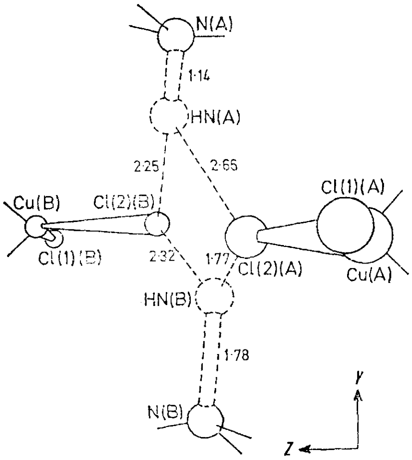

FIGURE 3 Intermolecular interactions near the amine sites in (I)

TABLE 8

Intra- and inter-molecular distances (Å) near the hydrogen-bonding site, with estimated standard deviations in parentheses

N(A) · · · Cl(2)(B)	3·13(2)	HN(B) · · · Cl(2)(B)	2·32(19)
N(A) · · · Cl(2)(A)	3·46(2)	HN(A) · · · HN(B)	2·64(20)
N(B) · · · Cl(2)(A)	3·13(2)	N(A) · · · Cl(1^{I})(B)	3·88(2)
N(B) · · · Cl(2)(B)	3·40(2)	N(A) · · · Cl(1^{II})(A)	4·41(2)
Cl(2)(A) · · · Cl(2)(B)	3·62(1)	N(B) · · · Cl(1^{II})(A)	3·94(2)
N(A) · · · N(B)	5·51(2)	N(B) · · · Cl(1)(B)	4·48(2)
HN(A) · · · N(A)	1·14(18)	Cl(1)(A) · · · Cl(1^{I})(B)	4·22(1)
HN(A) · · · Cl(2)(B)	2·25(18)	HN(A) · · · Cl(1^{III})(B)	4·89(18)
HN(A) · · · Cl(2)(A)	2·66(18)	HN(A) · · · Cl(1^{II})(A)	5·77(20)
HN(B) · · · N(B)	1·78(18)	HN(B) · · · Cl(1^{I})(B)	5·58(20)
HN(B) · · · Cl(2)(A)	1·77(19)	HN(B) · · · Cl(1^{II})(A)	6·79(20)

Roman numeral superscripts refer to the following equivalent positions:

I $\frac{1}{2} + x, \frac{1}{2} + y, z$
II $-\frac{1}{2} + x, \frac{1}{2} + y, z$
III $\frac{1}{2} + x, -\frac{1}{2} + y, z$

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[29] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' John Wiley & Sons, New York, 3rd edn., 1972, p. 120.

bond.[30] The overall solid-state structure of (I) may be visualized as being comprised of chains of these hydrogen-bonded sites running parallel to the crystallographic *b* axis.

The co-ordination polyhedron around the copper(II) ion can be described as a severaly distorted tetrahedron. However, the angles are somewhat larger than expected for a flattened tetrahedron. Theoretical calculations for Cs_2CuCl_4 have indicated that the Cl–Cu–Cl bond angles of 122 and 103° are the maximum expected for a Jahn-Teller distorted tetrahedron.[31] The corresponding angles in (I) are 130 and 105°. Because the deviations are somewhat larger than predicted both in this complex and the one studied by Trotter and Whitlow, it may be best to regard the co-ordination sphere for copper(II) in these species as deviations from square-planar rather than from tetrahedral geometry.

Undoubtedly the most informative structural data for (I) involves the magnitudes of the Cu–O and P–O bond distances and the Cu–O–P bond angle. The mean values (Cu–O 2·00, O–P 1·50 Å; Cu–O–P 145·5°) in (I) are nearly identical with those found for bis(triphenylphosphine oxide)copper(II) chloride[32] (Cu–O 1·96, O–P 1·49 Å; Cu–O–P 151°), yet the change in P–O stretchng frequency upon co-ordination is quite small for (I) ($\Delta\nu$ 11 cm^{-1}) and quite substantial for the latter complex ($\Delta\nu$ 53 cm^{-1}).[24] The small change in P–O stretching frequency in (I) is similar to the situation found for μ_4-oxo-hexa-μ-chloro-tetrakis[(triphenylphosphine oxide)-copper(II)] which has $\Delta\nu$ 1 cm^{-1}.[33] Interestingly, the Cu–O–P bond angle in this last complex is 180° and the Cu–O bond length is significantly shorter (1·89 Å).

Cotton *et al.* have listed three factors which they consider account for changes in the P–O bond order in co-ordination compounds: (i) the P–O σ-bonding is enhanced by increased positive charge on the metal ion; (ii) the p_π–d_π bonding between oxygen and phosphorus is decreased by increased positive charge on the metal ion; and (iii) the drift of metal electrons toward oxygen *via* d_π–p_π overlap enhances the oxygen–phosphorus multiple bonding. The second of these factors has usually been cited as dominant in accounting for the decrease in P–O stretching frequencies upon co-ordination. Bertrand[33] has rationalized the small change in P–O stretching frequency observed for $Cu_4OCl_6(Ph_3PO)_4$ as arising from the linear Cu–O–P bond angle, which ensures good overlap between the d_π orbitals on Cu with the p_π orbitals on oxygen, and consequently enhances the d_π–p_π overlap between oxygen and phosphorus [factor (iii)]. This explanation is consistent with the observed Cu–O bond length (*vide supra*). On the other hand, the relatively long P–O bond (1·51 Å) in $Cu_4OCl_6(Ph_3PO)_4$ is inconsistent with the fact that the normal P–O bond length in triphenylphosphine oxide itself is 1·46(1) Å.[28] Since the P–O stretching frequencies in these two species are identical, the significantly longer P–O bond length in the copper complex is disturbing. Recent structural results for tetranitratobis(triphenylphosphine oxide)-cerium(IV)[34] indicate a nearly linear Cu–O–P array (mean bond angle 171°), O–P 1·53 Å, yet a substantial change in the P–O stretching frequency upon co-ordination ($\Delta\nu$ 147 cm^{-1}). Thus even though the important bond angles and bond lengths in $Cu_4OCl_6(Ph_3PO)_4$ and $(Ph_3PO)_2Ce(NO_3)_4$ are virtually identical, the differences in P–O stretching frequencies are striking. Added to this are the results of the present study: a significantly bent Cu–O–P moiety, mean P–O bond length nearly identical with those in the aforementioned two complexes, and yet a small change in P–O stretching frequency. In order to rationalize this diverse data it seems necessary to include a fourth factor which, although mentioned in the literature, has apparently been overlooked. It has been pointed out[35] that the coupling of two oscillators, O–M and O–P, would be expected to increase the P–O stretching frequency by 50—150 cm^{-1}. The upper end of this range would be expected for a system with M–O–P 180°, the lower as the M–O–P angle reaches 90°. Therefore the small change in ν(P–O) for the copper(II) cluster can be attributed both to the coupling phenomenon as well as to enhanced d_π–p_π P–O bonding (*vide supra*). These two opposing effects should result in a small overall change in P–O stretching frequency upon co-ordination. On the other hand, the high positive charge on the cerium(IV) ion in $(Ph_3PO)_2Ce(NO_3)_4$ would greatly increase the significance of the second factor (see earlier). Apparently the P–O stretching frequency is extremely sensitive to the formal positive charge on the metal ion. The relatively small $\Delta\nu$ observed for (I) can be accounted for on the basis of a greatly diminished positive charge on the copper(II) ion because of the zwitterionic nature of the $CuCl_3^-$ moiety. In addition, the coupling of the Cu–O and O–P oscillators would be expected to be considerably less in this system because of the non-linearity of the Cu–O–P moiety. These two opposing effects result in an overall small decrease in the P–O stretching frequency.

It is therefore apparent that whereas the P–O stretching frequency is extremely sensitive to changes in electronic environment, the P–O bond length may remain nearly invariant. Because of this, from changes in P–O stretching frequencies alone, it is difficult to infer structural information about the metal–oxygen–phosphorus system and *vice versa*. Further structural information on a variety of phosphine oxide complexes is needed before correlations with i.r. data can be made with any degree of confidence.

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[3/2054 *Received, 5th October*, 1973]

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[30] G. C. Pimentel and A. L. McClellan, ' The Hydrogen Bond,' Freeman, London, 1960, p. 290.

[31] G. Felsenfeld, *Proc. Roy. Soc.*, 1956, **A236**, 506.

[32] J. A. Bertrand and A. R. Kalyanaraman, *Inorg. Chim. Acta*, 1971, **5**, 341.

[33] J. A. Bertrand, *Inorg. Chem.*, 1967, **6**, 495.

[34] Mazhar-Ul-Haque, C. N. Caughlan, F. A. Hart, and R. Van Nice, *Inorg. Chem.*, 1971, **10**, 115.

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