super-exchange.[42] If the orbitals used by the bridging oxygen atoms are pure p orbitals, the bond angle is expected to be 90° and the ground state is predicted to be a triplet (*i.e.*, $2J > 0$); if the orbitals are purely s, the ground state is predicted to be a singlet (*i.e.*, $2J < 0$). Hence, since an increased value of the bridging angle implies greater s character in the bridging orbitals, we would expect a decrease in $2J$ as the bridging angle is increased from 90°. For the three cases which have been studied in detail, this trend is observed.

Acknowledgments.—We are grateful to Dr. D. Y. Jeter for helpful discussions concerning the magnetic susceptibility data. This research was supported by the Materials Research Center of the University of North Carolina through Contract DAHC 15-67-C-0223 with the Advanced Research Projects Agency, and by the National Science Foundation through Grant No. GP-10300.

---

[42] J. B. Goodenough, "Magnetism and the Chemical Bond," Interscience, New York, N. Y., 1963, p 180 ff.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS,
VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE 37203

The Crystal and Molecular Structure of Tris(octamethylmethylenediphosphonic diamide)copper(II) Perchlorate[1a]

BY P. THOMAS MILLER,[1b] P. GALEN LENHERT,[1c] AND MELVIN D. JOESTEN*[1b]

Received January 27, 1972

Tris(octamethylmethylenediphosphonic diamide)copper(II) perchlorate, $Cu\{[(CH_3)_2N]_2P(O)CH_2P(O)[N(CH_3)_2]_2\}_3(ClO_4)_2$, crystallizes in the orthorhombic space group $Pna2_1$, with four molecules in the unit cell. The unit cell dimensions are a = 19.196 (4), b = 12.131 (2), and c = 22.868 (4) Å. Intensity data were collected with a four-circle computer-controlled diffractometer. Reflections were measured with the θ–2θ scan technique. All 62 nonhydrogen atoms were refined anisotropically and the 78 hydrogen atoms were included as fixed atoms. Refinement by full-matrix least squares using 6305 reflections gave a final R factor of 0.046. The CuO_6 group is a slightly distorted octahedron with each chelate ring in a boat conformation. The bend in one of the chelate rings is opposite that of the other two. Average bond distances and bond angles with rms deviations for the chelate rings are as follows: Cu–O, 2.085 Å (range 2.023–2.134 Å); P–O, 1.483 (5) Å; P–C(P), 1.798 (13) Å; O–Cu–O, 89.9 (12)°; Cu–O–P, 132.1 (14)°; O–P–C, 110.5 (6)°; P–C–P, 115.3 (15)°.

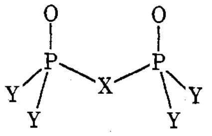
Introduction

During the past several years a number of six-coordinate Cu(II) complexes have been found to have higher symmetry than that allowed by the Jahn–Teller theorem. These include tris(octamethylpyrophosphoramide)copper(II) perchlorate, referred to as CuOMPA,[2] tris(ethylenediamine)copper(II) sulfate,[3] and potassium lead hexanitrocuprate(II).[4,5] The site symmetry of Cu(II) is 32 (D_3) in the first two and $m3$ (T_h) in the last one. Another example is $[Cu(H_2O)_6]SiF_6$ which crystallizes in space group $R\bar{3}$ with four molecules per unit cell. One of the cations is at a $\bar{3}$ (C_{3i}) symmetry site while the other three are at $\bar{1}$ (C_i) sites.[6]

CuOMPA was the first of a series of tris chelates of Cu(II) with organophosphorus bidentate ligands to be prepared in this laboratory. Members of this series (shown with their abbreviations in Table I) have similar physical and chemical properties.

The crystal structures of CuOMPA, previously reported,[2] and CuNIPA are isomorphous, based on a comparison of precession photographs.[7] This observation supports the conclusion that Cu(II) also has 32 (D_3) site symmetry in CuNIPA and has prompted us to investigate the structures of two additional systems, CuPCP and CuIPCP, which crystallize in lower symmetry space groups. The present report is a description of the structural results for CuPCP.

TABLE I
STRUCTURE OF LIGANDS



X	Y	Ligand	Abbreviation for tris chelate of $Cu(ClO_4)_2$	Ref
O	$N(CH_3)_2$	Octamethylpyrophosphoramide (OMPA)	CuOMPA	2
NCH_3	$N(CH_3)_2$	Nonamethylimidodiphosphoramide (NIPA)	CuNIPA	7, 8
CH_2	$N(CH_3)_2$	Octamethylmethylenediphosphonic diamide (PCP)	CuPCP	*a*
CH_2	$OCH(CH_3)_2$	Tetraisopropylmethylenediphosphonate (IPCP)	CuIPCP	7

[a] K. P. Lannert and M. D. Joesten, *Inorg. Chem.*, **8**, 1775 (1969).

Collection and Reduction of Data

Caution! Although the toxicity of PCP is not known, it should be handled with care because of its similarity to OMPA, a toxic anticholinesterase agent.

Crystals of CuPCP, $Cu\{[(CH_3)_2N]_2P(O)CH_2P(O)[N(CH_3)_2]_2\}_3(ClO_4)_2$, were obtained by evaporating an acetone solution of

---

(1) (a) Abstracted in part from the Ph.D. thesis of P. T. Miller, Vanderbilt University, Aug 1971. (b) Department of Chemistry. (c) Department of Physics.

(2) M. D. Joesten, M. S. Hussain, and P. G. Lenhert, *Inorg. Chem.*, **9**, 151 (1970).

(3) D. L. Cullen and E. C. Lingafelter, *ibid.*, **9**, 1858 (1970).

(4) N. W. Isaacs and C. H L Kennard, *J Chem Soc. A*, 386 (1969).

(5) D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, **10**, 1264 (1971).

(6) D. H. Templeton, S. Ray, and A. Zalkin, private communication.

(7) K. P. Lannert, Ph.D. Thesis, Vanderbilt University, 1969.

hydrated copper(II) perchlorate and ligand in a 1:4 mole ratio. Evaporation was carried out at room temperature in a desiccator since CuPCP is slightly hygroscopic. A number of transparent colorless crystals of CuPCP were selected from the original product synthesized and characterized by Lannert and Joesten.[8] The crystals deteriorated slowly in the presence of both atmospheric moisture and X-radiation. However, humidity control allowed the intensity data to be collected without special mounting procedures.

One large crystal of superior quality was cleaved across the needle axis to give a hexagonal prismatic section 0.81 × 0.59 × 0.69 mm along a^*, b^*, and c^*, respectively. It was mounted at the apex of the small faces on one end with the glass fiber parallel to a^* and to the ϕ axis of the diffractometer. The major faces parallel to the needle axis were (011), (01$\bar{1}$), (00$\bar{1}$), (0$\bar{1}\bar{1}$), and (001).

Precession photographs showed the crystals to be orthorhombic with $0kl$ reflections absent for $k + l$ odd, and $h0l$ reflections absent for h odd. The space group is therefore either $Pna2_1$ or $Pnam$[9] (an alternate setting of $Pnma$).

Accurate cell parameters were determined at 21° from 25 high-angle reflections ($2\theta > 80°$) centered manually on an accurately aligned four-circle diffractometer using the Cu Kα_1 line of the resolved doublet (λ 1.54051 Å) and a 1.0° X-ray tube takeoff angle. The six cell constants and three orientation parameters were obtained by least-squares refinement using 2θ, ω, and χ values as observations. All cell angles were constrained to 90° for the final refinement which gave a = 19.196 (4), b = 12.131 (2), and c = 22.868 (4) Å. The crystal density of 1.390 g/cm^3, measured by flotation in a mixture of 2-bromo-1-propane and 1-bromopentane, compares with the calculated value of 1.391 g/cm^3 based on four molecules per unit cell (volume 5325.1 Å^3) and a molecular weight of 1115.28. The centrosymmetric space group $Pnam$ with eight equivalent positions would have required the cation to possess either mirror or inversion symmetry, neither of which was expected. Consequently, the noncentrosymmetric space group $Pna2_1$, which imposed no symmetry on the cation, was chosen. This choice was later supported by a Karle–Hauptmann statistical treatment of the normalized structure factor magnitudes which clearly favored the noncentrosymmetric space group.[10,11]

Intensity data were collected with the four-circle computer-controlled Picker diffractometer (FACS-I system) using a Digital Equipment Corp. PDP-8/I with auxiliary disk memory. The computer programs, based on the FACS-I programs, were extensively modified and adapted for use with the disk memory in this laboratory.[12] The X-ray source was a standard-focus molybdenum tube set at a takeoff angle of 2.0° and operated at 50 kV (constant potential) and 12 mA. Both the source-to-crystal and crystal-to-detector distances were 23.5 cm and a 3.75 × 3.75 mm aperture defined the NaI detector opening. The pulse-height analyzer was set to a 95% window centered on the Mo Kα peak. Reflections were measured with the θ–2θ scan technique using a scan speed of 2°/min with 20-sec background measurements at each end point of the scan. Attenuation filters (constructed of one to five thicknesses of 0.0005-in. Ni foil) were automatically inserted in the diffracted beam when the count rate exceeded 8000 counts/sec.

Zr–Y–Al balanced filters[13,14] placed in the diffracted beam together with a 0.002-in. niobium incident-beam filter were used to collect reflections in the 2θ range 0–12°. In the 2θ range 12–55° a 0.001-in. niobium β filter was used without balanced filters. All reflections (except space group extinctions) out to the 55° limit in the hkl and $hk\bar{l}$ octants were measured once.

The scan range was given by $A + B \tan \theta$ where A is the base width and $B \tan \theta$ is the dispersion term. The balanced-filter data used A = 1.0 and B = 6.287, resulting in a scan from 0.5° below the filter band pass to 0.5° above it. Reflections above 12° in 2θ used A = 1.2 and B = 0.692.

During the course of data collection, three standard reflections were measured approximately every 2 hr to monitor X-ray source and detector stability. The intensity sum of each set was used to calculate the relative scale factor for the reflection measured between each set of standards. The three standards decreased slowly by about 20% during the course of data collection so the scaling also had the effect of correcting for crystal deterioration. A number of extra standards were measured every 400 reflections (approximately every 12 hr) to check for fluctuations remaining after the scaling procedure.

Data reduction included the usual background correction where, for a peak scan with I_p total counts, scan time t_p, and background counts B_1 and B_2, each measured for $t_p/2$ sec, the integrated intensity I was

$$I = I_p - (B_1 + B_2)(t_p/t_b)$$

I was taken as zero if the expression gave a negative value. The integrated intensities were multiplied by the usual Lorentz–polarization factor, the relative scale factors derived from the standard reflections, the attenuation-filter factors, and the X-ray absorption factor to obtain the F^2.

The absorption correction was calculated by numerical integration using the program ORABS.[15] The linear absorption coefficient calculated from mass absorption coefficients for Mo Kα[16] was 7.7131 cm^{-1}. The calculated absorption factors ranged from 0.646 to 0.746 with an average of 0.686. The crystal volume, also calculated by ORABS, was 0.227 mm^3.

The standard deviation for the integrated intensity, $\sigma(I)$, was considered to arise from two sources.[17] The first is the variance resulting from counting statistics, σ_c^2. The second, σ_x^2 (expressed in per cent) is that from all other sources which affect the value obtained by repeatedly measuring the same reflection (*e.g.*, short-term fluctuations in the X-ray source intensity). The combination gives $\sigma^2(I) = \sigma_c^2 + \sigma_x^2 I^2$ where

$$\sigma_c^2 = I_p + (B_1 + B_2)(t_p/t_b)^2$$

using the symbol definitions given above. σ_x^2 was obtained from the mean-square deviations of the extra standard reflections. The variance due to counting statistics, σ_c^2, was subtracted from the mean-square deviation for each extra standard, σ^2, and the difference, expressed as a per cent of I, was averaged over the different reflections to give σ_x^2, which for CuPCP was 1.0%.

The $\sigma(I)$ values were then converted to $\sigma(F^2)$ by multiplication with the same factors used to convert I. For all reflections, including those with $F^2 = 0$

$$\sigma(F) = -F + (F^2 + \sigma(F^2))^{1/2}$$

Finally, the 12,650 observations of the hkl and $hk\bar{l}$ reflections were averaged. $\sigma(F)$ for 6305 independent reflections was

$$\sigma(F) = [\sum \sigma_i^2(F)]^{1/2}(1/N)$$

where N individual measurements are averaged.

Solution and Refinement of the Structure

The CuPCP crystal structure was solved by the heavy-atom method using the Patterson function, F_o Fourier synthesis, and $F_o - F_c$ difference synthesis, with subsequent refinement of nonhydrogen atoms by full-matrix least squares.

A sharpened origin-removed Patterson function was calculated for CuPCP using preliminary data (2217 reflections with $8° < 2\theta < 38°$). All Cu–Cu peaks were identified and Fourier syntheses allowed the assignment of six phosphorus and six oxygen atoms (R = 0.39). Alternating least-squares and difference syntheses were used to locate the remainder of the 62 nonhydrogen atoms. Several additional full-matrix least-squares calculations were carried out using the full data set. Various blocks of up to 200 parameters were selected from the 558 heavy-atom parameters for each cycle and R was reduced to about 0.065.

---

[8] K. P. Lannert and M. D. Joesten, *Inorg. Chem.*, **7**, 2048 (1968).

[9] "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1962.

[10] H. Hauptmann and J. Karle, "Solution of the Phase Problem. I. The Centrosymmetric Crystal," ACA Monograph No. 3, Polycrystal Book Service, Pittsburgh, Pa., 1953, and references therein.

[11] C. Dickinson, J. M. Stewart, and J. R. Holden, *Acta Crystallogr.*, **21**, 663 (1966).

[12] Modifications by Douglas Henry and P. G. Lenhert. A program write-up is available from P. G. L.

[13] T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966, Chapter 10.

[14] P. K. Kirkpatrick, *Rev. Sci. Instrum.*, **10**, 186 (1939).

[15] D. J. Wehe, W. R. Busing, and H. A. Levy, "ORABS, a Fortran Program for Calculating Single Crystal Absorption Corrections," Oak Ridge National Laboratory Report ORNL-TM-229, Oak Ridge, Tenn., 1962.

[16] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

[17] T. J. Shaffner, Ph.D. Dissertation, Vanderbilt University, Nashville, Tenn., 1969.

Table II

Atomic Parameters for CuPCP[a]

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
CU	.09469(2)	.20050(3)	.25000	3.43(2)	3.07(2)	2.65(2)	.27(2)	.10(2)	-.05(2)
P(1)	.02792(6)	.22368(9)	.11769(5)	4.87(6)	4.28(6)	3.70(5)	.14(5)	.70(4)	.23(4)
P(2)	.14727(6)	.37234(10)	.14951(5)	4.73(6)	5.71(7)	3.45(5)	-.42(5)	-.05(5)	.78(5)
P(3)	.15144(6)	.26833(9)	.37979(5)	4.25(5)	4.35(5)	3.17(4)	-.02(4)	-.12(4)	-.54(4)
P(4)	-.00313(5)	.29046(8)	.35370(5)	4.19(5)	3.92(5)	2.94(4)	.39(4)	.28(4)	.02(4)
P(5)	.17488(5)	-.01172(9)	.19284(5)	3.62(5)	4.00(5)	4.54(5)	.04(4)	-.22(4)	-.68(4)
P(6)	.05375(6)	-.05935(8)	.27673(5)	4.20(5)	3.36(5)	4.45(5)	-.02(4)	-.24(4)	-.57(4)
O(1)	.02716(14)	.17433(22)	.17717(12)	5.03(15)	4.80(14)	4.60(14)	.37(12)	1.38(12)	1.57(12)
O(2)	.12850(15)	.34594(23)	.21068(11)	6.45(16)	5.10(15)	2.94(12)	.20(13)	.21(12)	.25(11)
O(3)	.16430(13)	.23054(20)	.31914(11)	4.34(13)	4.43(14)	3.50(12)	-.06(11)	.33(11)	-.34(10)
O(4)	.01864(13)	.28535(21)	.29154(10)	4.52(13)	4.56(14)	2.96(11)	.82(11)	.23(10)	.27(10)
O(5)	.16773(13)	.10706(20)	.20615(11)	4.20(13)	3.35(12)	5.01(14)	-.42(11)	-.25(11)	-.25(11)
O(6)	.06014(14)	.05850(22)	.29441(11)	5.01(15)	4.10(14)	4.99(15)	.37(12)	-.05(12)	-1.32(11)
N(10)	.0085(2)	.1388(3)	.0649(2)	6.51(23)	6.98(24)	6.08(22)	-.79(19)	1.49(19)	-1.80(19)
N(14)	-.0287(2)	.3230(3)	.1139(2)	5.90(20)	5.41(19)	4.08(17)	1.09(16)	-.35(15)	.62(15)
N(20)	.1139(2)	.4922(3)	.1303(2)	8.67(26)	4.42(19)	4.98(20)	-.80(18)	-.97(18)	.80(16)
N(24)	.2298(2)	.3822(5)	.1416(2)	4.68(21)	14.47(40)	6.88(26)	-.65(24)	.53(19)	2.66(26)
N(30)	.1642(2)	.3994(3)	.3873(2)	6.46(22)	4.91(19)	5.34(20)	-1.24(16)	.53(17)	-1.48(16)
N(34)	.2017(2)	.2037(3)	.4259(2)	4.80(19)	6.37(22)	5.54(20)	.72(17)	-1.35(16)	-.02(17)
N(40)	-.0203(2)	.4180(3)	.3696(2)	6.76(22)	3.94(17)	5.79(20)	1.33(16)	.95(17)	-.20(15)
N(44)	-.0738(2)	.2221(3)	.3704(2)	3.84(16)	5.77(20)	5.47(19)	.27(15)	.22(14)	1.39(16)
N(50)	.2384(2)	-.0607(3)	.2312(2)	4.54(17)	4.83(18)	7.11(23)	1.54(15)	-.86(16)	-.75(16)
N(54)	.1909(2)	-.0367(3)	.1247(2)	5.40(20)	6.35(21)	4.93(19)	-.74(17)	1.13(16)	-1.57(17)
N(60)	-.0285(2)	-.0908(3)	.2731(2)	4.39(17)	5.58(19)	5.39(19)	-.55(15)	.27(15)	-.29(16)
N(64)	.0875(2)	-.1452(3)	.3227(2)	8.03(24)	5.28(20)	5.14(19)	1.95(19)	-.49(19)	.01(17)
C(1)	.1139(2)	.2713(3)	.1000(2)	4.63(21)	4.82(22)	3.09(17)	.61(17)	.86(15)	.44(16)
C(3)	.0628(2)	.2357(3)	.4008(2)	4.55(20)	4.50(20)	3.02(16)	.37(17)	.03(16)	-.09(15)
C(5)	.0945(2)	-.0815(3)	.2060(2)	4.16(19)	4.09(20)	5.22(21)	.09(17)	.04(18)	-1.15(17)
C(11)	-.0627(3)	.0935(6)	.0644(3)	7.96(36)	12.05(48)	15.01(58)	-6.05(36)	3.15(39)	-5.84(45)
C(12)	.0489(4)	.0895(8)	.0223(4)	10.76(49)	17.72(70)	14.37(59)	-2.75(48)	3.58(45)	-10.97(54)
C(15)	-.0561(2)	.3784(4)	.1653(2)	5.48(24)	6.66(27)	5.03(24)	1.81(22)	-.44(20)	-.02(21)
C(16)	-.0511(3)	.3696(5)	.0579(2)	9.95(38)	8.49(36)	6.39(30)	2.65(32)	.45(29)	2.39(27)
C(21)	.1091(4)	.5770(4)	.1726(3)	16.24(57)	5.53(30)	8.58(40)	1.20(34)	-2.87(38)	-.71(28)
C(22)	.1067(5)	.5329(5)	.0719(3)	24.88(85)	7.21(38)	6.64(35)	.50(45)	-4.36(46)	2.12(30)
C(25)	.2764(3)	.3226(7)	.1793(5)	4.74(30)	14.19(56)	22.56(82)	-.01(35)	-1.26(43)	5.03(59)
C(26)	.2639(4)	.4264(17)	.0955(6)	4.70(39)	68.86(278)	23.11(107)	.00(88)	1.70(54)	25.17(155)
C(31)	.2021(3)	.4617(4)	.3440(3)	10.08(38)	4.16(23)	8.99(36)	-.72(25)	.58(30)	-.29(25)
C(32)	.1412(3)	.4629(5)	.4389(3)	10.50(42)	8.34(35)	7.40(33)	-1.68(32)	1.43(29)	-4.94(29)
C(35)	.1967(3)	.0850(5)	.4296(3)	9.92(41)	7.00(32)	10.16(40)	2.17(30)	-4.12(34)	.50(30)
C(36)	.2410(3)	.2535(6)	.4724(2)	8.16(35)	13.22(48)	5.31(26)	-1.79(34)	-2.07(26)	1.22(30)
C(41)	-.0067(3)	.5075(4)	.3288(3)	10.47(38)	4.38(23)	9.28(37)	-.01(25)	-1.42(32)	.08(25)
C(42)	-.0556(3)	.4473(5)	.4236(3)	10.28(42)	7.45(35)	9.43(39)	2.52(30)	2.46(33)	-3.97(30)
C(45)	-.1360(2)	.2473(5)	.3357(3)	4.40(25)	8.71(33)	9.73(39)	.83(24)	-.77(25)	2.33(30)
C(46)	-.0783(3)	.1206(4)	.4020(3)	5.02(26)	7.48(31)	9.13(35)	-1.03(23)	.48(24)	3.18(27)
C(51)	.2682(3)	-.0030(5)	.2799(3)	6.89(30)	8.05(34)	9.48(37)	1.96(26)	-4.01(28)	-1.33(29)
C(52)	.2746(3)	-.1643(5)	.2149(3)	6.51(30)	7.84(33)	11.82(44)	3.88(27)	-.89(29)	-1.19(31)
C(55)	.1592(4)	-.1188(6)	.0867(3)	11.99(48)	14.49(56)	7.89(38)	-4.25(43)	2.18(36)	-5.85(40)
C(56)	.2557(3)	.0088(5)	.0992(2)	6.53(29)	10.63(40)	6.26(29)	.55(29)	1.63(24)	-1.04(28)
C(61)	-.0774(2)	-.0168(5)	.2472(3)	4.65(24)	10.11(37)	8.71(34)	.22(23)	-.66(27)	1.49(36)
C(62)	-.0524(3)	-.2050(4)	.2727(3)	7.97(32)	7.08(31)	9.97(40)	-2.96(28)	.87(29)	.29(29)
C(65)	.1336(4)	-.2348(5)	.3104(3)	11.24(44)	6.99(35)	12.63(48)	1.87(33)	.41(41)	3.93(34)
C(66)	.0631(5)	-.1443(6)	.3823(3)	21.50(73)	9.36(42)	5.68(33)	3.80(46)	1.06(43)	1.21(31)
CL(1)	.19574(14)	.24391(18)	-.06845(8)	16.89(20)	11.19(14)	8.17(11)	1.80(14)	5.88(13)	2.75(11)
CL(2)	-.06176(9)	-.24800(13)	.08611(7)	9.45(10)	6.38(7)	6.93(8)	-.28(8)	-2.70(8)	-1.01(7)
O(10)	.1439(5)	.3064(6)	-.0463(3)	37.03(98)	19.85(62)	13.73(46)	20.58(68)	12.20(58)	8.32(44)
O(11)	.2564(8)	.2898(11)	-.0547(6)	41.14(153)	36.71(144)	35.35(156)	-19.64(129)	5.41(142)	-14.35(128)
O(12)	.2017(4)	.2351(8)	-.1248(3)	23.07(75)	37.26(102)	8.65(36)	6.74(70)	5.12(45)	1.99(52)
O(13)	.2014(4)	.1559(6)	-.0390(4)	23.01(72)	17.37(54)	33.06(96)	10.44(53)	17.58(71)	14.02(61)
O(15)	-.1203(3)	-.1885(5)	.0893(5)	11.03(40)	14.12(48)	40.60(115)	4.07(36)	-7.82(61)	-3.13(61)
O(16)	-.0161(3)	-.2122(6)	.1239(3)	13.34(40)	27.74(75)	12.28(41)	-3.25(44)	-5.09(35)	-7.07(44)
O(17)	-.0790(3)	-.3445(4)	.0897(6)	13.32(45)	6.57(29)	59.86(160)	-1.08(30)	2.54(74)	.81(63)
O(18)	-.0283(6)	-.2345(11)	.0399(3)	35.22(114)	50.76(165)	5.17(28)	-7.84(112)	1.91(50)	-1.67(60)

	x/a	y/b	z/c	B
H(11)	.1467	.2063	.1004	5.07
H(12)	.1200	.2972	.0613	5.07
H(31)	.0584	.1539	.4024	4.79
H(32)	.0617	.2667	.4356	4.79
H(51)	.1050	-.1500	.1997	5.08
H(52)	.0667	-.0528	.1825	5.08
H(111)	-.0967	.1565	.0599	13.57
H(112)	-.0683	.0433	.0295	13.57
H(113)	-.0722	.0531	.1006	13.57
H(121)	.0831	.0402	.0408	17.04
H(122)	.0174	.0465	-.0044	17.04
H(123)	.0727	.1486	-.0005	17.04
H(151)	-.0433	.4581	.1627	6.88
H(152)	-.1073	.3698	.1664	6.88
H(153)	-.0344	.3452	.2009	6.88
H(161)	-.1003	.3549	.0508	10.06
H(162)	-.0420	.4518	.0586	10.06
H(163)	-.0213	.3364	.0262	10.06
H(211)	.1496	.6285	.1669	12.32
H(212)	.0648	.6176	.1684	12.32
H(213)	.1124	.5429	.2124	12.32
H(221)	.0645	.5025	.0534	14.91
H(222)	.1029	.6155	.0730	14.91
H(223)	.1484	.5126	.0491	14.91
H(251)	.3038	.2656	.1550	16.72
H(252)	.3111	.3721	.1982	16.72
H(253)	.2503	.2807	.2099	16.72
H(261)	.2989	.4776	.1056	38.51
H(262)	.2896	.3575	.0743	38.51
H(263)	.2297	.4519	.0663	38.51
H(311)	.1696	.5189	.3265	8.88
H(312)	.2416	.4993	.3631	8.88
H(313)	.2181	.4113	.3128	8.88
H(321)	.1813	.5132	.4510	10.44
H(322)	.1007	.5107	.4283	10.44
H(323)	.1297	.4131	.4711	10.44
H(351)	.2443	.0523	.4290	10.41
H(352)	.1716	.0630	.4657	10.41
H(353)	.1700	.0585	.3943	10.41

	x/a	y/b	z/c	B
H(361)	.2123	.2520	.5096	10.94
H(362)	.2850	.2126	.4788	10.94
H(363)	.2508	.3317	.4619	10.94
H(411)	-.0428	.5652	.3318	9.63
H(412)	.0404	.5414	.3390	9.63
H(413)	-.0038	.4789	.2879	9.63
H(421)	-.0255	.5043	.4443	10.70
H(422)	-.1016	.4771	.4157	10.70
H(423)	-.0577	.3799	.4486	10.70
H(451)	-.1527	.1777	.3155	9.01
H(452)	-.1740	.2733	.3625	9.01
H(453)	-.1252	.3040	.3063	9.01
H(461)	-.1260	.1139	.4204	8.97
H(462)	-.0712	.0563	.3751	8.97
H(463)	-.0424	.1184	.4336	8.97
H(511)	.2758	-.0572	.3129	9.81
H(512)	.3155	.0272	.2684	9.81
H(513)	.2380	.0574	.2931	9.81
H(521)	.3256	-.1477	.2085	10.47
H(522)	.2704	-.2175	.2484	10.47
H(523)	.2539	-.1950	.1793	10.47
H(551)	.1657	-.0993	.0449	13.29
H(552)	.1782	-.1936	.0948	13.29
H(553)	.1066	-.1208	.0950	13.29
H(561)	.2921	-.0498	.0964	9.51
H(562)	.2461	.0398	.0595	9.51
H(563)	.2733	.0696	.1253	9.51
H(611)	-.0904	-.0435	.2072	9.92
H(612)	-.1205	-.0117	.2718	9.92
H(613)	-.0560	.0585	.2438	9.92
H(621)	-.1024	-.2082	.2817	10.21
H(622)	-.0416	-.2377	.2342	10.21
H(623)	-.0252	-.2455	.3041	10.21
H(651)	.1827	-.2129	.3205	11.92
H(652)	.1206	-.3019	.3330	11.92
H(653)	.1325	-.2535	.2671	11.92
H(661)	.0236	-.1972	.3868	15.49
H(662)	.1019	-.1649	.4087	15.49
H(663)	.0465	-.0679	.3917	15.49

[a] Fractional coordinates and thermal parameters are shown with standard deviations. An additional figure has been retained to avoid rounding errors in derived quantities and improve correspondence with the calculated structure factors. Isotropic B values are given in Å² and anisotropic temperature factors are in the form: $T = \exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}\cdot hla^*c^* + 2B_{23}klb^*c^*)]$.

Hydrogen atoms were located from difference maps with the aid of calculated positions based on the known geometry of the carbon atoms. A C–H distance of 1.0 Å and tetrahedral geometry were used for the three methylene groups. For methyl groups, the hydrogen atoms were assigned a C–C–H angle of 109.5° and a C–H distance of 1.00 Å and were assumed to lie on the circle traced out when the methyl group was rotated about the C–C bond. This procedure, suggested by Paton, Maslen, and Watson,[18] was programmed for the computer. A difference synthesis (with hydrogen atoms omitted from F_c) was stored in the computer and values of the electron density were interpolated at intervals along the locus of possible hydrogen positions. The points, spaced by 120°, which gave the maximum electron density values were chosen as the best hydrogen positions. Most of the 72 methyl hydrogen atoms were located with reasonable certainty although a few, especially those on C(26), are unreliable. The hydrogen atom temperature factors were taken as 1.2 times the isotropic equivalent of the methyl carbon temperature factor.

After further refinement of all heavy-atom parameters, hydrogen positions were determined as described above. At this point in the refinement ($R = 0.048$), it was noted that several intense reflections seemed to be affected by extinction, since F_o was significantly smaller than F_c. The extinction corrections, based upon a value of 0.1124×10^{-4} cm for r^* (Zachariasen's[19] extinction parameter), resulted in a maximum change (ΔF) of 23.7 and in changes of 0.5% or more for 32 reflections.

The final cycles of full-matrix least squares reduced the conventional R factor, $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, to 0.046 and the weighted R factor, $R' = \{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma wF_o^2\}^{1/2}$, to 0.035. This final set of data included reflections with $F_o = 0$ and allowed 11 observations for each of the 558 parameters refined. All 62 nonhydrogen atoms were refined anisotropically and the 78 hydrogen atoms were included as fixed atoms.

Atomic scattering factors for Cu(II), Cl, P, O, N, and C were those tabulated by Cromer and Mann.[20] The Cu(II), Cl, and P scattering factors were corrected for the real part of anomalous dispersion. Hydrogen scattering factors were those of Stewart, Davidson, and Simpson.[21]

Structure factor, electron density, bond distance–angle, and least-squares calculations were carried out with the X-Ray 67 programs.[22] The quantity minimized in the least-squares calculation was $\Sigma w(|F_o| - |F_c|)^2$ where the weights were

$$w = 0.8/\sigma^2(F)$$

and ranged from 0.14 to 4.17. The atomic parameters (calculated from the inverse matrix of the normal equations) and their standard deviations are displayed in Table II. The values shown were used (before rounding) in the calculation of the final structure factors.[23] The large thermal parameters for the perchlorate oxygen atoms and some of the terminal methyl groups on the CuPCP cation suggest local disorder. The average shift-to-error ratio for the final cycle was 0.17 but several perchlorate parameters had ratios as high as 1.1. The maximum ratio for the CuPCP cation was 0.71 for the x coordinate of N(60). A final difference synthesis using all 6305 reflections showed a maximum residual electron density of 0.30 e/Å^3 and a minimum of −0.32 e/Å^3, both in the vicinity of the disordered perchlorate anions. Residual densities of 0.25 e/Å^3 maximum and −0.27 e/Å^3 minimum were noted in the vicinity of N(24), near C(25) and C(26).

Magnitudes and directions of thermal ellipsoid principal axes (Table III) are included to permit comparison with published values for CuOMPA,[2] $Cu(en)_3SO_4$,[3] and $K_2PbCu(NO_2)_6$.[5]

TABLE III

THERMAL ELLIPSOID PRINCIPAL-AXIS MAGNITUDES (Å) AND DIRECTIONS FOR SELECTED ATOMS

	Axis	$\sqrt{u^2}$	Angle (deg) from		
			a	b	c
Cu	1	0.213	28	63	86
	2	0.194	65	149	73
	3	0.182	101	77	17
O(1)	1	0.298	57	58	49
	2	0.241	138	49	85
	3	0.189	67	58	139
O(2)	1	0.288	10	81	86
	2	0.254	99	11	85
	3	0.191	87	84	173
O(3)	1	0.242	57	138	67
	2	0.233	38	53	86
	3	0.205	106	74	23
O(4)	1	0.262	46	46	81
	2	0.217	135	45	89
	3	0.192	84	83	171
O(5)	1	0.252	74	86	164
	2	0.234	29	116	78
	3	0.199	66	26	80
O(6)	1	0.275	74	54	140
	2	0.251	18	92	72
	3	0.199	98	36	55

Description of the Structure

The orientation of the cations and anions in the unit cell is shown in Figure 1. The shortest copper–copper separation (9.673 Å) is between cations related by the a-glide operation. The next nearest copper neighbor is related by translation along b (12.131 Å). The spaces between a cation and its nearest neighbors (along the pseudotrigonal axis) are free of perchlorate anions, as are the spaces between next nearest neighbors.

TABLE IV

INTRAMOLECULAR BOND DISTANCES (Å) AND STANDARD DEVIATIONS FOR CuPCP[a]

Distances in Cation	
Cu–O(1)	2.134 (3)
Cu–O(2)	2.084 (3)
Cu–O(3)	2.102 (3)
Cu–O(4)	2.023 (2)
Cu–O(5)	2.063 (3)
Cu–O(6)	2.107 (3)
O(1)–P(1)	1.486 (3)
O(2)–P(2)	1.480 (3)
O(3)–P(3)	1.481 (3)
O(4)–P(4)	1.483 (3)
O(5)–P(5)	1.479 (3)
O(6)–P(6)	1.491 (3)
P(1)–C(1)	1.795 (4)
P(2)–C(1)	1.787 (4)
P(3)–C(3)	1.812 (4)
P(4)–C(3)	1.790 (4)
P(5)–C(5)	1.785 (4)
P(6)–C(5)	1.817 (5)
P(1)–N(10)	1.630 (4)
P(1)–N(14)	1.625 (4)
P(2)–N(20)	1.648 (4)
P(2)–N(24)	1.599 (4)
P(3)–N(30)	1.618 (4)
P(3)–N(34)	1.630 (4)
P(4)–N(40)	1.623 (4)
P(4)–N(44)	1.635 (4)
P(5)–N(50)	1.615 (4)
P(5)–N(54)	1.617 (5)
P(6)–N(60)	1.626 (4)
P(6)–N(64)	1.615 (4)
N(10)–C(11)	1.473 (7)
N(10)–C(12)	1.381 (10)
N(14)–C(15)	1.453 (6)
N(14)–C(16)	1.464 (7)
N(20)–C(21)	1.415 (7)
N(20)–C(22)	1.431 (8)
N(24)–C(25)	1.437 (10)
N(24)–C(26)	1.352 (15)
N(30)–C(31)	1.443 (7)
N(30)–C(32)	1.477 (8)
N(34)–C(35)	1.446 (7)
N(34)–C(36)	1.437 (7)
N(40)–C(41)	1.455 (7)
N(40)–C(42)	1.453 (8)
N(44)–C(45)	1.466 (6)
N(44)–C(46)	1.430 (7)
N(50)–C(51)	1.434 (8)
N(50)–C(52)	1.484 (7)
N(54)–C(55)	1.455 (8)
N(54)–C(56)	1.481 (7)
N(60)–C(61)	1.427 (7)
N(60)–C(62)	1.459 (6)
N(64)–C(65)	1.430 (8)
N(64)–C(66)	1.441 (8)
Distances in Anion	
Cl(1)–O(10)	1.35 (1)
Cl(1)–O(11)	1.33 (2)
Cl(1)–O(12)	1.30 (1)
Cl(1)–O(13)	1.27 (1)
Cl(2)–O(15)	1.34 (1)
Cl(2)–O(16)	1.31 (1)
Cl(2)–O(17)	1.22 (1)
Cl(2)–O(18)	1.25 (1)

[a] Several of the N–C distances and all of the Cl–O distances are affected by local disorder (see thermal parameters in Table II).

---

[18] M. G. Paton, E. N. Maslen, and K. J. Watson, *Acta Crystallogr.*, **22**, 120 (1967).

[19] W. H. Zachariasen, *Acta Crystallogr., Sect. A*, **24**, 212 (1968).

[20] D. T Cromer and J. B. Mann, *ibid.*, **24**, 321 (1968).

[21] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175(1965).

[22] J. M. Stewart, "X-Ray 67 Program System for X-Ray Crystallography for the Univac 1108, CDC 3600/6600, IBM 360/50, 65, 75, IBM 7094," Technical Report TR-67-58, Computer Science Center, University of Maryland,College Park, Md., 1967.

[23] A listing of structure factors will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society,1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2221. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

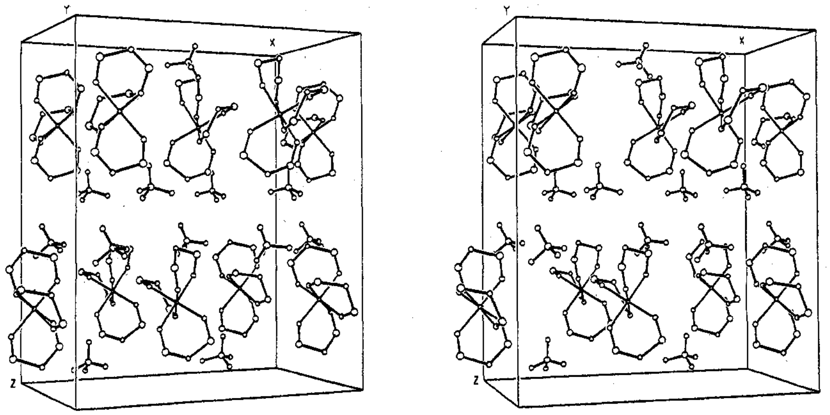


Figure 1.—Stereogram of unit cells showing the cations (with side groups omitted) and the perchlorate anions.

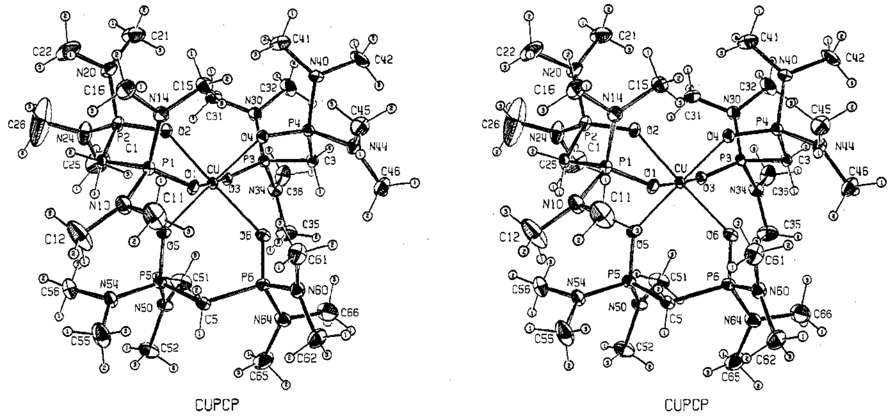


Figure 2.—Stereogram of cation. The thermal ellipsoids are shown at the 12% probability level.

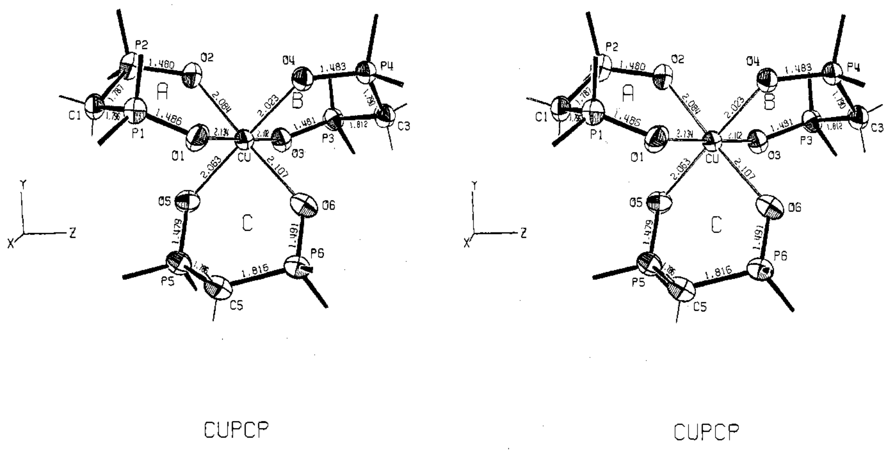


Figure 3.—Stereogram of chelate ring.

A number of intermolecular contact distances are smaller than the sum of van der Waals radii for the adjacent atoms. The perchlorate anions are near the methylene bridge atoms of the chelate ring and there are two contacts of the C–H···O type with H···O contacts of 2.50 Å. The cations are closely packed as indicated by the 26 methyl–methyl contacts (with 12 different cations) which are less than the sum of the van der Waals radii (4.0 Å for methyl groups). Of these, the six shortest are less than 3.6 Å and result from interactions between the cation and six different neighboring cations.

Bond distances and bond angles are shown in Tables IV and V; the stereogram, Figure 2, shows the thermal motion and the numbering scheme. The stereoscopic drawing of the chelate rings in Figure 3 illustrates two points about the geometry of the cation. First, the preferred conformation of each chelate ring is that of a slightly twisted boat with the bend in ring A opposite to that of rings B and C. Second, the Cu(II) is distorted from octahedral symmetry but the distortions are not large.

The degree of twist in the rings is shown by the least-squares plane calculations given in Table VI. The P_2O_2 combination is approximately planar and it makes dihedral angles of about 21° with the O–Cu–O plane and 44° with the P–C–P plane. This conformation is quite different from that in CuOMPA[2] where the Cu(II) is coplanar with the chelate rings. In the $(OMPA)_2$[24] complex, however, the O–P–O–P–O backbones are es-

---

[24] M. S. Hussain, M. D. Joesten, and P. G. Lenhert, *Inorg. Chem.*, **9**, 162 (1970).

TABLE V

INTRAMOLECULAR BOND ANGLES (DEG) AND STANDARD DEVIATIONS FOR CuPCP

Angles about the Metal Ion		Other Angles in Chelate Rings	
Type I[a]		Cu-O(1)-P(1)	130.4 (2)
O(1)-Cu-O(2)	88.8 (1)	Cu-O(2)-P(2)	131.8 (2)
O(3)-Cu-O(4)	91.0 (1)	Cu-O(3)-P(3)	130.7 (2)
O(5)-Cu-O(6)	89.9 (1)	Cu-O(4)-P(4)	132.4 (2)
		Cu-O(5)-P(5)	134.3 (2)
Type II[b]		Cu-O(6)-P(6)	132.8 (2)
O(1)-Cu-O(4)	90.2 (1)	O(1)-P(1)-C(1)	110.2 (2)
O(1)-Cu-O(6)	93.6 (1)	O(2)-P(2)-C(1)	111.3 (2)
O(2)-Cu-O(3)	88.8 (1)	O(3)-P(3)-C(3)	109.7 (2)
O(2)-Cu-O(5)	92.5 (1)	O(4)-P(4)-C(3)	111.2 (2)
O(3)-Cu-O(5)	91.7 (1)	O(5)-P(5)-C(5)	110.3 (2)
O(4)-Cu-O(6)	87.9 (1)	O(6)-P(6)-C(5)	110.4 (2)
Type III[c]		P(1)-C(1)-P(2)	114.1 (3)
O(1)-Cu-O(5)	87.2 (1)	P(3)-C(3)-P(4)	115.1 (3)
O(2)-Cu-O(4)	89.8 (1)	P(5)-C(5)-P(6)	116.9 (3)
O(3)-Cu-O(6)	88.8 (1)		
Other Angles in Cation			
O(1)-P(1)-N(10)	114.9 (2)	C(1)-P(1)-N(10)	104.3 (2)
O(1)-P(1)-N(14)	109.9 (2)	C(1)-P(1)-N(14)	111.4 (2)
O(2)-P(2)-N(20)	110.4 (2)	C(1)-P(2)-N(20)	107.3 (2)
O(2)-P(2)-N(24)	111.4 (2)	C(1)-P(2)-N(24)	109.6 (2)
O(3)-P(3)-N(30)	112.2 (2)	C(3)-P(3)-N(30)	109.2 (2)
O(3)-P(3)-N(34)	111.0 (2)	C(3)-P(3)-N(34)	106.2 (2)
O(4)-P(4)-N(40)	108.2 (2)	C(3)-P(4)-N(40)	111.3 (2)
O(4)-P(4)-N(44)	115.9 (2)	C(3)-P(4)-N(44)	104.9 (2)
O(5)-P(5)-N(50)	108.5 (2)	C(5)-P(5)-N(50)	112.7 (2)
O(5)-P(5)-N(54)	113.5 (2)	C(5)-P(5)-N(54)	103.8 (2)
O(6)-P(6)-N(60)	108.6 (2)	C(5)-P(6)-N(60)	109.8 (2)
O(6)-P(6)-N(64)	114.1 (2)	C(5)-P(6)-N(64)	108.1 (2)
N(10)-P(1)-N(14)	106.0 (2)	C(11)-N(10)-C(12)	110.7 (5)
N(20)-P(2)-N(24)	106.8 (2)	C(15)-N(14)-C(16)	115.0 (4)
N(30)-P(3)-N(34)	108.3 (2)	C(21)-N(20)-C(22)	112.4 (4)
N(40)-P(4)-N(44)	105.2 (2)	C(25)-N(24)-C(26)	111.5 (7)
N(50)-P(5)-N(54)	108.1 (2)	C(31)-N(30)-C(32)	115.2 (4)
N(60)-P(6)-N(64)	105.7 (2)	C(35)-N(34)-C(36)	114.2 (4)
P(1)-N(10)-C(11)	117.0 (4)	C(41)-N(40)-C(42)	116.5 (4)
P(1)-N(10)-C(12)	131.9 (5)	C(45)-N(44)-C(46)	113.8 (4)
P(1)-N(14)-C(15)	122.8 (4)	C(51)-N(50)-C(52)	114.9 (5)
P(1)-N(14)-C(16)	122.0 (4)	C(55)-N(54)-C(56)	111.8 (5)
P(2)-N(20)-C(21)	119.0 (4)	C(61)-N(60)-C(62)	112.8 (4)
P(2)-N(20)-C(22)	126.2 (4)	C(65)-N(64)-C(66)	113.1 (5)
P(2)-N(24)-C(25)	120.7 (5)	P(5)-N(50)-C(51)	122.9 (4)
P(2)-N(24)-C(26)	126.7 (6)	P(5)-N(50)-C(52)	121.9 (4)
P(3)-N(30)-C(31)	121.2 (4)	P(5)-N(54)-C(55)	128.6 (4)
P(3)-N(30)-C(32)	123.5 (4)	P(5)-N(54)-C(56)	118.0 (3)
P(3)-N(34)-C(35)	118.5 (4)	P(6)-N(60)-C(61)	120.8 (4)
P(3)-N(34)-C(36)	126.0 (4)	P(6)-N(60)-C(62)	121.9 (4)
P(4)-N(40)-C(41)	122.1 (4)	P(6)-N(64)-C(65)	127.6 (4)
P(4)-N(40)-C(42)	121.2 (4)	P(6)-N(64)-C(66)	118.7 (5)
P(4)-N(44)-C(45)	116.3 (4)		
P(4)-N(44)-C(46)	127.2 (4)		

[a] Between bonds of the same ligand. [b] Between bonds related by pseudo threefold axis. [c] Between bonds in different ligands.

TABLE VI

LEAST-SQUARES PLANES FOR CuPCP

Ring A		Ring B		Ring C	
Atom	Dev, Å	Atom	Dev, Å	Atom	Dev, Å
P$_2$O$_2$ Ligand Planes					
Cu[a]	+0.55	Cu[a]	−0.49	Cu[a]	−0.50
O(1)	+0.11	O(3)	−0.11	O(6)	−0.06
P(1)	−0.11	P(3)	+0.10	P(5)	+0.06
C(1)[a]	+0.69	C(3)[a]	−0.66	C(5)[a]	−0.63
P(2)	+0.11	P(4)	−0.10	P(6)	−0.06
O(2)	−0.11	O(4)	+0.11	O(6)	+0.06
Nitrogen Atom Deviation from (Å) the PC$_2$ Planes for the Dimethylamino Groups[b]					
N(10) (e)	0.056	N(30) (a)	0.019	N(50) (a)	0.043
N(14) (a)	0.040	N(34) (e)	0.098	N(53) (e)	0.109
N(20) (a)	0.134	N(40) (a)	0.038	N(60) (e)	0.185
N(24) (e)	0.088	N(44) (e)	0.141	N(64) (a)	0.063

[a] Omitted from calculations of the plane. [b] (a) axial nitrogen; (e) equatorial nitrogen.

sentially planar, with the Cu(II) out of the plane by 0.3 Å.

This difference in ring conformation is not surprising since the tetrahedral geometry of the bridging carbon atom in CuPCP requires a P–C–P angle of about 110° while the bridging oxygen atom in CuOMPA permits much larger angles (134°). The movement of the carbon bridge atom out of the P$_2$O$_2$ plane and the slight twist about the bridge bonds relieves the steric strain which would otherwise be present. The increase in the dihedral angle between the O–Cu–O plane and the P$_2$O$_2$ plane from 14° for the (OMPA)$_2$ complex to 21° in CuPCP appears to reflect the greater importance of intramolecular interactions in CuPCP.

One also observes that the slightly twisted boat conformation places the dimethylamino groups in either axial or equatorial positions. Although this relieves steric strain in the ring, it gives rise to interactions between the dimethylamino groups on adjacent ligands. These are minimized when the bridge atom of one chelate ring points in the opposite direction from the other two. In the observed conformation, rings A and B, A and C, and B and C show respectively 0, 1, and 4 methyl–methyl contacts less than 4.0 Å between ligands (Table VII). If all three bridge atoms pointed in the same direction, there would be several additional contacts between ligands.

TABLE VII

METHYL–METHYL INTRAMOLECULAR CONTACTS

Intraligand			Interligand		
Ring	Atoms	Distance, Å	Rings	Atoms	Distance, Å
A	C(12)–C(16)	3.99	A–C	C(12)–C(55)	3.61
	C(16)–C(22)	3.63	B–C	C(45)–C(61)	3.95
	C(15)–C(21)	3.98		C(46)–C(61)	3.91
	C(11)–C(16)	3.36[a]		C(66)–C(35)	3.93
	C(22)–C(26)	3.27[a]		C(51)–C(35)	3.84
	C(21)–C(26)	3.91			
B	C(32)–C(41)	3.83			
	C(42)–C(32)	3.80			
	C(31)–C(36)	3.94			
	C(42)–C(45)	3.51[a]			
	C(32)–C(36)	3.27			
C	C(62)–C(65)	3.69			
	C(62)–C(66)	3.43[a]			
	C(52)–C(55)	3.72			
	C(52)–C(56)	3.40[a]			
	C(52)–C(65)	3.58			
	C(51)–C(65)	3.88			

[a] Contacts between substituents on the same phosphorus atom.

All intramolecular methyl–methyl contacts (C–C distance less than 4.0 Å) are listed in Table VII). Five of these are *interligand* contacts but only one of these (C(12)–C(55)) is substantially less than the normal van der Waals distance. The six shortest *intraligand* contacts range from 3.51 to 3.27 Å. These are between methyl groups on the dimethylamino substituents attached to the same phosphorus atom. The two shortest intraligand contacts (C(32)–C(36) and C(22)–C(26)) involve atoms with the shortest intermolecular contacts (C(22), C(26), and C(36)).

There is a strong tendency for the nitrogen bonds to be trigonal. The nitrogen atoms deviate 0.085 Å on the average from the plane defined by the phosphorus and two carbon atoms of the PNC_2 groups. In both the $(OMPA)_2$ and $(OMPA)_3$ complexes of Cu(II)[2,24] the PNC_2 groups which are coplanar with the P–O (donor) bond are more nearly planar than the other PNC_2 groups. In CuPCP, this tendency, if present, is much less pronounced. Instead, there is a correlation between the planarity of the nitrogen bonds and the presence of the PNC_2 group in axial or equatorial positions (see Table VI). In every case except one (N(20) and N(24)), the axial PNC_2 groups are more nearly planar than the corresponding equatorial group involving the same phosphorus atom. On the average, the nitrogen atom deviates 0.056 Å from the PC_2 plane for axial and 0.113 Å for equatorial groups.

The average bond distances and mean deviations for CuPCP are as follows: phosphoryl P–O, 1.483 (5) Å; bridging P–C–(P), 1.798 (13) Å; P–N, 1.623 (12) Å; N–C, 1.443 (30) Å.[25] The P–O distance is nearly identical with the corresponding distance in CuOMPA[2] and the $(OMPA)_2$ complex;[24] the short distance has been accounted for in terms of multiple bonding.[26,27] The P–C–(P) bond distances are consistent with literature values of 1.83 Å for $P\text{–}CH_2$[28] and 1.80–1.83 Å for $P\text{–}CH_3$[29–31] single bonds. The P–N bond distances are comparable to values of 1.56–1.63 Å which have been reported for delocalized systems involving P–N linkages.[32] The accepted value for a P–N single bond is 1.77–1.78 Å.[33,34]

In CuPCP the Cu–O distances range from 2.023 to 2.134 Å and the O–Cu–O angles are in the range 87.2–93.6°. In CuOMPA[2] the Cu–O distances are equal (2.065 Å) and the angles about Cu(II) are in the range 88.4–90.6°. Thus, the symmetry of Cu(II) in CuPCP is definitely lower than that of Cu(II) in CuOMPA, although the distortion from octahedral symmetry is not large.

At present, it is not possible to say whether the distortions of CuPCP from octahedral geometry arise because of the Jahn–Teller effect or because of steric effects. It is conceivable that the several short intra- and intermolecular atomic distances, through the distortions they introduce, affect the Cu–O distances. The present work, however, provides additional evidence that tris chelates of Cu(II) possess either trigonal symmetry or approximate octahedral geometry.

Acknowledgments.—This research was supported by the Public Health Service (Grants GM-15451-03 and AM-09085), The Common Research Computer Facility of Houston, Texas (USPHS Grant FR00254), and Vanderbilt University. We thank Dr. G. A. Mair for reading a draft of this paper and making several useful suggestions.

[25] Several N–C distances are appreciably affected by the substantial "thermal" motion of the terminal methyl groups.

[26] D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

[27] D. P. Craig and N. L. Paddock, *ibid.*, 4118 (1962).

[28] G. R. Clark and C. J. Palenik, *Inorg. Chem.*, **9**, 2754 (1970).

[29] M. W. Doughill, *J. Chem. Soc.*, 5471 (1961).

[30] P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, **21**, 957 (1966).

[31] H. L. Carrell and J. Donahue, *Acta Crystallogr., Sect. B*, **24**, 699 (1968).

[32] A. J. Wagner and A. Vos, *ibid.*, **24**, 1423 (1962); and references therein.

[33] D. W. J. Cruickshank, *Acta Crystallogr.*, **17**, 671 (1964).

[34] L. N. Beard and P. G. Lenhert, *Acta Crystallogr., Sect. B*, **24**, 1529 (1968).

CONTRIBUTION FROM THE MOBIL RESEARCH AND DEVELOPMENT CORPORATION, RESEARCH DEPARTMENT,
PAULSBORO, NEW JERSEY 08066

The Crystal Structure of *catena*-Bis[μ-(*O,O'*-diisopropyldithiophosphato)-digold(I)](*Au–Au*), $\{[Au(i\text{-}C_3H_7O)_2PS_2]_2\}_n$, a Polymeric Complex Containing Weak Gold–Gold Interactions

BY STEPHEN L. LAWTON,* WAYNE J. ROHRBAUGH, AND GEORGE T. KOKOTAILO

Received January 11, 1972

The crystalline compound *catena*-bis[μ-(*O,O'*-diisopropyldithiophosphato)-digold(I)](*Au–Au*), $\{[Au(i\text{-}C_3H_7O)_2PS_2]_2\}_n$, forms yellow needles in the triclinic space group $P\bar{1}$ (C_i^1) with unit cell parameters $a = 12.495 \pm 0.004$, $b = 17.251 \pm 0.004$, $c = 12.167 \pm 0.004$ Å, $\alpha = 99.33 \pm 0.03°$, $\beta = 102.17 \pm 0.05°$, $\gamma = 72.79 \pm 0.02°$. The observed and calculated densities are 2.21 and 2.238 ± 0.002 g/cm^3 (for $Z = 4$ formula weights/unit cell), respectively. A full-matrix anisotropic–isotropic least-squares refinement has resulted in a discrepancy index of 0.062 using three-dimensional X-ray diffraction counter data. The crystal structure is comprised of two crystallographically independent dimers each of which contains one gold–gold bond bridged through sulfur by two bidentate $S_2P(OC_3H_7)_2$ ligands. These dimers are joined together through the metal atoms in a staggered arrangement to form linear chains of weak gold–gold bonds extending the full length of the crystal. The gold–gold separations along the chain *within* and *between* the $[Au(dtp)]_2$ dimers range from 2.914 (5) to 3.109 (6) Å, with the average, 3.04 Å, being equivalent to $c/4$. Each gold atom is therefore surrounded by four atoms, two of which are sulfur and two are gold, in a slightly distorted square-planar configuration. The Au–S bonds average 2.28 (rms, 0.03) Å in length, a value which is comparable with that in gold(III) sulfur-ligated complexes. This material has been found to be dimeric in benzene solution by vapor pressure osmometry.

Introduction

The development of oil-soluble compounds which will deposit soft metallic films on rubbing metal surfaces for the reduction of wear has long been an objective in lubricant science. Investigation of metal *O,O'*-dialkylphosphorodithioates in this laboratory has resulted in the finding that gold derivatives exhibit excellent lubrication performance in this regard. These