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Structure Studies of Pyrophosphate Chelate Rings. II. The Crystal Structure of Bis(perchlorato)bis(octamethylpyrophosphoramid)copper(II)

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The compound $\text{Cu}\{[(\text{CH}_3)_2\text{N}]_2\text{P}(\text{O})\text{OP}(\text{O})[\text{N}(\text{CH}_3)_2]_2\}_2(\text{ClO}_4)_2$ crystallizes in the monoclinic space group $\text{P}2_1/\text{c}$. The unit cell contains two formula units with $a = 10.797 \pm 0.001$, $b = 8.865 \pm 0.001$, $c = 20.047 \pm 0.001$ Å, and $\beta = 109.9 \pm 0.1^\circ$. All atoms (including hydrogen) were refined and the final R factor is 0.048 for 3306 observed reflections. The copper is octahedrally coordinated (crystallographic symmetry C_1) with equatorial Cu–O bond distances to the pyrophosphate chelate rings of 1.946 (1) and 1.936 (2) Å and axial Cu–O bond distances to two perchlorate oxygen atoms of 2.546 (3) Å. The chelate rings in this bis complex are more puckered than those reported for the corresponding tris complex, with Cu, P(1), and P(2) lying 0.30, 0.13, and -0.12 Å from the plane of the three oxygen atoms of the ligand. Although the chelate ring in the bis complex is more puckered, the P–O, P–O–(P), and P–N distances are the same as those in the tris complex. The structural results for the bis and tris complexes of OMPA are discussed in terms of a negligible amount of $\text{d}\pi\text{-p}\pi$ delocalization in the chelate ring.

Introduction

The previous paper in this series² described the (isomorphous) crystal structures of the tris chelates of octamethylpyrophosphoramid (OMPA) with Co(II), Mg(II), and Cu(II).

The structural analysis of $\text{Cu}(\text{OMPA})_2(\text{ClO}_4)_2$ was undertaken to investigate whether the planarity of the chelate rings in the tris chelates was a result of $\text{d}\pi\text{-p}\pi$ delocalization or the steric requirements of three ligands around Cu(II). Since delocalization has been proposed for β -ketoenolate chelate rings,³ we were interested in making a comparison between bis chelates of OMPA and β -ketoenolates.

Experimental Section

Preparation of the Complex.—The metal perchlorate, $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0045 mol), was dissolved in 15 ml of acetone and dehydrated with 2,2-dimethoxypropane (15 ml) by stirring for 1.5 hr. To the resulting solution 0.009 mol of freshly distilled OMPA⁴ was added dropwise with vigorous stirring. The stirring was continued for 20–30 min. Excess anhydrous ether was added (2–3 ml at a time with stirring) until a light blue crystalline precipitate formed. The mixture was filtered, washed several times with anhydrous ether under suction, and dried *in vacuo*. *Anal.* Calcd for $\text{CuC}_{16}\text{H}_{48}\text{N}_8\text{P}_4\text{O}_{14}\text{Cl}_2$: C, 23.03; H, 5.75; N, 13.43. Found:⁵ C, 23.43; H, 5.74; N, 13.40. Attempts to recrystallize the bis complex from acetone resulted in the formation of the tris complex. Therefore, it was necessary to choose a suitable crystal from freshly precipitated bis complex for X-ray structure analysis.

Crystal Data.—Preliminary precession photographs of $hk0$, $h0l$, $h1l$, and $h2l$ layers (taken with zirconium-filtered Mo $\text{K}\alpha$ radiation) indicated monoclinic symmetry. The systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ are consistent with the space group $\text{P}2_1/\text{c}$ (no. 14).

The cell dimensions were refined by the method of least squares from 2θ values for 14 high-angle reflections measured on a manual

Picker four-circle diffractometer, using a crystal of approximately $0.21 \times 0.21 \times 0.34$ mm size. The resolved Cu $\text{K}\alpha_1$ line was used (wavelength 1.54051 Å). The cell constants were found to be $a = 10.797 \pm 0.001$ Å, $b = 8.865 \pm 0.001$ Å, $c = 20.047 \pm 0.001$ Å, and $\beta = 109.9 \pm 0.1^\circ$.

The unit cell volume of 1804 Å³ with two formula units per unit cell gives a density of 1.539 g/cm³. This compares with an observed density, determined by flotation in a mixture of tetrachloroethane and 1,2,3-trichloropropane, of 1.532 g/cm³ (average of four determinations).

Collection and Reduction of Intensity Data.—These data were obtained from a crystal of approximate dimensions $0.2 \times 0.2 \times 0.25$ mm with a manual four-circle Picker diffractometer, the θ - 2θ scan method, and Mo $\text{K}\alpha$ radiation. The scan speed was $1^\circ/\text{min}$ and the takeoff angle was 2° . The intensities were measured with a scintillation counter with pulse height discriminator set at $\sim 100\%$. The crystal was mounted so that the b axis coincided with the ϕ axis of the instrument. A 0.001-in. Nb filter was used in the incident beam collimator for all reflections except those measured with the balanced filter technique. Some 15 strong reflections with $2\theta < 10^\circ$ were measured with the balanced filter method by using Zr and Y filters in the diffracted beam. The scan range for each reflection was calculated as described previously.² Stationary counter, stationary crystal background counts of 30–40 sec were taken at each end of the scan.

A standard reflection (304) was measured after each 18–20 reflection measurements. In addition, eight other preselected check reflections were measured once a day. Crystal alignment was checked daily, using the (020) and (200) reflections as reference. Both $hk0$ and $\bar{h}k0$ data, equivalent by the twofold symmetry of the monoclinic lattice, were measured to provide an internal check and an averaged value was used. A total of 3534 independent reflections out to $(\sin \theta)/\lambda = 0.62$ Å⁻¹ were measured with 3306 of these recorded as observed. A measurement was considered if the value of the measured intensity was greater than zero.

The diffractometer data were treated for background as in part I and a preliminary set of F^2 and $\sigma(F^2)$ were obtained. The standard deviation $\sigma(F^2)$ at this stage was from counting statistics alone.

Conventional Lorentz and polarization corrections were applied and the measurements were corrected for absorption by the crystal. The value of the absorption coefficient μ was calculated to be equal to 10.23 cm⁻¹ for Mo $\text{K}\alpha$ radiation (λ 0.7107 Å). For the absorption correction, the crystal shape was described by six planar faces appropriate to a rectangular parallelepiped of volume 0.015 mm³ and correction was made for each reflection

(1) (a) Department of Chemistry. (b) Department of Physics.

(2) Part I: M. D. Joesten, M. S. Hussain, and P. G. Lenhart, *Inorg. Chem.*, **9**, 151 (1970).(3) F. A. Cotton and J. S. Wood, *ibid.*, **3**, 245 (1964).(4) A 70% solution of OMPA obtained from K & K Laboratories, Inc., Plainview, N. Y., was purified by fractional vacuum distillation. The fraction distilling between 130 and 135° (0.2 mm) was used. *Caution!* This compound is highly toxic.

(5) Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

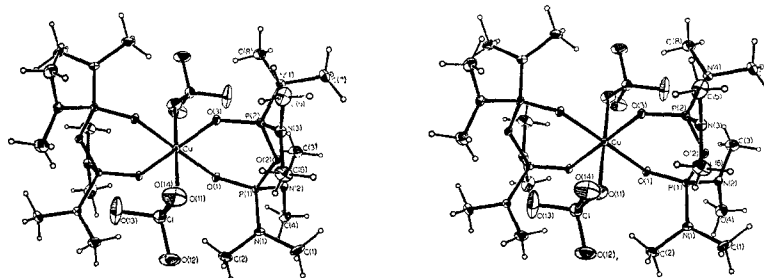


Figure 1.—Stereoscopic illustration of one molecule of $\text{Cu}(\text{OMPA})_2(\text{ClO}_4)_2$ viewed approximately along the c axis.

with the OR-ABS Fortran program of Wehe, Busing, and Levy.^{6a} The maximum and minimum calculated transmission factors were 0.87 and 0.82, respectively.

The effects on X-ray intensity due to counter and high-voltage instability and crystal misalignments were incorporated into the standard deviations of the measured F^2 . The method^{6b} made use of the check reflections that were monitored daily throughout the experiment and calibrated with respect to the (304) reflection. The standard deviation can be divided into two components

$$\sigma_t^2 = \bar{\sigma}_x^2 + \sigma_c^2$$

where σ_x represents the fluctuations in addition to counting statistics. In a perfectly stable system, σ_t should depend on the counting statistics alone. The values for σ_x were calculated for each set of the check reflections and were expressed on a per cent basis and then averaged. The averaged value $\bar{\sigma}_x$ was assumed constant for each intensity measurement.

Solution and Refinement of the Structure.—The atomic scattering factors used for Cu(II), Cl, P, C, N, and O were taken from ref 7. The Cu(II), P, and Cl factors were corrected for the real part of the anomalous dispersion using values of $\Delta f'$ given by Cromer.⁸ The hydrogen scattering factors were those of Stewart, *et al.*⁹ The calculations were performed with the crystal structure calculation system of Stewart¹⁰ on the IBM 7094 computer. In the least-squares refinements the function minimized was $\sum w(|F_o| - S|F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and weight w was estimated as $w = 1/\sigma^2(F_o)$. The agreement factor R is defined as $R = \sum ||F_o| - S|F_c|| / \sum |F_o|$ and weighted R is defined as $R_w = [\sum w(|F_o| - S|F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

In the space group $P2_1/c$ (no. 14) the two copper atoms occupy special positions $(0, 0, 0; 0, 1/2, 1/2)$ which are inversion centers. The asymmetric unit consists of half of the copper atom, one chelate, and one perchlorate group. Two phosphorus atoms were easily located in a three-dimensional Patterson function. Because of the location of a copper atom at the origin, the Patterson synthesis can be regarded as partly equivalent to a Fourier synthesis. From 15 large Patterson vectors representing tentative atomic locations, eight could be selected which satisfied known structural features of the complex. The conventional crystallographic R factor with these atoms included was 0.445. A difference Fourier synthesis phased with these eight atoms (copper, two phosphorus, three oxygen, and two nitrogen atoms) was computed which revealed atomic positions for all nonhydrogen atoms. Three cycles of full-matrix least-squares refinement¹⁰ in which scale factors, anisotropic temperature factors for

copper(II), and positional and isotropic thermal parameters for all other atoms were varied, reduced R to 0.102. Large discrepancies existed between F_o and F_c values for certain reflections. Some 34 of these intensities were remeasured. Of these, 19 reflections were corrected for scan time or intensity. The other 15 reflections had incorrect hkl values. Then with 3306 observed F 's and anisotropic temperature factors for all atoms, the R value dropped to 0.068 in two cycles of least-squares refinement. Because of the computer limitations the positional parameters and anisotropic thermal parameters had to be varied separately.

At this stage a three-dimensional difference synthesis, including all nonhydrogen atoms, was computed using low-angle reflection data ($(\sin \theta)/\lambda < 0.54 \text{ \AA}^{-1}$; 2265 reflections) to locate the hydrogen atoms. In this map the hydrogen atoms were the highest peaks with $0.25\text{--}0.45 \text{ e}^- \text{ \AA}^{-3}$. Hydrogen atoms were located by a procedure described by Paton, Maslen, and Watson.¹¹ The position of a given hydrogen atom is constrained to a circle described by the rotation of the tetrahedral methyl group about the N-C bond and C-H distance of 1.0 \AA . The electron density on a difference synthesis was evaluated along the constraining circle at 15° intervals in ϕ , the angle of rotation from the staggered position, for each of the eight methyl groups. The plot of the electron density as a function of ϕ for all methyl groups has three maxima approximately 120° apart. The three-electron density values at the points $\phi = \alpha, \alpha + 120^\circ$, and $\alpha + 240^\circ$ at 15° intervals in α were averaged. The plots of the averaged electron density as a function of ϕ has a period of 120° . The maximum was located graphically to give the desired rotation angle ϕ , from which the three hydrogen positions for each methyl group were calculated. These positions were refined by three cycles of least-squares refinement using low-angle reflection data.

For final stages of refinement the parameters were divided into two subgroups. Subgroup A contained the scale factor, the positional and anisotropic temperature factors for Cu(II), O(1), P(1), N(1), N(2), and C(1)–C(4), and positional and isotropic factors for hydrogen atoms bonded to C(1) through C(4). Subgroup B contained the corresponding parameters for P(2), O(2), O(3), Cl, O(11)–O(14), N(3), N(4), C(5)–C(8), and hydrogen atoms attached to C(5) through C(8). The total number of parameters refined per cycle (two runs) was 302. The final R at the conclusion of refinement was 0.048 and the weighted R was 0.035, both based on the observed reflections only. Coordinate shifts on the final cycle averaged 0.017 times the esd with a maximum shift of 0.131σ .

The tabulation of the observed and calculated structure factors is given in Table I. Fractional coordinates and temperature factors for all atoms are given in Tables II–IV.

Discussion

Figure 1 is a stereoscopic illustration of $\text{Cu}(\text{OMPA})_2(\text{ClO}_4)_2$ made with ORTEP.¹² The labeled small spheres represent hydrogen atoms.

(11) M. G. Paton, E. N. Maslen, and K. J. Watson, *Acta Cryst.*, **22**, 120 (1967).

(12) C. K. Johnson, "ORTEP, Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," Oak Ridge National Laboratory Report ORNL-3794 U.C.-4-Chemistry, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(6) (a) D. J. Wehe, W. R. Busing, and H. A. Levy, "OR-ABS: A Fortran Program for Calculating Single-Crystal Absorption Corrections," Oak Ridge National Laboratory Report ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962; (b) T. J. Shaffner, Ph.D. Thesis, Vanderbilt University, 1969.

(7) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 210–212.

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

(10) J. M. Stewart, "Crystal Structure Calculation System for the IBM 7090, 7094," Technical Report TR-64-6, Computer Science Center, University of Maryland, and Research Computer Laboratory, University of Washington.

TABLE I
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR (X10) Cu(OMPA)2(CIO4)2

Table with multiple columns of numerical data representing observed and calculated structure factors for various reflections. The table is organized into several sections, each with a header indicating the reflection indices (e.g., -13,0,1, 12, 67, 77, 73, 13, 54, -80, etc.).

TABLE I (Continued)

18	0	-1.6L	1	0.34L	5 314	306	5 993	957	1 628	619	9	32	-43	6 151	-147	18	-0	4	2 285	-304	5,9L	1	3 105	-122	8 558	544	6 28	-10

The anisotropic temperature factors for all of the heavy atoms were used to calculate the principal axes for the vibrational ellipsoids. The chelate atoms (OPO) generally have a maximum amplitude roughly along [100]. The root-mean-square amplitudes for the atoms of the chelate ring (Table V) are from 0.01 to 0.08 Å smaller than the amplitudes reported for chelate ring atoms in tris-OMPA chelates.² Among the oxygens of the perchlorate ion, the smallest vibrations are for O(11). This is the expected result since the perchlorate ion is coordinated to Cu(II) through O(11).

The average C-H distance is 0.97 Å with a minimum value of 0.83 Å and a maximum value of 1.14 Å. The

average H-C-H angle is 110° with a minimum value of 101° and a maximum value of 125°. The other intramolecular bond lengths and angles are listed in Tables VI and VII. It was found that all chemically equivalent bond lengths were equivalent to their mean to within three standard deviations. The angles are also equivalent to their mean to within three standard deviations except for the P-N(3)-C and O-Cu-O(11) angles. While the average of the P-N-C angles was close to that expected for a planar array, several angles showed significant deviations from the mean. The P=O, P-O, P-N, and N-C bond lengths are similar to those obtained for the tris complexes.² The mean equatorial Cu-O

TABLE II
 ANISOTROPIC TEMPERATURE FACTORS OF NONHYDROGEN ATOMS OF $\text{Cu}(\text{OMPA})_2\text{ClO}_4$

Atom	B_{11}^a	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2.50 (2)	1.90 (2)	2.29 (2)	-0.17 (1)	0.03 (1)	0.16 (1)
P(1)	2.49 (3)	2.23 (3)	2.14 (3)	0.03 (2)	0.47 (2)	0.31 (2)
P(2)	2.39 (2)	1.88 (2)	2.52 (2)	-0.10 (2)	0.59 (2)	0.15 (2)
Cl	4.01 (3)	5.07 (4)	4.69 (4)	0.29 (3)	1.80 (3)	-0.82 (3)
O(1)	2.99 (9)	1.87 (8)	2.56 (9)	-0.02 (7)	-0.27 (7)	0.23 (7)
O(2)	3.07 (7)	2.13 (7)	2.22 (7)	-0.51 (6)	0.12 (6)	0.15 (6)
O(3)	2.69 (7)	2.10 (7)	2.75 (7)	-0.37 (6)	-0.26 (6)	0.40 (6)
O(11)	6.55 (14)	10.03 (18)	6.52 (14)	3.62 (13)	3.90 (12)	0.95 (13)
O(12)	10.15 (20)	12.86 (24)	8.08 (18)	1.16 (18)	6.67 (17)	1.63 (17)
O(13)	5.84 (15)	19.35 (38)	12.62 (27)	-0.27 (19)	-1.97 (16)	-7.41 (27)
O(14)	15.59 (30)	5.09 (15)	13.99 (27)	1.28 (18)	8.20 (24)	0.72 (17)
N(1)	4.16 (13)	4.36 (14)	2.93 (12)	-0.28 (12)	1.57 (10)	0.65 (11)
N(2)	2.57 (12)	3.61 (13)	3.22 (13)	0.65 (10)	0.41 (10)	0.54 (11)
N(3)	3.95 (11)	2.13 (10)	4.22 (12)	0.20 (8)	1.31 (10)	-0.34 (9)
N(4)	3.12 (10)	3.92 (11)	3.00 (11)	-0.85 (9)	1.02 (8)	0.10 (9)
C(1)	9.75 (36)	6.71 (29)	2.58 (17)	-0.77 (26)	2.50 (20)	-0.51 (17)
C(2)	4.52 (22)	10.12 (39)	6.01 (31)	0.02 (25)	2.41 (23)	3.81 (29)
C(3)	4.42 (23)	7.71 (32)	6.96 (30)	1.90 (23)	3.12 (23)	1.22 (27)
C(4)	5.38 (28)	4.70 (21)	6.03 (26)	1.62 (10)	0.87 (22)	1.93 (20)
C(5)	8.58 (34)	2.69 (14)	7.69 (29)	1.67 (17)	0.45 (25)	-0.02 (17)
C(6)	8.97 (29)	5.47 (27)	8.40 (27)	-0.31 (23)	5.90 (25)	-2.30 (23)
C(7)	4.00 (18)	7.29 (25)	5.80 (21)	-2.37 (18)	1.56 (16)	-0.42 (19)
C(8)	7.24 (25)	7.89 (26)	4.34 (16)	-2.12 (23)	3.45 (17)	-1.50 (18)

^a B_{ij} values are in square ångströms and the expression is $\exp[-1/4(h^2a^*B_{11} + k^2b^*B_{22} + \dots + 2klb^*c^*B_{23})]$.

 TABLE III^a
 FRACTIONAL ATOMIC COORDINATES OF THE NONHYDROGEN
 ATOMS FOR $\text{Cu}(\text{OMPA})_2\text{ClO}_4$

	x	y	z
Cu	0	0	0
P(1)	0.23183 (6)	-0.01108 (7)	0.14860 (3)
P(2)	0.20065 (6)	0.26929 (7)	0.06669 (3)
Cl	-0.22991 (8)	0.17938 (10)	0.08653 (4)
O(1)	0.13636 (16)	-0.07840 (18)	0.08375 (8)
O(2)	0.26242 (15)	0.16043 (18)	0.13406 (8)
O(3)	0.09057 (15)	0.19190 (18)	0.01193 (8)
O(11)	-0.11727 (23)	0.11177 (30)	0.07923 (13)
O(12)	-0.23949 (27)	0.14436 (37)	0.15261 (14)
O(13)	-0.34159 (27)	0.12864 (45)	0.03252 (18)
O(14)	-0.22458 (34)	0.33618 (31)	0.08150 (18)
N(1)	0.17657 (22)	-0.01369 (26)	0.21327 (11)
N(2)	0.37952 (20)	-0.08025 (25)	0.17768 (11)
N(3)	0.17159 (21)	0.41784 (23)	0.10519 (12)
N(4)	0.31326 (20)	0.31375 (25)	0.03504 (11)
C(1)	0.24867 (37)	0.05695 (42)	0.28158 (15)
C(2)	0.05408 (32)	-0.09133 (47)	0.20892 (18)
C(3)	0.47259 (30)	-0.05408 (43)	0.13973 (19)
C(4)	0.40803 (31)	-0.21558 (37)	0.22237 (17)
C(5)	0.15023 (38)	0.56203 (36)	0.06801 (20)
C(6)	0.12121 (39)	0.41116 (41)	0.16452 (21)
C(7)	0.42883 (30)	0.40551 (41)	0.07551 (18)
C(8)	0.31357 (33)	0.26528 (44)	-0.03474 (16)

^a Numbers in parentheses here and in succeeding tables are the standard deviations in the least significant digits.

bond length (1.946 Å) is somewhat shorter than the corresponding bond length (2.065 Å) in the tris-OMPA complexes.

The coordination polyhedron about the copper is a distorted octahedron with equatorial Cu-O distances of 1.946 and 1.936 Å. The axial Cu-O distance is 2.546 Å. The O(1)-Cu-O(11) angle (89.4°) is close to the expected value of 90°, but the O(3)-Cu-O(11) angle is $85.3 \pm 0.1^\circ$. As shown in Figure 1, perchlorate oxygen [O(11)] is tilted in the direction of the

 TABLE IV
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC
 TEMPERATURE FACTORS OF THE HYDROGEN ATOMS FOR
 $\text{Cu}(\text{OMPA})_2(\text{ClO}_4)_2$

	x	y	z	$B, \text{Å}^2$
H(11) ^a	0.3409 (47)	0.0976 (55)	0.2825 (24)	12.3 (1.7)
H(12)	0.1992 (58)	0.1195 (74)	0.2903 (32)	7.1 (2.6)
H(13)	0.2717 (39)	-0.0225 (47)	0.3245 (23)	7.6 (1.2)
H(21)	0.0029 (65)	-0.0219 (73)	0.2195 (32)	8.2 (2.8)
H(22)	0.0099 (52)	-0.1050 (68)	0.1625 (30)	10.5 (2.3)
H(23)	0.0813 (38)	-0.1767 (49)	0.2466 (22)	7.8 (1.3)
H(31)	0.4761 (48)	-0.1537 (64)	0.1188 (27)	10.8 (2.0)
H(32)	0.4368 (62)	0.0154 (81)	0.1050 (37)	7.7 (2.7)
H(33)	0.5617 (60)	-0.0458 (69)	0.1768 (32)	12.6 (2.3)
H(41)	0.4906 (62)	-0.2062 (78)	0.2499 (36)	3.6 (2.6)
H(42)	0.3481 (43)	-0.2318 (54)	0.2490 (23)	7.2 (1.6)
H(43)	0.4058 (37)	-0.3131 (49)	0.1865 (21)	10.3 (1.2)
H(51)	0.1881 (46)	0.6434 (60)	0.0963 (24)	14.2 (1.7)
H(52)	0.1656 (41)	0.5539 (48)	0.0196 (24)	10.0 (1.6)
H(53)	0.0590 (46)	0.5822 (56)	0.0543 (25)	8.3 (1.9)
H(61)	0.0264 (49)	0.4637 (59)	0.1399 (27)	19.1 (2.0)
H(62)	0.1172 (34)	0.3159 (42)	0.1797 (18)	12.9 (1.1)
H(63)	0.1748 (45)	0.4801 (54)	0.1995 (25)	9.8 (1.6)
H(71)	0.4253 (41)	0.5007 (52)	0.0471 (23)	12.2 (1.5)
H(72)	0.4311 (38)	0.4457 (46)	0.1300 (23)	11.6 (1.3)
H(73)	0.4988 (42)	0.3427 (54)	0.0779 (24)	8.9 (1.8)
H(81)	0.2427 (36)	0.2121 (44)	-0.0554 (19)	5.2 (1.2)
H(82)	0.3038 (46)	0.3542 (60)	-0.0649 (26)	12.3 (1.9)
H(83)	0.3917 (43)	0.2139 (54)	-0.0327 (22)	11.9 (1.6)

^a The first number in parentheses corresponds to the carbon atom to which the hydrogen is attached.

 TABLE V
 MAGNITUDE OF THERMAL ELLIPSOIDS FOR THE CHELATE RING

Atom	Root-mean-square amplitude, Å		
	$(\mu_{11}^2)^{1/2}$	$(\mu_{22}^2)^{1/2}$	$(\mu_{33}^2)^{1/2}$
Cu	0.215	0.153	0.151
O(1)	0.243	0.159	0.147
P(1)	0.192	0.173	0.153
O(2)	0.229	0.160	0.154
P(2)	0.191	0.169	0.152
O(3)	0.244	0.156	0.152

TABLE VI
BOND DISTANCES^a

Atoms	Distances, Å	Atoms	Distances, Å	Nonbonding contacts	
				Atoms	Distances, Å
Cu-O(1)	1.946 (1)	N(1)-C(1)	1.466 (4)	O(1)-O(3)	2.753 (2)
Cu-O(3)	1.936 (2)	N(1)-C(2)	1.466 (4)	O(1)-O(3)*	2.736 (2)
		N(2)-C(3)	1.471 (5)	O(1)-O(11)	3.189 (3)
Cu-O(11)	2.546 (3)	N(2)-C(4)	1.466 (4)	O(1)-O(11)*	3.219 (3)
		N(3)-C(5)	1.458 (4)	O(3)-O(11)	3.069 (3)
P(1)-O(1)	1.482 (1)	N(3)-C(6)	1.469 (5)	P(1)-P(2)	2.934 (2)
		N(4)-C(7)	1.478 (4)	O(11)-O(12)	2.305 (4)
P(2)-O(3)	1.483 (1)	N(4)-C(8)	1.466 (4)	O(11)-O(13)	2.283 (4)
		Av N-C	1.467 (8)	O(11)-O(14)	2.310 (4)
P(1)-O(2)	1.604 (2)	Cl-O(11)	1.407 (3)	O(12)-O(13)	2.287 (4)
P(2)-O(2)	1.609 (2)	Cl-O(12)	1.399 (3)	O(12)-O(14)	2.261 (5)
P(1)-N(1)	1.602 (3)	Cl-O(13)	1.392 (3)	O(13)-O(14)	2.258 (5)
P(2)-N(4)	1.600 (3)	Cl-O(14)	1.396 (3)		
P(1)-N(2)	1.619 (2)	Av Cl-O	1.398 (4)		
P(2)-N(3)	1.611 (2)				
Av P-N	1.608 (3)				

^a Standard deviations are given in parentheses. Atoms marked with an asterisk are related to atoms of the same number by an inversion center.

TABLE VII
BOND ANGLES^a

Atoms	Angles, deg	Atoms	Angles, deg	Atoms	Angles, deg
O(1)-Cu-O(3)	90.3 (1)	P(1)-N(2)-C(3)	121.1 (2)	C(1)-N(1)-C(2)	115.9 (3)
O(1)-Cu-O(3)*	89.7 (1)	P(1)-N(2)-C(4)	120.4 (2)	C(3)-N(2)-C(4)	114.1 (3)
O(1)-Cu-O(11)	89.4 (1)	P(2)-N(3)-C(5)	119.6 (2)	C(5)-N(3)-C(6)	114.4 (3)
O(3)-Cu-O(11)	85.3 (1)	P(2)-N(3)-C(6)	122.8 (2)	C(7)-N(4)-C(8)	114.2 (3)
Cu-O(1)-P(1)	135.1 (1)	O(1)-P(1)-N(1)	111.5 (1)	O(11)-Cl-O(12)	110.5 (2)
Cu-O(3)-P(2)	137.8 (1)	O(3)-P(2)-N(4)	110.2 (1)	O(11)-Cl-O(13)	109.3 (2)
				O(11)-Cl-O(14)	111.0 (2)
O(1)-P(1)-O(2)	110.3 (1)	O(1)-P(1)-N(2)	117.9 (1)	O(12)-Cl-O(13)	110.0 (2)
O(3)-P(2)-O(2)	110.1 (1)	O(3)-P(2)-N(3)	119.7 (1)	O(12)-Cl-O(14)	107.9 (2)
P(1)-O(2)-P(2)	132.1 (1)	O(2)-P(1)-N(1)	108.5 (1)	O(13)-Cl-O(14)	108.2 (2)
		O(2)-P(2)-N(4)	109.2 (1)		
				Nonbonding	
P(1)-N(1)-C(1)	121.7 (2)			O(3)*-O(1)-O(3)	89.7 (1)
P(1)-N(1)-C(2)	122.4 (2)	O(2)-P(1)-N(2)	100.7 (1)	O(1)-O(3)-O(1)*	90.3 (1)
P(2)-N(4)-C(7)	122.0 (2)	O(2)-P(2)-N(3)	100.4 (1)	Cu-O(1)-O(3)	44.7 (1)
P(2)-N(4)-C(8)	123.8 (2)			Cu-O(3)-O(1)	45.0 (1)
		N(1)-P(1)-N(2)	107.1 (1)		
		N(3)-P(2)-N(4)	106.7 (1)		

^a Standard deviations are given in parentheses. Atoms marked with an asterisk are related to atoms of the same number by an inversion center.

Cu-O(3) bond. The Cu-O(11)-Cl angle of 149.5° indicates that the perchlorate tetrahedron is tilted about 30° from the Cu-O axis. As required by the special position of the copper atom in this space group, the metal atom lies at the center of symmetry of the six surrounding oxygen atoms.

The Cu-O(11) distance of 2.546 Å is perhaps 0.2-0.4 Å longer than the corresponding M-O bond length in other complexes¹³⁻¹⁶ with perchlorate ion as monodentate ligand and nickel or cobalt as the central metal atom. However, this distance is similar to the Cu-O(ClO₄) distance of 2.61 Å observed in the Cu(en)₂(ClO₄)₂ complex.¹⁷ This difference in degree of tetragonal distortion is as expected for Cu(II) complexes.

The dimensions of the perchlorate ion are all reasonable within experimental error and are a fair approximation to the tetrahedral ion expected in spite of rather large values for the temperature factors. The O(11) atom is positioned more precisely than any other atom of the perchlorate. The mean value of 1.398 Å for Cl-O distances in the perchlorate ion is shorter than the normal bond length of 1.43 Å for a regular tetrahedral perchlorate ion.¹⁸ Judging from the temperature parameters, the Cl-O distances observed may be too short because of the large amplitude vibrations of the atoms.

Results of the least-squares plane calculations are given in Table VIII. The pyrophosphate chelate ring is more puckered in the bis complex than in the tris complex of OMPA.² The data in Table VIII can be used to illustrate the degree of puckering. The first plane was defined by the three oxygen atoms of the

chelate ring so that a direct comparison could be made with the results for the tris complex. The Cu(II) ion and P(1) atom are 0.296 and 0.135 Å below the plane defined by the three oxygen atoms while P(2) is 0.123 Å above the plane. In the tris chelate of OMPA the Cu(II) ion and three oxygen atoms lie in the plane with P(1) 0.056 Å above and P(2) 0.056 Å below the plane.

The dihedral angle between OMO and OPOPO planes is 166.4°. This angle is similar to that found for chelate rings of some of the metal complexes with β-ketoenolates where the OCCCO portion of the ring is planar or almost planar but the OMO plane is often canted to the mean plane of the ligand atoms. All of the six-coordinate monomeric or polymeric complexes of β-ketoenolates have similar dihedral angles between

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TABLE VIII
 LEAST-SQUARES PLANE CALCULATIONS^{a, b}

	Atom	Dev, Å
A. Chelate Ring		
1. $q_1 = 0.8782$ $q_2 = -0.2345$ $q_3 = -0.6911$ $D = 0.2936$	*Cu ²⁺	-0.296
	O(1)	0.000
	*P(1)	-0.135
	O(2)	0.000
	*P(2)	0.123
2. $q_1 = 0.8781$ $q_2 = -0.2743$ $q_3 = -0.6679$ $D = 0.2946$	O(3)	0.000
	*Cu ²⁺	-0.295
	O(1)	0.065
	P(1)	-0.063
	O(2)	0.004
	P(2)	0.057
	O(3)	-0.063
B. N(1) Dimethylamino Group		
$q_1 = -0.4178$	P(1)	-0.004
$q_2 = 0.8483$	N(1)	0.013
$q_3 = -0.1634$	C(1)	-0.004
$D = -1.6110$	C(2)	-0.004
C. N(2) Dimethylamino Group		
$q_1 = 0.1413$	P(1)	-0.046
$q_2 = 0.6694$	N(2)	0.141
$q_3 = 0.6375$	C(3)	-0.047
$D = 2.2340$	C(4)	-0.047
D. N(3) Dimethylamino Group		
$q_1 = 0.8133$	P(2)	-0.038
$q_2 = 0.1677$	N(3)	0.118
$q_3 = 0.2467$	C(5)	-0.039
$D = 2.5292$	C(6)	-0.040
E. N(4) Dimethylamino Group		
$q_1 = -0.3886$	P(2)	-0.003
$q_2 = 0.8283$	N(4)	0.008
$q_3 = -0.2471$	C(7)	-0.003
$D = 0.8086$	C(8)	-0.003

^a Atoms marked with asterisks were not included in the calculation of the plane. ^b The equation of the plane is $q_1X + q_2Y + q_3Z = D$ where X , Y , and Z are in ångströms and refer to the crystallographic axes. The last term is the plane-to-origin distance in ångströms.

158 and 172°.^{19,20} In four-coordinate planar complexes of β -ketoenolates such as Cu(acac)₂²¹ or Ni(DPM)₂²² the metal atoms lie in the plane of the ligand atoms. This is similar to the planarity of the entire chelate ring in the tris-OMPA complexes.²

The arrangement and planarity of the dimethylamino groups is of special interest in view of the average P-N bond length of 1.608 Å. The two dimethylamino groups on a particular phosphorus atom are staggered with respect to each other, thus avoiding any non-bonding interactions. The planarity of these groups was checked by defining a least-squares plane with PNCC atoms of a particular group. The results are given in Table VIII. The groups with N(1) and N(4) are much closer to planarity (0.011-0.017 Å) than the

N(3) and N(2) groups (0.158-0.188 Å). The P-N-C and O-P-N angles involving N(1) and N(4) atoms are identical (Table VII), whereas those involving N(2) and N(3) atoms are identical with each other but differ from the first pair of atoms. The groups attached to N(1) and N(4) are much closer to planarity than the corresponding groups in the tris-OMPA complexes. In fact, these groups are more planar than the dimethylamino groups in P₄N₄[N(CH₃)₂]₈²³ and P₆N₆[N(CH₃)₂]₁₂.²⁴ However, the P-N distance in the bis-OMPA complex is the same (within experimental error) as the P-N distances in the tris-OMPA complexes.

Nordman and coworkers have reported a similar observation of the coplanarity of dimethylamino groups attached to phosphorus in (CH₃)₂NPF₂B₄H₈²⁵ and (CH₃)₂NPF₂.²⁶ The P-N bond lengths in these two compounds are 1.593 (6) and 1.628 (5) Å, respectively. The first of these agrees within experimental error with the P-N bond lengths determined in the present work. Thus additional evidence is provided for the tendency of dimethylamino groups to be planar when the P-N bond length is near 1.60 Å.

Conclusions

It is difficult to account for the pucker in the chelate ring of Cu(OMPA)₂(ClO₄)₂. Consider that (1) bond distances and angles are similar in the bis and tris complexes of OMPA, (2) the P=O bond distances of 1.48 Å and the P-N distance of 1.61 Å are indicative of p π -d π bonding in these bonds and would be expected to change as the chelate ring becomes puckered, and (3) all intermolecular contacts in both bis and tris complexes are greater than the normal van der Waals distance.

Although the conformation of the bis-OMPA chelate ring is similar to that reported for β -ketoenolates,³ there is no evidence for either full or partial delocalization of electron density in the OPOPO chelate ring. This conclusion is indicated by the lack of change in the length of the P=O, P-O-(P), and P-N bonds and the slight change in the Cu-O bond length in going from the tris chelate to the bis chelate. One would expect such a change since electronic delocalization would be less efficient in the puckered ring.

Although no special steric crowding is indicated, the tetragonal distortion of the bis chelate is considerable with a difference of 0.6 Å between the axial and equatorial Cu-O distances. Thus, the chelate rings in the bis complex may have more flexibility to assume a puckered conformation.

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