

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS,
VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE 37203**Structure Studies of Pyrophosphate Chelate Rings. I. The Crystal Structures of Tris-Octamethylpyrophosphoramidate Complexes of Cobalt(II), Magnesium(II), and Copper(II) Perchlorates¹**BY MELVIN D. JOESTEN,^{2a} M. SAKHAWAT HUSSAIN,^{2a} AND P. GALEN LENHERT^{2b}

Received March 20, 1969

The crystal structures of tris(octamethylpyrophosphoramidate)metal(II) perchlorates $M\{[(CH_3)_2N]_2P(O)OP(O)[N(CH_3)_2]_2\}_3 \cdot (ClO_4)_2$, where M is Co, Mg, and Cu, have been determined by single-crystal X-ray diffraction analysis. All three compounds crystallize in the trigonal space group $P\bar{3}c1$ with two formula units per unit cell. The cell constants are: $a = 12.858$ (1) Å, $c = 18.267$ (2) Å, $D_m = 1.416$ g/cm³, $D_{\text{calcd}} = 1.417$ g/cm³ for Co(II); $a = 12.849$ (a) Å, $c = 18.285$ (2) Å, $D_m = 1.372$ g/cm³, $D_{\text{calcd}} = 1.374$ g/cm³ for Mg(II); and $a = 12.855$ (1) Å, $c = 18.260$ (3) Å, $D_m = 1.421$ g/cm³, $D_{\text{calcd}} = 1.425$ g/cm³ for Cu(II). Hydrogen atoms were located and included in the refinement. The final R factors for reflections having $F \geq 2\sigma_F$ are 0.059 and 0.056 for the complexes of Co(II) and Mg(II), respectively. The final R factor for 1993 observed reflections for the Cu(II) complex is 0.048. Bond distances and angles are in close agreement for all three structures. The M–O distances are 2.085 (3), 2.061 (2), and 2.065 (2) Å for Co(II), Mg(II), and Cu(II), respectively. Two observations are of special significance. (1) The site symmetry of the metal ions is D_3 . This symmetry should be unstable in the case of Cu(II) according to the Jahn–Teller theorem. (2) The chelate rings are planar (within 0.06 Å) in all three cases. The geometry of Cu(II) is closest to octahedral with an O–Cu–O chelate angle of 88.4° and other O–Cu–O angles of 90.5 and 90.6°. Since the Mg(II) chelate rings are as close to planarity as those of Co(II) and Cu(II), the planarity cannot be attributed to $d\pi$ – $d\pi$ delocalization in the chelate ring.

Introduction

The synthesis and characterization of complexes of octamethylpyrophosphoramidate (OMPA) with over 30 metal ions have been reported previously.³ Infrared data for these complexes supported the presence of a chelate ring structure in which the metal ions are coordinated to the phosphoryl oxygen atoms of OMPA.

We undertook the X-ray structure analysis of several OMPA complexes to obtain information about the orientation of the pyrophosphate linkage with respect to the metal ions. Such structural information may aid in understanding the role of metal ions in biological phosphorylation reactions of adenosine phosphates.

The present paper is a discussion of the tris-octamethylpyrophosphoramidate (OMPA) complexes of the formula $M\{[(CH_3)_2N]_2P(O)OP(O)[N(CH_3)_2]_2\}_3 \cdot (ClO_4)_2$, where M is Co(II), Mg(II), and Cu(II). These compounds will be referred to as CoOMPA, MgOMPA, and CuOMPA, respectively.

Collection and Reduction of Data

Crystals of all three compounds were grown from acetone solution by slow evaporation at room temperature. *Complexes of OMPA are toxic anticholinesterase agents so skin contact should be avoided.* Both CoOMPA and MgOMPA crystallized as needles with a hexagonal prismatic shape. CuOMPA crystallized in the form of hexagonal platelets. The structure of CoOMPA was studied first. Since the same method was used to collect the data for all three compounds, a detailed description will be given only for CoOMPA.

(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. Preliminary communication: *J. Am. Chem. Soc.*, **90**, 5623 (1968).

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

(3) M. D. Joesten, *Inorg. Chem.*, **6**, 1598 (1967), and references cited therein.

Preliminary precession photographs of the $h\bar{k}0$, $h\bar{k}1$, $h\bar{k}2$, $h0l$ levels of CoOMPA were taken. The upper level photographs exhibited threefold symmetry. The systematic absence of $h\bar{h}0l$ when l is odd indicated the space group was either $P\bar{3}c1$ or $P3c1$. The precession photographs for MgOMPA and CuOMPA could be superimposed on those for CoOMPA, indicating all three structures are isomorphous.

The cell parameters were refined by the method of least squares⁴ from 2θ values for 16 high-angle reflections measured with a Picker four-circle diffractometer using Cu $K\alpha$ radiation (1.54051 Å). These measurements were made at room temperature (25°) using a takeoff angle of 2°. The central maximum of the profile of each peak was determined by carefully adjusting χ , ω , and 2θ with the diffracted beam aperture only slightly open. The negative and positive 2θ values for some of the selected high-angle reflections were measured and used in the least-squares refinement. Densities were measured in mixtures of 1,2,3-trichloropropane and 1,3-dibromopropane. Table I lists the crystal data for all three complexes.

Intensity data were collected with the four-circle diffractometer by the 2θ -scan technique. Molybdenum $K\alpha$ radiation was used. An NaI scintillation detector and a pulse height discriminator set to include essentially 90% of the Mo $K\alpha$ radiation were used. The crystals were mounted with the long dimension (c) parallel to the ϕ axis on the four-circle diffractometer. The scan speed was 1°/min and the takeoff angle was 2°.

The 2θ settings for background were calculated from the equation $2\theta_{\mp} = 2 \arcsin(\lambda_{\mp} \sin \theta_0 / \lambda_0) + C_{\mp}$ with C_{\mp} empir-

(4) W. R. Busing and H. A. Levy, Oak Ridge National Laboratory Report No. ORNL-TM-271, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

TABLE I
 CRYSTAL DATA AT 25°

Cell dimensions	CoOMPA ^a	MgOMPA ^a	CuOMPA ^a
<i>a</i> , Å	12.858 ± 0.001	12.849 ± 0.001	12.855 ± 0.001
<i>c</i> , Å	18.267 ± 0.002	18.285 ± 0.002	18.260 ± 0.003
Cell vol, Å ³	2616	2614	2613
Formula weight	1116.6	1082.0	1121.3
<i>Z</i>	2	2	2
<i>D_m</i> , g/cm ³	1.416	1.372	1.421
<i>D_{calcd}</i> , g/cm ³	1.417	1.374	1.425
<i>F</i> (000)	1174	1144	1178
Abs coeff (Mo Kα), cm ⁻¹	6.94	3.94	7.85

^a Formula is M(C₈H₂₄O₈N₄P₂)₃(ClO₄)₂, where M is Co, Mg, or Cu.

ically determined from a careful examination of several intensity profiles. In the equation $\lambda_0 = 0.7107 \text{ \AA}$, $\lambda_+ = 0.7177 \text{ \AA}$, $\lambda_- = 0.7037 \text{ \AA}$. The values of C_{\mp} are -0.50 and 0.70° for CoOMPA, -0.45 and 0.45° for MgOMPA, and -0.50 and 0.70° for CuOMPA. Stationary background counts were measured at the end points of the 2θ scan. The length of background count varied from 25 to 40 sec in different 2θ ranges.

A reference reflection was recorded after every hour (about 17 reflections) as a check on the stability of the crystal and the instrument. The alignment of the crystal was checked daily. In addition to the reference or main standard reflection several check reflections were measured once a day. Both $hk0$ and $kh0$ reflections were measured but an averaged value was used for calculations.

Preliminary values of F^2 and $\sigma_e(F^2)$ were obtained from the diffractometer data using the data reduction equation $I = N - (B_1 + B_2)T/2T_B$, where I is the integrated intensity, N is the count recorded in scanning the reflection, T is the time for the scan in seconds, B_1 and B_2 are the background counts recorded at the high and low ends of the scan, and T_B is the time for one background count in seconds. Conventional Lorentz and polarization corrections were then applied.

Since the CoOMPA crystal was small with a hexagonal shape, the absorption correction was estimated to be less than $\pm 5\%$ in F^2 . Therefore, no absorption correction was made. This estimate was verified later by an absorption correction calculation based on 545 selected reflections. The maximum change in transmission factors was only 2%. Absorption corrections were made for MgOMPA and CuOMPA by the method of Busing and Levy.⁵

The standard deviation, $\sigma_e(F^2)$, was determined from counting statistics, including a term for detector and X-ray source fluctuations. The fluctuation term was determined from an analysis of the extra standards. The resulting values were 0.9, 0.5, and 1.4% for CoOMPA, MgOMPA, and CuOMPA, respectively. The standard deviation was divided into two components $\sigma_t^2 = \sigma_x^2 + \sigma_e^2$, where σ_x represents the fluctuation in addition to counting statistics. In a perfectly stable system σ_t should depend upon only the counting

statistics. Each σ_x was expressed on a percentage basis and then averaged to obtain $\bar{\sigma}_x$ which was assumed to be constant for each intensity measurement. This procedure⁶ allowed the effects of X-ray fluctuations and slight crystal misalignment to be incorporated into the standard deviations of the measured F^2 . The final structure factor F and corresponding standard deviation $\sigma(F)$ were calculated from F^2 and $\sigma_e(F^2)$ values obtained from preliminary data reduction.

Experimental Section

CoOMPA.—The crystal used for intensity measurements was cut from a larger one to a size $0.25 \times 0.25 \times 0.5$ mm with the long axis of the crystal parallel to the c axis. The volume of the crystal was 0.0195 mm^3 . The standard reflection was (212) and three other reflections were used as extra standards. A total of 1799 reflections out to $(\sin \theta)/\lambda = 0.62 \text{ \AA}^{-1}$ were measured with 1659 of these recorded as observed and 1314 having $F_o \geq 2\sigma$. A measurement was considered as observed if the value of the measured intensity was greater than zero. A 0.001-in. Nb incident beam filter was used for reflections with $2\theta > 10^\circ$. Balanced filter technique with Zr and Y filters in the diffracted beam were used for reflections with 2θ less than 10° .

MgOMPA.—Two crystals were used. The long dimension of both crystals is parallel to the c axis. The large crystal with maximum dimensions of $0.4 \times 0.4 \times 0.6$ mm and a volume of 0.0663 mm^3 was used for $10^\circ < 2\theta < 58^\circ$. The small crystal with maximum dimensions of $0.12 \times 0.15 \times 0.30$ mm and a volume of 0.0032 mm^3 was used for reflections with $2\theta < 10^\circ$ and for all reflections with a count rate of greater than 10,000 cps on the large crystal.

A balanced filter pair of Y and Zr was used for reflections measured with the small crystal. A 0.001-in. Nb incident beam filter was used for reflections with $2\theta > 10^\circ$. The standard reflection was (143) with seven additional reflections as extra standards. Intensity data for 2338 reflections out to $(\sin \theta)/\lambda = 0.68 \text{ \AA}^{-1}$ were collected with 2138 of these recorded as observed and 1669 having $F_o \geq 2\sigma$.

CuOMPA.—For CuOMPA, a crystal with maximum dimensions of $0.5 \times 0.5 \times 0.6$ mm and a volume of 0.1631 mm^3 was chosen for intensity measurements. The c axis is parallel to the long dimension of the crystal. A 0.001-in. Nb incident beam filter was used for reflections with $2\theta > 10^\circ$. Balanced filter techniques with Zr and Y filters in the diffracted beam were used for reflections in the 2θ range of $0-15^\circ$ and several other strong reflections. A total of 2124 reflections out to $(\sin \theta)/\lambda = 0.66 \text{ \AA}^{-1}$ were measured with 1993 of these recorded as observed. The reflection (432) was used as the standard with seven other reflections of medium intensities as extra standards.

Solution and Refinement

The X-ray 63 program system was used for most of the remaining calculations.⁷ The least-squares refinement of the structure was based on F , the parameters being varied to minimize the function $\sum w(|F_o| - S|F_c|)^2$. The variable S was included to place the observed structure factors (F_o) and the calculated structure factors (F_c) on a common scale. The reliability of each term in the sum was weighted by the factor w , which was estimated as $w = 1/\sigma^2(F_o)$. Progress in the analyses was indicated by the value of the residual index $R = \sum ||F_o| - S|F_c|| / \sum |F_o|$. The analysis of the three structures was carried out as follows.

CoOMPA.—The analysis began with a trial structure

(5) (a) W. R. Busing and H. A. Levy, *Acta Cryst.*, **10**, 180 (1959); (b) D. J. Wehe, W. R. Busing, and H. A. Levy, "A Fortran Program for Calculating Single Crystal Absorption Corrections," Report No. 229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(6) T. J. Shaffner, Ph.D. Thesis, Vanderbilt University, 1969.

(7) J. M. Stewart, Technical Report Tr 64-6, NSG-398, Computer Science Center, University of Maryland, College Park, Md., April 1964.

based on assumed geometry for the pyrophosphate-metal rings. Both $P\bar{3}c1$ and $P3c1$ are compatible with the molecular model. We therefore began the analysis with $P\bar{3}c1$ (D_{3d}^4 , no. 165)⁸ in order to take advantage of the higher symmetry. Cobalt(II) was assumed to occupy the Wyckoff position a and the middle oxygen atom of the ring, f.⁸ These choices fix the position and orientation of the molecule in the unit cell. Structure factors calculated for cobalt(II), phosphorus, and the two independent oxygen atoms of the chelate ring indicate that the orientation chosen was not greatly in error.

The chlorine atoms of the four perchlorate groups must be located in either of the Wyckoff positions c or d. Since the c axis is too short to permit four perchlorate groups to pack between the CoOMPA molecules along $0,0,z$, they must occupy position d. The approximate value of z was determined by trial and error. About 100 low-angle reflections with $l = 2n$ were selected and the residual was calculated for trial structures including Co(II) and the other atoms of the chelate ring together with chlorine placed successively with different z coordinates. When the minimum residual had been located, additional $l = 2n$ reflections were included with higher values for l . The z coordinate which gave a minimum value for this set of reflections differed from the final value by 0.05 Å.

At this point in the analysis a Fourier synthesis program which could handle trigonal space groups became available. The Patterson function calculated at this time was compatible with our choice of space group. We then proceeded to locate the remaining oxygen, carbon, and nitrogen atoms by difference synthesis.

Atomic scattering factors used in the refinement were taken from ref 9. Refinement proceeded normally by full-matrix least squares. The independent parameters correspond to half of one OMPA ligand and one-third of one perchlorate anion. Anisotropic thermal motion was allowed for all nonhydrogen atoms. The only parameter restrictions applied were those required by the symmetry of the special positions. Temperature factor restrictions imposed by symmetry on atoms in special positions were determined by the method of Levy.¹⁰ The least-squares program used treats symmetry-related B_{ij} 's as separate parameters. It was therefore necessary to refine only one of the related B_{ij} 's. After every cycle those refined were averaged with unrefined but related B_{ij} 's and the averaged values were used for the subsequent cycle.

The difference map obtained after all nonhydrogen atoms were refined still had areas of residual electron density near the perchlorate oxygen positions. In order to assess the amount of disorder in the perchlorate oxygen atoms, a difference synthesis was calculated in which the coordinates of all atoms except the perchlorate oxygen atoms were included. After examining

the resulting map, two sets of coordinates for the perchlorate oxygen atoms were assigned to allow for the disorder and/or fairly high thermal motion. The population parameters chosen were 0.6 for O(31) and O(41) and 0.4 for O(32) and O(42). A difference map with these parameters still contained residual electron density ($\pm 0.3 \text{ e}^-/\text{Å}^3$ near perchlorate oxygen positions). An attempt to obtain an improved model for the disordered perchlorate groups was made by using a procedure similar to that described below for locating hydrogen atoms. However, not much improvement resulted and the above model was used for final refinements.

Hydrogen atoms were located from a difference synthesis computed with data out to $(\sin \theta)/\lambda = 0.54 \text{ Å}^{-1}$ (1093 observed reflections). The procedure used was similar to that reported by Paton, Maslen, and Watson.¹¹ Tetrahedral geometry and a carbon hydrogen distance of 1.00 Å were used. Eight equally spaced rotations were made and 24 points on a circle of possible hydrogen positions were marked on the difference map. Difference density values were interpolated from the map and plotted as a function of the rotation angle. In most cases the hydrogen positions were indicated by peaks of about $0.35 \text{ e}^-/\text{Å}^3$ spaced 120° apart. Calculated hydrogen atom positions corresponding to the best orientation were refined by three cycles of least squares. Difference density values for hydrogen atoms on C(2) were smaller ($0.2 \text{ e}^-/\text{Å}^3$) and the peaks were rather broad. Two sets of coordinates were assigned to the C(2) hydrogen atoms to allow for the disorder or hindered rotation.

All heavy-atom parameters were refined as noted above along with coordinates and isotropic temperature factors for all hydrogen atoms except those bonded to C(2). The final cycle of full-matrix least squares was calculated with 1314 reflections having $F_o \geq 2\sigma$. Coordinate shifts for all atoms on the final cycle averaged 0.11 times the esd with a maximum shift of 0.63σ . The final value of R is 0.059 for reflections with $F_o > 2\sigma$ and 0.074 for 1659 observed reflections.

The observed and calculated structure factors for all reflections are given in Table II. The final positional and thermal parameters are given in Tables VA, VIA, and VIIA.

MgOMPA.—Refined coordinates of CoOMPA were used as starting parameters for MgOMPA. Atomic scattering factors used in the refinement were taken from ref 9. The structure was refined for nonhydrogen atoms by the same method used for CoOMPA. The perchlorate disorder model used for CoOMPA was also used for MgOMPA. Three cycles of ORFLS gave $R = 0.069$. At this point 149 reflections which had the poorest agreement of F_o with F_c were remeasured. The refinement was then continued and the hydrogen atoms were located by the same method used for CoOMPA. Fixed positions for H(21), H(22), and H(23) were assigned since these parameters did not converge. The

(8) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 271.

(9) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 210-212.

(10) H. A. Levy, *Acta Cryst.*, **9**, 879 (1956).

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

TABLE II
MAGNITUDES OF OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times 10$) FOR $\text{Co}(\text{OMPA})_3(\text{ClO}_4)_2$

0.0,1	2	28	-3	18	154	-47	2	128	-117	2	180	-188	19	31	-42	12	42	-55	3	33	42	8	287	268	17	41	65	10	242	-233	6	136	-116	14	134	-125
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final cycle of full-matrix least-squares refinement was calculated with 1669 reflections having $F_o > 2\sigma$. Coordinate shifts for all atoms on the final cycle averaged 0.05 times the esd with a maximum shift of 0.32 σ .

The final value for R is 0.056 for 1669 reflections with $F_o > 2\sigma$ and 0.069 for 2138 observed reflections. The observed and calculated structure factors for all reflections are given in Table III. The final positional

TABLE III
OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR Mg(OMPA)₂(ClO₄)₂

0.01L	2.54	42	11	67	70	2.1L	0.28L	0.37L	0.46L	0.55L	0.64L	0.73L	0.82L	0.91L	1.00L	1.09L	1.18L	1.27L	1.36L	1.45L	1.54L	1.63L	1.72L	1.81L	1.90L	1.99L	2.08L	2.17L	2.26L	2.35L	2.44L	2.53L	2.62L	2.71L	2.80L	2.89L	2.98L	3.07L	3.16L	3.25L	3.34L	3.43L	3.52L	3.61L	3.70L	3.79L	3.88L	3.97L	4.06L	4.15L	4.24L	4.33L	4.42L	4.51L	4.60L	4.69L	4.78L	4.87L	4.96L	5.05L	5.14L	5.23L	5.32L	5.41L	5.50L	5.59L	5.68L	5.77L	5.86L	5.95L	6.04L	6.13L	6.22L	6.31L	6.40L	6.49L	6.58L	6.67L	6.76L	6.85L	6.94L	7.03L	7.12L	7.21L	7.30L	7.39L	7.48L	7.57L	7.66L	7.75L	7.84L	7.93L	8.02L	8.11L	8.20L	8.29L	8.38L	8.47L	8.56L	8.65L	8.74L	8.83L	8.92L	9.01L	9.10L	9.19L	9.28L	9.37L	9.46L	9.55L	9.64L	9.73L	9.82L	9.91L	10.00L	10.09L	10.18L	10.27L	10.36L	10.45L	10.54L	10.63L	10.72L	10.81L	10.90L	10.99L	11.08L	11.17L	11.26L	11.35L	11.44L	11.53L	11.62L	11.71L	11.80L	11.89L	11.98L	12.07L	12.16L	12.25L	12.34L	12.43L	12.52L	12.61L	12.70L	12.79L	12.88L	12.97L	13.06L	13.15L	13.24L	13.33L	13.42L	13.51L	13.60L	13.69L	13.78L	13.87L	13.96L	14.05L	14.14L	14.23L	14.32L	14.41L	14.50L	14.59L	14.68L	14.77L	14.86L	14.95L	15.04L	15.13L	15.22L	15.31L	15.40L	15.49L	15.58L	15.67L	15.76L	15.85L	15.94L	16.03L	16.12L	16.21L	16.30L	16.39L	16.48L	16.57L	16.66L	16.75L	16.84L	16.93L	17.02L	17.11L	17.20L	17.29L	17.38L	17.47L	17.56L	17.65L	17.74L	17.83L	17.92L	18.01L	18.10L	18.19L	18.28L	18.37L	18.46L	18.55L	18.64L	18.73L	18.82L	18.91L	19.00L	19.09L	19.18L	19.27L	19.36L	19.45L	19.54L	19.63L	19.72L	19.81L	19.90L	20.00L
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and thermal parameters are given in Tables VB, VIB, and VIIB.
CuOMPA.—The values of the atomic parameters (thermal parameters used were isotropic for hydrogen and anisotropic for other atoms) found for MgOMPA

were used as the initial parameters in the refinement procedure. The perchlorate disorder model used for CoOMPA was also used for CuOMPA. Structure factor calculations with these parameters gave a residual index of 0.110 for 1993 observed reflections. Two

TABLE IV
MAGNITUDES OF OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR Cu(OMPA)3(C104)2

Table with multiple columns containing numerical data for observed and calculated structure factors. The table is organized into several sections, each starting with a label like 'O,10L' or 'O,21L' and followed by columns of numbers representing different reflections.

cycles of least-squares refinement determined the R value to 0.052. Hydrogen atoms were located with a difference synthesis computed with data out to (sin theta)/lambda = 0.54 A^-1 (939 observed reflections) by the same method used for CoMPA. The hydrogen atoms were refined by three cycles of full-matrix least squares starting with isotropic temperature factors of 8.00 A^2 and holding

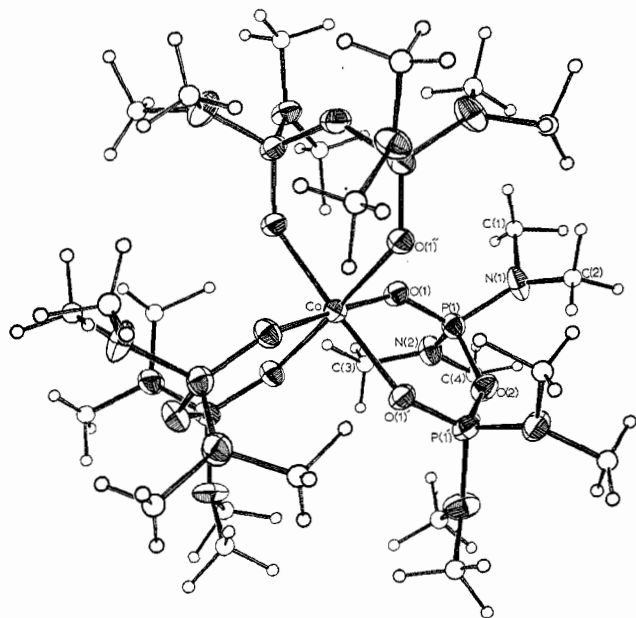


Figure 1.—Projection of $\text{Co}(\text{OMPA})_3^{2+}$. The a axis is directed from Co to O(2) and the ion is viewed approximately along the c axis.

all nonhydrogen parameters fixed. The scattering factor curves for Cu(II), phosphorus, and chlorine were corrected for the real part of anomalous dispersion.¹² Neutral-atom factors listed by Cromer, *et al.*,¹³ were used for nitrogen, oxygen, and carbon. The scattering factors for the hydrogen atoms were from Table II of ref 14.

Two more least-squares refinement cycles were performed with adjustment of anisotropic temperature factors and positional coordinates of all nonhydrogen atoms. Hydrogen atoms were assigned a fixed-atom contribution. The value of R reduced to 0.049. A final cycle of least-squares refinement in which all parameters were allowed to vary brought R to 0.048. The maximum and minimum values of the final electron difference density were $\pm 0.3 \text{ e}^-/\text{\AA}^3$ in the vicinity of the disordered atoms of the perchlorate group and $\pm 0.15 \text{ e}^-/\text{\AA}^3$ everywhere else. Coordinate shifts on the final full-matrix least-squares refinement averaged 0.17 times the esd with a maximum shift of 1.2 times the esd for one of the disordered perchlorate oxygen atoms.

The observed and calculated structure factors are given in Table IV. The final positional and thermal parameters are given in Tables VC, VIC, and VIIC.

The similarity in the corresponding temperature factors for O(31), O(32), O(41), and O(42) for CoOMPA, MgOMPA, and CuOMPA shows our assumption of the same disorder ratio for the perchlorate ion in all three compounds is valid.

Description of Structures

Figure 1 is a projection of the $\text{Co}(\text{OMPA})_3^{2+}$ cation

(12) (a) M. G. Paton, E. N. Maslen, and K. J. Watson, *Acta Cryst.*, **22**, 213 (1967); D. T. Cromer, *ibid.*, **18**, 17 (1965).

(13) D. T. Cromer and J. B. Mann, *ibid.*, **A24**, 321 (1968).

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

TABLE V^a

FRACTIONAL ATOMIC COORDINATES OF THE NONHYDROGEN ATOMS FOR TRIS-CHELATE COMPLEXES OF OMPA

Atom	x	y	z
A. $[\text{Co}(\text{OMPA})_3](\text{ClO}_4)_2$			
Co	0	0	0
P(1)	0.26708 (14)	0.07171 (14)	0.18166 (9)
Cl	$1/3$	$2/3$	0.05306 (18)
O(1)	0.15356 (29)	0.07392 (32)	0.18486 (17)
O(2)	0.27941 (37)	0	$1/4$
O(31) ^b	$1/3$	$2/3$	-0.0202 (14)
O(32) ^b	$1/3$	$2/3$	0.1286 (14)
O(41) ^b	0.3283 (14)	0.5630 (12)	0.07950
O(42) ^b	0.3280 (26)	0.5674 (19)	0.02660
N(1)	0.39097 (42)	0.19622 (51)	0.18727 (28)
N(2)	0.27460 (43)	0.00886 (44)	0.10716 (25)
C(1)	0.4265 (11)	0.2858 (11)	0.1283 (7)
C(2)	0.44524 (66)	0.24701 (66)	0.25125 (53)
C(3)	0.3833 (10)	0.0058 (13)	0.0848 (8)
C(4)	0.16546 (87)	-0.07549 (95)	0.06872 (52)
B. $[\text{Mg}(\text{OMPA})_3](\text{ClO}_4)_2$			
Mg	0	0	$1/4$
P(1)	0.26660 (7)	0.07087 (8)	0.18183 (5)
Cl	$1/3$	$2/3$	0.05302 (10)
O(1)	0.15252 (16)	0.07098 (17)	0.18629 (10)
O(2)	0.28035 (20)	0	$1/4$
O(31) ^b	$1/3$	$2/3$	-0.02139 (77)
O(32) ^b	$1/3$	$2/3$	0.12602 (76)
O(41) ^b	0.32514 (88)	0.56130 (68)	0.07950
O(42) ^b	0.3280 (15)	0.5700 (11)	0.02660
N(1)	0.39024 (22)	0.19739 (27)	0.18795 (16)
N(2)	0.27483 (24)	0.00869 (24)	0.10715 (14)
C(1)	0.42420 (69)	0.28357 (65)	0.12797 (43)
C(2)	0.44876 (37)	0.25064 (39)	0.25544 (26)
C(3)	0.38350 (54)	0.00933 (75)	0.08373 (42)
C(4)	0.16706 (45)	-0.07584 (48)	0.06760 (28)
C. $[\text{Cu}(\text{OMPA})_3](\text{ClO}_4)_2$			
Cu	0	0	$1/4$
P(1)	0.26581 (5)	0.07174 (6)	0.18184 (3)
Cl	$1/3$	$2/3$	0.05306 (6)
Q(1)	0.15212 (14)	0.07392 (15)	0.18531 (8)
O(2)	0.27795 (16)	0	$1/4$
O(31) ^b	$1/3$	$2/3$	-0.02004 (63)
O(32) ^b	$1/3$	$2/3$	0.12723 (61)
O(41) ^b	0.32720 (65)	0.56361 (53)	0.07950
O(42) ^b	0.3284 (12)	0.5693 (8)	0.02660
N(1)	0.39070 (20)	0.19734 (21)	0.18845 (12)
N(2)	0.27372 (18)	0.00967 (19)	0.10699 (11)
C(1)	0.42557 (58)	0.28297 (43)	0.12697 (29)
C(2)	0.44695 (62)	0.24991 (57)	0.25715 (33)
C(3)	0.38292 (40)	0.00800 (57)	0.08528 (28)
C(4)	0.16581 (33)	-0.07402 (34)	0.06736 (19)

^a Numbers in parentheses for the parameters here and in succeeding tables are the standard deviations in the least significant digits. No standard deviations are listed for the fixed parameters. ^b Oxygen atoms O(31) and O(41) define one orientation of the perchlorate group and are assigned an occupancy factor of 0.6. O(32) and O(42) are assigned an occupancy factor of 0.4.

drawn with ORTEP¹⁵ showing 70% probability thermal vibration ellipsoids of all nonhydrogen atoms except carbons.¹⁶ The carbon and hydrogen atoms are plotted as spheres for clarity. Since the structures of

(15) C. K. Johnson, "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(16) The atoms are numbered according to the system used in the tables. Chelate ring atoms with a prime are related by a twofold axis through Co(II) and O(2).

TABLE VI^{a-c}
 ANISOTROPIC TEMPERATURE FACTORS OF NONHYDROGEN ATOMS FOR THE TRIS-CHELATE COMPLEXES OF OMPA

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
A. [Co(OMPA) ₃](ClO ₄) ₂						
Co	2.99 (7)	2.99	4.17 (8)	1.49		
P(1)	3.17 (7)	4.09 (8)	4.39 (7)	1.54 (6)	0.36 (6)	0.31 (6)
Cl	5.93 (16)	5.93	4.75 (16)	2.97		
O(1)	3.37 (16)	4.27 (19)	4.10 (16)	2.05 (16)	0.64 (14)	0.73 (16)
O(2)	3.84 (22)	5.84 (32)	5.15 (30)	2.92	0.50	1.00 (25)
O(31)	17.7 (23)	17.7	7.8 (14)	8.84		
O(32)	17.9 (31)	17.9	4.0 (14)	8.97		
O(41)	9.34 (71)	9.55 (96)	15.3 (12)	5.34 (77)	1.82 (93)	6.63 (93)
O(42)	17.1 (17)	12.4 (19)	17.9 (23)	9.1 (18)	-4.5 (20)	-12.2 (19)
N(1)	3.89 (24)	4.94 (29)	4.84 (25)	0.12 (24)	-0.94 (21)	-1.00 (26)
N(2)	3.61 (24)	5.37 (28)	4.94 (27)	1.96 (23)	0.48 (21)	-0.96 (23)
C(1)	8.24 (69)	6.16 (59)	7.59 (67)	0.20 (53)	0.72 (56)	1.04 (55)
C(2)	6.59 (45)	5.59 (45)	13.41 (66)	0.98 (36)	0.50 (46)	1.08 (45)
C(3)	5.59 (53)	9.34 (77)	8.85 (67)	3.79 (54)	1.88 (51)	-0.92 (67)
C(4)	7.13 (54)	6.15 (54)	4.72 (44)	2.17 (42)	-0.56 (39)	-1.04 (42)
B. [Mg(OMPA) ₃](ClO ₄) ₂						
Mg	3.90 (9)	3.90	4.94 (11)	1.95		
P(1)	3.78 (4)	4.87 (4)	5.22 (4)	1.88 (3)	0.32 (3)	0.08 (4)
Cl	6.71 (9)	6.71	5.57 (8)	3.35		
O(1)	4.25 (9)	4.89 (10)	5.05 (9)	2.31 (8)	0.45 (8)	0.61 (16)
O(2)	4.54 (12)	6.73 (17)	6.26 (16)	3.37	0.36	0.72 (14)
O(31)	18.6 (14)	18.6	8.57 (72)	9.30		
O(32)	19.3 (16)	19.3	4.98 (69)	9.63		
O(41)	11.31 (42)	9.34 (48)	16.11 (65)	5.74 (41)	1.46 (54)	5.61 (49)
O(42)	15.75 (91)	13.8 (12)	21.7 (15)	7.6 (10)	-2.4 (13)	-13.7 (12)
N(1)	4.78 (13)	5.86 (15)	6.36 (14)	1.24 (13)	-0.04 (12)	-0.12 (13)
N(2)	4.50 (13)	6.42 (15)	6.20 (15)	2.41 (12)	0.52 (12)	-0.74 (12)
C(1)	7.69 (34)	7.39 (31)	9.81 (41)	0.44 (30)	0.51 (31)	1.76 (28)
C(2)	8.47 (26)	8.64 (28)	11.32 (30)	1.17 (22)	-3.03 (25)	-2.07 (25)
C(3)	6.64 (28)	11.53 (45)	9.25 (38)	4.72 (30)	1.31 (28)	-1.98 (35)
C(4)	7.08 (27)	7.43 (30)	6.19 (23)	2.91 (23)	-0.36 (19)	-1.06 (21)
C. [Cu(OMPA) ₃](ClO ₄) ₂						
Cu	3.24 (2)	3.24	3.90 (2)	1.62		
P(1)	3.61 (2)	3.36 (2)	4.47 (2)	1.87 (2)	0.06 (2)	-0.06 (2)
Cl	6.25 (5)	6.25	4.87 (5)	3.13		
O(1)	4.56 (7)	5.30 (8)	4.84 (6)	3.03 (6)	-0.07 (5)	0.21 (6)
O(2)	3.93 (8)	6.19 (12)	5.43 (11)	3.10	0.49	0.97 (11)
O(31)	18.0 (10)	18.0	9.16 (59)	9.00		
O(32)	18.1 (13)	18.1	4.29 (49)	9.03		
O(41)	10.17 (31)	9.14 (39)	17.10 (56)	5.17 (32)	2.26 (42)	6.55 (40)
O(42)	16.79 (76)	12.41 (76)	21.3 (11)	8.20 (75)	-1.76 (93)	-12.27 (80)
N(1)	5.03 (10)	5.07 (10)	5.77 (10)	0.86 (9)	-0.40 (8)	-0.20 (9)
N(2)	4.38 (9)	5.69 (10)	5.25 (9)	2.23 (8)	0.59 (7)	-0.71 (8)
C(1)	9.73 (30)	6.14 (20)	8.48 (26)	0.38 (21)	0.29 (23)	1.29 (19)
C(2)	7.54 (25)	7.52 (26)	9.33 (27)	0.48 (23)	-2.54 (22)	-1.10 (22)
C(3)	6.26 (19)	9.72 (29)	8.74 (25)	3.95 (20)	1.86 (18)	-1.52 (23)
C(4)	6.58 (17)	6.35 (17)	5.06 (14)	2.45 (14)	-0.25 (12)	-1.08 (13)

^a B_{ij} values are in square ångströms and the expression is $\exp[-1/4(h^2a^*2B_{11} + k^2b^*2B_{22} + \dots + 2klb^*c^*B_{23})]$. ^b The restrictions on the thermal parameters for M, Cl, O(31), and O(32) atoms were: $B_{11} = B_{22} = 2B_{12}$; $B_{13} = B_{23} = 0$. Only B_{11} and B_{33} were allowed to refine. ^c The restrictions on thermal parameters for O(2) atoms were: $2B_{12} = B_{22}$; $2B_{13} = B_{33}$. Here B_{12} and B_{13} were not refined.

CoOMPA, MgOMPA, and CuOMPA are essentially identical, the figures in this paper are applicable to all three compounds. Figure 2 is a stereoscopic view of the cation environment in these complexes. Although the metal ions have trigonal symmetry, the deviations from octahedral symmetry are small. A comparison of the O-M-O angles in Table IX shows that CuOMPA has the smallest deviation from octahedral geometry.

The average C-H distances are 0.97, 0.93, and 0.97 Å and the H-C-H angles are 112, 105, and 114° for CoOMPA, MgOMPA, and CuOMPA, respectively. The C(2)-H bond distances and angles are not included in

these averages since the hydrogen coordinates for this group were fixed in CoOMPA and MgOMPA during the refinement.

Bond distances and angles for nonhydrogen atoms are in close agreement for all three structures. These are compared in Tables VIII and IX. Of particular interest are the similarities in distances for the complex of a nontransition metal, Mg(II), with those for the complexes of Co(II) and Cu(II). All corresponding distances in the chelate ring are within experimental error with the exception of the M-O distance.

Figures 1 and 2 also illustrate the planarity of the

TABLE VII

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF THE HYDROGEN ATOMS FOR THE TRIS-CHELATE COMPLEXES OF OMPA

Atom ^a	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
A. [Co(OMPA) ₃](ClO ₄) ₂				
H(11)	0.3954 (75)	0.3405 (74)	0.1489 (46)	13.1 (37)
H(12)	0.5295 (86)	0.3296 (72)	0.1263 (42)	13.9 (29)
H(13)	0.4158 (64)	0.2515 (60)	0.0917 (34)	5.0 (24)
H(211) ^b	0.4781 ^c	0.1997	0.2795	8.0
H(221)	0.5190	0.3324	0.2462	8.0
H(231)	0.3907	0.2570	0.2887	8.0
H(212)	0.5345	0.2691	0.2543	8.0
H(222)	0.4471	0.3264	0.2635	8.0
H(232)	0.4062	0.1936	0.2968	8.0
H(31)	0.3707 (95)	-0.0695 (97)	0.1077 (55)	15.5 (46)
H(32)	0.4129 (76)	0.0549 (75)	0.0492 (41)	9.7 (33)
H(33)	0.4507 (69)	0.0605 (69)	0.1162 (38)	8.7 (26)
H(41)	0.1704 (57)	-0.0589 (55)	0.0290 (30)	5.7 (21)
H(42)	0.1494 (62)	-0.1529 (64)	0.0820 (34)	8.0 (24)
H(43)	0.0761 (85)	-0.0720 (78)	0.0915 (44)	16.4 (30)

B. [Mg(OMPA)₃](ClO₄)₂

H(11)	0.3874 (46)	0.3290 (44)	0.1346 (30)	14.4 (26)
H(12)	0.5083 (45)	0.3132 (38)	0.1193 (22)	11.1 (15)
H(13)	0.3880 (43)	0.2472 (42)	0.0894 (25)	11.2 (20)
H(21)	0.5267 ^c	0.3161	0.2509	13.5
H(22)	0.4252	0.2687	0.2749	14.9
H(23)	0.4619	0.2048	0.2798	20.2
H(31)	0.3737 (39)	-0.0627 (39)	0.0959 (23)	9.8 (18)
H(32)	0.4073 (39)	0.0234 (39)	0.0327 (23)	11.4 (15)
H(33)	0.4405 (34)	0.0443 (33)	0.1157 (18)	7.6 (13)
H(41)	0.1715 (28)	-0.0509 (28)	0.0144 (21)	8.7 (10)
H(42)	0.1535 (34)	-0.1504 (35)	0.0801 (18)	8.6 (13)
H(43)	0.0955 (38)	-0.0784 (36)	0.0790 (22)	10.5 (15)

C. [Cu(OMPA)₃](ClO₄)₂

H(11)	0.3974 (43)	0.3358 (40)	0.1470 (25)	12.4 (17)
H(12)	0.5062 (43)	0.3259 (40)	0.1237 (23)	12.2 (15)
H(13)	0.3946 (43)	0.2367 (44)	0.0784 (26)	13.8 (15)
H(21)	0.4382 (44)	0.1912 (48)	0.2865 (27)	13.9 (20)
H(22)	0.5135 (44)	0.2933 (41)	0.2465 (23)	10.5 (15)
H(23)	0.4132 (71)	0.2845 (73)	0.2642 (42)	24.1 (42)
H(31)	0.3718 (35)	-0.0653 (38)	0.0957 (20)	9.7 (13)
H(32)	0.3999 (36)	0.0375 (35)	0.0295 (20)	10.8 (11)
H(33)	0.4477 (33)	0.0618 (32)	0.1121 (18)	8.7 (10)
H(41)	0.1754 (25)	-0.0532 (23)	0.0174 (17)	7.1 (8)
H(42)	0.1534 (24)	-0.1504 (27)	0.0788 (13)	6.0 (7)
H(43)	0.0942 (31)	-0.0751 (30)	0.0852 (17)	9.2 (10)

^a The first number in parentheses corresponds to the carbon atoms to which the hydrogen is attached. ^b Two sets of hydrogen atoms were used for C(2) in the case of [Co(OMPA)₃](ClO₄)₂ to allow for disorder. The third number in parentheses corresponds to the possible position for the hydrogen atom. ^c Coordinates and temperature factors of hydrogen atoms on C(2) were not allowed to refine.

chelate rings. Least-squares plane calculations for the chelate rings of CoOMPA, MgOMPA, and CuOMPA indicate that one phosphorus atom is 0.06 Å above and the other 0.06 Å below the plane defined by the metal and the three oxygen atoms which are required by symmetry to lie in a plane. The planarity of the chelate rings in CoOMPA and CuOMPA would be consistent with electron delocalization in the chelate ring through $d\pi-p\pi$ bonding. However, planar chelate rings would not be expected for MgOMPA where $d\pi-p\pi$ delocalization cannot occur. In addition, the

TABLE VIII

BOND DISTANCES FOR MgOMPA, CoOMPA, AND CuOMPA

Atoms	Distances, Å		
	CoOMPA	MgOMPA	CuOMPA
M-O(1)	2.084 (3)	2.061 (2)	2.065 (2)
P-O(1)	1.476 (5)	1.471 (3)	1.477 (2)
P-O(2)	1.606 (3)	1.604 (1)	1.602 (1)
P-N(1)	1.602 (4)	1.614 (2)	1.615 (2)
P-N(2)	1.610 (5)	1.611 (3)	1.611 (2)
N(1)-C(1)	1.47 (1)	1.461 (9)	1.476 (6)
N(1)-C(2)	1.35 (1)	1.428 (9)	1.437 (6)
N(2)-C(3)	1.48 (2)	1.459 (9)	1.469 (7)
N(2)-C(4)	1.46 (1)	1.456 (5)	1.454 (4)
Cl-O(31)	1.34 (3)	1.36 (1)	1.33 (1)
Cl-O(32)	1.38 (3)	1.33 (1)	1.35 (1)
Cl-O(41)	1.39 (2)	1.39 (1)	1.37 (1)
Cl-O(42)	1.33 (3)	1.30 (1)	1.31 (1)

TABLE IX

BOND ANGLES FOR MgOMPA, CoOMPA, AND CuOMPA

Atoms	Angles, deg		
	CoOMPA	MgOMPA	CuOMPA
O(1)-M-O(1')	87.9 (1)	86.1 (1)	88.4 (1)
O(1')-M-O(1'')	91.7 (1)	91.3 (1)	90.5 (1)
O(1)-M-O(1'')	90.8 (1)	91.5 (1)	90.6 (1)
M-O(1)-P	137.3 (2)	139.5 (1)	137.2 (1)
P(1)-O(2)-P(1')	134.6 (3)	133.5 (2)	134.7 (1)
O(1)-P-O(2)	111.3 (2)	110.6 (1)	111.1 (1)
O(1)-P-N(1)	118.5 (3)	118.4 (2)	118.4 (1)
O(1)-P-N(2)	110.6 (3)	111.1 (1)	110.7 (1)
O(2)-P-N(1)	101.0 (2)	100.8 (1)	100.6 (1)
O(2)-P-N(2)	108.6 (3)	108.7 (1)	109.0 (1)
N(1)-P-N(2)	106.1 (3)	106.5 (1)	106.3 (1)
P-N(1)-C(1)	120.0 (6)	118.9 (3)	117.9 (2)
P-N(1)-C(2)	123.7 (4)	124.1 (4)	123.4 (3)
P-N(2)-C(3)	122.8 (6)	123.1 (3)	122.2 (2)
P-N(2)-C(4)	120.3 (6)	121.1 (3)	121.0 (2)
C(1)-N(1)-C(2)	111.8 (6)	113.4 (5)	114.8 (3)
C(3)-N(2)-C(4)	114.9 (6)	114.3 (5)	114.8 (3)
O(31)-Cl-O(41)	110.3 (3)	110.3 (1)	110.6 (1)
O(31)-Cl-O(42)	111.2 (5)	111.7 (2)	111.6 (2)
O(41)-Cl-O(41')	108.6 (7)	108.6 (4)	108.4 (3)
O(42)-Cl-O(42')	107 (1)	107.1 (7)	107.3 (6)

P-O(1) bond distance of 1.476 Å is too short and the P-O(2) bond distance of 1.606 Å is too long to be consistent with appreciable electron delocalization in the ring. Bond distances for other metal complexes of ligands with phosphoryl oxygen donor sites are given in Table X. Neither the P-O nor the P-O(P) bond distances in these compounds are influenced to any significant extent by the metal ions.

Since Mg(II) cannot utilize *d* orbitals for $d\pi-p\pi$ delocalization in the chelate ring, packing forces may be causing planarity of the chelate rings. Figure 3 is a stereoscopic packing diagram for MgOMPA. No unusual packing effects are apparent. Contact distances between methyl groups of ligands attached to the same Mg(II) are all greater than the sum of van der Waals radii (4.0 Å). Contact distances between methyl groups and perchlorate oxygen atoms and chelate ring oxygen atoms are greater than the range suggested for C-H...O hydrogen bonds (H...O > 2.6 Å).¹⁷ Thus, there appear to be no significant

(17) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968, p 16.

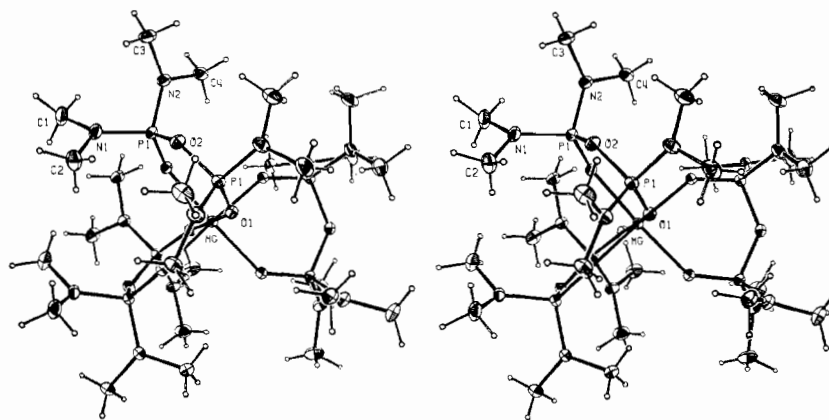


Figure 2.—Stereoscopic projection of $\text{Mg}(\text{OMPA})_3^{2+}$. The a axis is directed from Mg to O(2). Coordinates given in Table V are related to the lettered atoms by $y, x, 1/2 - z$.

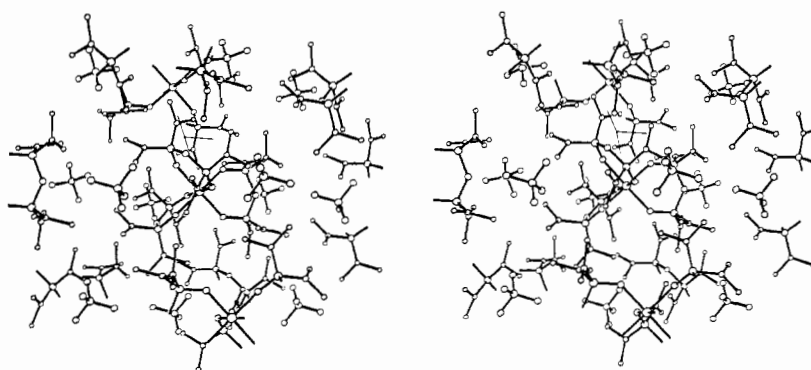


Figure 3.—Stereoscopic packing diagram. Unit cell axes are drawn in to show orientation of the packing diagram. The a axis is directed from Mg to O(2).

packing forces or hydrogen bonds which are affecting the chelate ring geometry.

The P–N distance of 1.6 Å is much shorter than the single bond distance^{18,19} of 1.77 Å and is between that observed for P–N(*exo*) and P–N(*endo*) in $\text{P}_4\text{N}_4[\text{N}(\text{CH}_3)_2]_8$ (Table X). These distances suggest that $d\pi$ – $p\pi$ bonding is quite important between phosphorus and nitrogen. The importance of $d\pi$ – $p\pi$ bonding is also indicated by the flattened dimethylamino groups. In all three complexes one nitrogen atom [N(1)] is 0.17 Å away from the plane defined by P(1), C(1), and C(2) while N(2) is 0.11 Å away from the plane defined by P(1), C(3), and C(4). This suggests that the hybridization at the nitrogen atoms approximates sp^2 .

The D_3 site symmetry of Cu(II) in CuOMPA should be unstable according to the Jahn–Teller theorem.²⁰ The only previous tris-chelate complex of Cu(II) for which structure data are available is tris(ethylenediamine)copper(II) sulfate.^{21,22} Since no static Jahn–Teller distortions are present in CuOMPA, we decided to examine the anisotropic thermal parameters for evidence to support the presence of dynamic Jahn–

Teller distortions. Table XI lists the root-mean-square amplitudes of vibration for atoms in the chelate ring for CoOMPA, MgOMPA, and CuOMPA. Of particular interest is the comparison of thermal parameters for Cu(II) with Mg(II) where Jahn–Teller distortions are absent. The root-mean-square amplitudes for O(1)–Cu and O(1)–Mg are equal within experimental error. The root-mean-square vibration amplitudes of all atoms in the chelate ring do not differ significantly for the three complexes of OMPA. The values for the amplitudes are those expected if the thermal motions of the chelate atoms are nearly isotropic. This comparison of thermal parameters indicates that any oscillation among three nontrigonal distortions (dynamic Jahn–Teller effect) is not sufficient to be detected by X-ray analysis.

Electron paramagnetic resonance spectroscopy provides a more sensitive method of detecting small distortions in the immediate environment of Cu(II). We are proceeding with epr and X-ray studies of single crystals of $\text{Cu}(\text{OMPA})_3(\text{ClO}_4)_2$ at low temperature in an attempt to learn more about the importance of Jahn–Teller distortions in trigonal systems.

Conclusions

Although the close agreement of bond distances in these three compounds may be surprising, previous spectroscopic studies of Ni(II) and Cu(II) complexes of

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TABLE X
 COMPARISON OF BOND DISTANCES (Å)

Compound	P-O	P-O-(P)	P-N	M-O
CoOMPA ^a	1.476 (5)	1.606 (3)	1.606 (5) ^m	2.084 (3)
[(CH ₃) ₂ PO] ₂ Co(NO ₃) ₂ ^b	1.54 (3) ^m			1.93 (2) ^m
Co ₃ [(C ₂ H ₅) ₂ O] ₂ P(O)CHC(O)CH ₃] ₆ ^c	1.464 (5) ^m			2.061 (5) ^m
[(C ₂ H ₅) ₂ O] ₂ PO] ₂ UO ₂ (NO ₃) ₂ ^d	1.52 ^m			2.44 ^m
[(C ₂ H ₅) ₂ PO]UO ₂ (C ₂ H ₅ O ₂) ₂ ^e	1.48 (3)			2.37 (2)
Na ₄ P ₂ O ₇ · 10H ₂ O ^f	1.523 (4) ^m	1.612 (5)		2.48 (6) ^m
α-Cu ₂ P ₂ O ₇ ^g	1.53 (2) ^m	1.576 (7)		1.95 (4) ^m (equatorial); 2.322 (6), 2.947 (6) (axial)
α-Mg ₂ P ₂ O ₇ ^h	1.52 (2) ^m	1.59 (2) ^m		2.08 (2) ^m
NaHPO ₃ NH ₂ ⁱ	1.522 (11)		1.769 (19)	
P ₄ O ₁₀ ^j	1.40 (2)	1.60 (2) ^m		
P ₄ N ₄ [N(CH ₃) ₂] ₈ ^k			1.58 (1) ^m (<i>endo</i>) 1.68 (1) ^m (<i>exo</i>)	
N ₃ (CH ₃) ₃ P ₃ O ₃ (O(CH ₃)) ₃ ^l	1.44		1.69 ^m	

^a This work. ^b F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963). ^c F. A. Cotton, R. Hugel, and R. Eiss, *Inorg. Chem.*, **7**, 18 (1968). ^d J. E. Fleming and H. Lynton, *Chem. Ind. (London)*, 1415 (1960). ^e C. Pavattoni, *et al.*, *Chem. Commun.*, 278 (1968). ^f W. S. McDonald and D. W. J. Cruickshank, *Acta Cryst.*, **22**, 43 (1967). ^g B. E. Robertson and C. Calvo, *ibid.*, **22**, 665 (1967). ^h C. Calvo, *ibid.*, **23**, 289 (1967). ⁱ D. W. J. Cruickshank, *ibid.*, **17**, 671 (1964). ^j D. W. J. Cruickshank, *ibid.*, **17**, 677 (1964). ^k G. J. Bullens, *J. Chem. Soc.*, 3193 (1962). ^l G. B. Ansell and G. J. Bullens, *Chem. Commun.*, 493 (1965). ^m Mean value with average esd in parentheses.

 TABLE XI
 MAGNITUDE OF THERMAL ELLIPSOIDS FOR
 CHELATE RINGS OF OMPA

Atom	Root-mean-square amplitude, Å		
	(\bar{u}_1^2) ^{1/2}	(\bar{u}_2^2) ^{1/2}	(\bar{u}_3^2) ^{1/2}
Cu	0.203	0.203	0.222
Mg	0.225	0.225	0.249
Co	0.195	0.195	0.229
O(1)Cu	0.263	0.248	0.215
O(1)Mg	0.264	0.244	0.225
O(1)Co	0.253	0.217	0.191
O(2)Cu	0.295	0.246	0.200
O(2)Mg	0.304	0.271	0.220
O(2)Co	0.289	0.241	0.205
P(1)Cu	0.242	0.237	0.214
P(1)Mg	0.261	0.256	0.219
P(1)Co	0.240	0.239	0.199

OMPA indicated the metal-oxygen bond was essentially electrostatic. The characteristic band for Cu(II) complexes is shifted into the near-infrared region for the tris-OMPA complex.²³ The spectrochemical parameters for the tris-OMPA complex of Ni(II) place this ligand at the low end of both the spectrochemical and the nephelauxetic series.

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Although the planarity of the chelate rings would be consistent with electron delocalization in the ring, the fact that the P-O and P-O-(P) bond lengths are unaffected by the type of metal ion lends further support to the electrostatic character of the metal-oxygen bond. The function of the metal ion appears to be one of orientation of the pyrophosphate linkage by electrostatic interaction. Partial dπ-pπ delocalization in the pyrophosphate portion of the chelate ring may be a contributing factor to the planarity of the chelate ring.

Acknowledgments.—The authors are indebted to Dr. T. J. Shaffner and Mrs. Johnetta Smith for assistance in various stages of this analysis and to Dr. J. M. Stewart for help in the use of the X-ray 63 program system for crystallography. The computing was done at the Common Research Computer Facility, Houston, Texas, under USPHS Grant FR00254. Other stages of the work were supported by grants from the Public Health Service (GM-15451-01 and AM-09085-04), American Cancer Society, and Vanderbilt University Research Council.