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CRYSTAL STRUCTURE AND MAGNETIC STUDIES OF BIS (MU-DIBUTYLPHOSPH--ETC(U)  
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CRYSTAL STRUCTURE AND MAGNETIC STUDIES OF  
BIS ( $\mu$ -DIBUTYLPHOSPHINATO)COPPER(II)

by

R. Cini, P. Colamarino, P. L. Orioli, L. S. Smith,  
P. R. Newman, H. D. Gillman, and P. Nannelli

Prepared for publication

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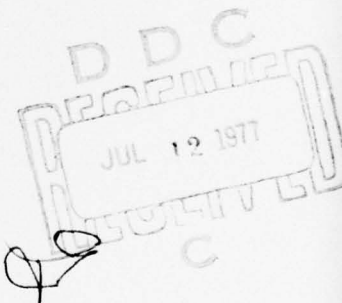
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br><br>The structure of $\text{Cu}[\text{OP}(\text{C}_4\text{H}_9)_2\text{O}]_2$ in the solid state has<br>been determined by three-dimensional single-crystal x-ray<br>techniques. The compound crystallizes in the triclinic space<br>group P1 with two formula units in a cell of dimensions:<br>$a = 12.245(6)$ , $b = 9.863(5)$ , $c = 9.819(5)$ Å; $\alpha = 101.18(4)$ ,<br>$\beta = 105.78(5)$ , $\gamma = 93.77(4)^\circ$ ; $V = 1110.7$ Å <sup>3</sup> , $d_c = d_m =$ |                       |                                                                |

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### Abstract

The structure of  $\text{Cu}[\text{OP}(\text{C}_4\text{H}_9)_2\text{O}]_2$  in the solid state has been determined by three-dimensional single-crystal x-ray techniques. The compound crystallizes in the triclinic space group  $\text{P}\bar{1}$  with two formula units in a cell of dimensions:  $\underline{a} = 12.245(6)$ ,  $\underline{b} = 9.863(5)$ ,  $\underline{c} = 9.819(5)$  Å;  $\underline{\alpha} = 101.18(4)$ ,  $\underline{\beta} = 105.78(5)$ ,  $\underline{\gamma} = 93.77(4)^\circ$ ;  $V = 1110.7$  Å<sup>3</sup>,  $d_c = d_m = 1.25$  g cm<sup>-3</sup>. The structure was solved by the heavy-atom technique, and least squares refinement gave an R factor of 0.061. The structure consists of polymeric chains of copper atoms linked by double phosphinate bridges. The coordination around each copper atom can be described as a very flattened tetrahedron. The g tensors for oriented single crystals were determined by ESR and range from 2.07 to 2.41, with the larger value in a direction nearly normal to a mean plane formed by the copper atoms and the ligands. The spin orbit coupling constant suggests considerable mixing of metal and ligand orbitals in this polymer.

## Introduction

The poly(metal phosphinates), which are inorganic coordination polymers consisting of metal ions linked by phosphinate (OPO) bridges, have been extensively studied because of their potential in a variety of high temperature applications including coatings and grease thickeners.<sup>2</sup> Recently we have become interested in the magnetic properties of these unique one dimensional inorganic complexes and initiated an investigation of these properties. In this regard we studied the temperature dependent magnetic susceptibilities of a number of these materials and found that the OPO bridges provided a path for antiferromagnetic superexchange  $J/K \sim 0-5K$ .<sup>3,4</sup> In addition, more extensive studies of some chromium phosphinates also indicated that disorder plays an important role in determining the magnetic properties of these polymers by limiting the range of spin correlation.<sup>3</sup> In order to extend our understanding of this system further, we report here a single crystal study of  $Cu[OP(C_4H_9)_2O]_2$  including its complete crystallographic structure and the orientation of the electronic  $\vec{g}$  tensor relative to the atomic configuration.

## Experimental Section

The preparation of  $Cu[OP(C_4H_9)_2O]_2$  has previously been reported.<sup>5</sup> Some crystals were obtained from dilute aqueous solutions, whereas other larger crystals were obtained from dilute ethanol solutions.

Crystal Structure Data Collection. The title compound crystallizes in the triclinic space group  $P\bar{1}$  with two formula units in a cell with dimensions  $[\lambda(\text{Mo-K}\alpha) = 0.7107 \text{ \AA}^\circ, \mu(\text{Mo-K}\alpha) = 11.40 \text{ cm}^{-1}]$ :  $a = 12.245(6)$ ,  $b = 9.863(5)$ ,  $c = 9.819(5) \text{ \AA}$ ;  $\alpha = 101.18(4)$ ,  $\beta = 105.78(5)$ ,  $\gamma = 93.77(4)^\circ$ ;  $V = 1110.7 \text{ \AA}^3$ . The calculated density of  $1.249 \text{ g/cm}^3$  agrees well with that of  $1.253 \text{ g/cm}^3$  measured by flotation in potassium tetraiodomercurate. Intensity data were collected on a Philips automatic diffractometer with the  $\omega - 2\theta$  scan technique, at a scan speed of  $0.05^\circ/\text{sec}$  and a scan width of  $1.20^\circ$  in  $\omega$ . Stationary-counter stationary-crystal background counts of 15 sec were taken at each end of the scan range. The 2462 reflections having  $I > 2\sigma(I)$  were collected in the range  $6 < 2\theta < 50^\circ$  and used for the structure determination and refinement. The standard deviation  $\sigma(I)$  of the corrected intensity  $I$  was taken as:  $\sigma(I) = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (KI)^2]^{1/2}$  where  $P$  is the peak count,  $B_1$  and  $B_2$  are the background counts, and  $T_p$  and  $T_b$  are the count times on the peak and background, respectively. The factor  $K$  was found to be 0.02 by a least squares fit of three standard reflections monitored at regular intervals. Intensities were corrected for Lorentz-polarization effects; absorption effects were neglected.

Structure Solution and Refinement. The structure was solved by the heavy-atom technique with the use of Patterson and Fourier syntheses, which gave all the non-hydrogen atom posi-

tions. Two cycles of least squares with isotropic temperature factors for all the atoms, followed by two cycles with anisotropic temperature factors for Cu, P and O atoms reduced the R factor to 0.061. The function minimized was  $\sum w (|F_o| - |F_c|)^2$  with weights taken as  $w = 4F_o^2/\sigma^2(F_o^2)$ . At this point a difference electron density synthesis showed 26 out of 36 hydrogen atoms. The positions of the other hydrogen atoms were calculated. Introduction of hydrogen atoms with the temperature factors of the carbon atoms to which they are attached, followed by two cycles of least squares, gave final values for R and R' factors of 0.050 and 0.053 respectively (R' is defined as  $[\sum w (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ ). Atomic scattering factors were taken from Cromer and Waber<sup>6</sup> for Cu, P, O, and C atoms and from Stewart, et al.,<sup>7</sup> for H atoms. Cu and P scattering factors were corrected for the real and imaginary part of anomalous dispersion effects. All the calculations were performed with the use of the X-RAY 72 system of programs, adapted for the C11 10070 computer of the University of Florence. Final atomic parameters with their estimated standard deviations are listed in Table 1.

## Electron Spin Resonance

Single crystals were selected after observation under cross polarizers to eliminate twinned samples. Alignment was accomplished by using x-ray precession photographs of the zero-level reflections (hk0) and (0kl). The aligned crystal was then fixed to the wall of a rectangular TE<sub>102</sub> cavity which was cooled to 77K and operated at 10 GHz. The magnitude of the resonant field was calibrated by inserting a small amount of diphenyl picryl hydrazyl (DPPH) in the cavity. The resonant magnetic fields as a function of magnet angle were measured for three orthogonal rotations. The resulting data for each rotation (see Fig. 1) were fit to the expression.

$$g^2 = \alpha + \beta \cos^2 \theta + \gamma \sin^2 \theta$$

with

$$\alpha = \frac{g_+^2 + g_-^2}{2} \quad \beta = \frac{g_+^2 - g_-^2}{2} \cos 2\theta_+ \quad \gamma = \frac{g_+^2 - g_-^2}{2} \sin 2\theta_+$$

where  $g_+$  and  $g_-$  are the maximum and minimum  $g$  values occurring at  $\theta_+$  and  $\theta_-$  for each rotation. The parameters  $\alpha^i$ ,  $\beta^i$ , and  $\gamma^i$  ( $i$  denotes the rotation axis) are then used to define a matrix  $\overline{\overline{w}}$ . The eigenvalues of the  $\overline{\overline{w}}$  matrix are the squares of the principal values of the  $\overrightarrow{g}$  tensor. In addition the eigenvectors are composed of the directional cosines of the principal axes of the  $\overrightarrow{g}$  tensor relative to the fixed (laboratory) coordinates used to index the external magnetic field

orientation. The previous alignment of the crystal was then used to relate the orientation of the principal axes of the  $g$  tensor to the atomic coordination surrounding each  $\text{Cu}^{2+}$  ion.<sup>8</sup>

#### Magnetic Susceptibility

Approximately 11 mg of polycrystalline material was used for measurement of the magnetic susceptibility in a Faraday balance over the temperature range from  $77\text{K} \leq T \leq 300\text{K}$ . The details of the experimental apparatus are described elsewhere.<sup>9</sup>

Description of the Structure. The overall structure of bis-(dibutylphosphinato)copper(II) is similar to that of the analogous bis(diphenylphosphinato)lead(II),<sup>10</sup> i.e., it consists of polymeric chains in which the phosphinate groups form double bridges between copper atoms (Figure 2). The endless chains wind around the crystallographic  $c$  axis. The coordination around the copper atom can be described as a very flattened tetrahedron with approximate  $D_{2d}$  symmetry (Figure 3). This type of coordination geometry is rather common in four-coordinate copper(II) compounds. The average Cu-O distance is  $1.920(4)\text{\AA}$ , a value in agreement with other Cu-O bond lengths in four-coordinate copper compounds. The Cu-Cu distance along the chain is  $4.938(2)$ . Bond lengths and angles in the phosphinate group are in agreement with the values found in bis(diphenylphosphinato)lead(II) (Table 2).

The single crystal x-ray studies of a few zinc phosphinates showed them all to consist of tetrahedral metal atoms linked by alternating single and triple phosphinate bridges.<sup>11</sup> Some cobalt phosphinates have been shown to be isomorphous with their zinc analogs,<sup>12</sup> and x-ray fiber studies have indicated that a beryllium phosphinate also has the single-triple bridged structure.<sup>13</sup> This copper phosphinate is the first definitively characterized poly(metal phosphinate) with tetrahedral metal centers (albeit distorted) and double phosphinate bridging.

#### ESR and The g-Tensor

The x-ray precession photographs were used to relate the principal g values and orientation of the g-tensor to the atomic coordination of the  $\text{Cu}^{2+}$  ions as shown in Fig. 4. The largest g-value, 2.41, is found in a direction nearly in the bc plane of the crystal, approximately normal to a plane formed by completely flattening the tetrahedron of four oxygens surrounding the copper.

This g-tensor is consistent with those normally seen for  $\text{Cu}^{2+}$  in an approximate square planar ligand field. For  $\text{Cu}^{2+}$  in a tetragonal field the principal g values are given by:

$$g_{zz} = 2 - \frac{8\lambda}{\Delta_0} \quad g_{xx} = g_{yy} = 2 - \frac{2\lambda}{\Delta_1}$$

in which  $\Delta_0$  is the splitting between  $d_{x^2-y^2}$  and  $d_{xy}$  and  $\Delta_1$  is the difference in energy between  $d_{x^2-y^2}$  and the (degenerate)  $d_{xz}$  and  $d_{yz}$  orbitals. Thus the largest  $g$  value should occur along the  $z$ -axis or perpendicular to the square planar arrangement. If we assume  $\Delta_0$  is approximately equal to  $\Delta = 13000 \text{ cm}^{-1}$  (estimated from absorption spectra), we calculate a value of  $\lambda = -500 \pm 100 \text{ cm}^{-1}$  (with the variation due to anisotropy). This is somewhat less than the free ion value of  $-830 \text{ cm}^{-1}$  and indicates significant mixing of metal and ligand orbitals.

#### ESR - Linewidth

The resonance line was a single-well resolved absorption at all temperatures in the range  $1.1\text{K} \leq T \leq 300\text{K}$ . The linewidth and  $g$  value are both anisotropic but nearly temperature independent. Fig. 5 shows the range of linewidth anisotropy for a typical rotation. The angular dependence is reminiscent of magnetic dipolar interaction with functional dependence on angle given by  $(3 \cos^2\theta - 1)^2$  in three dimensions and  $(3 \cos^2\theta - 1)^{4/3}$  in one dimension. The solid and dash lines show the best fits of these functions to the data. The approximate agreement and the linear character to the crystal structure suggest the possibility of one-dimensional magnetic dipolar interactions competing with an (isotropic) exchange mechanism.

### Magnetic Susceptibility

The high temperature magnetic susceptibility is Curie like with  $C = 0.485(1)$ . The  $g$  value of  $\chi_{\text{susc}} = 2.18(1)$  derived from the Curie constant compares well with the geometric average of the ESR  $g$  values.

Acknowledgement. We thank Prof. P. Zanazzi for the use of the diffractometer at the Istituto di Mineralogia, University of Perugia. We also thank Profs. A. J. Heeger and A. F. Garito and Dr. B. P. Block for discussions. The work was supported at Pennwalt in part by the Office of Naval Research and at the University of Pennsylvania by NSF-MRL grant No. DMR76-00678.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 x 148 mm, 24x reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$0.00 for photocopy or \$2.50 for microfiche, referring to code number AIC000000.

### Figure Captions

- Figure 1. The measured g values as a function of magnet angle for three orthogonal rotations.
- Figure 2. ORTEP drawing showing the polymeric chain of bis(dibutylphosphinato)copper(II).
- Figure 3. ORTEP drawing of the bis(dibutylphosphinato)-copper(II) moiety. The numbering scheme is the same as that used in the tables. Superscripts 1 and 11 refer respectively to atoms related through the centers of symmetry at 0,0,0 and 0,0,1/2.
- Figure 4. The orientation of the principal g values.
- Figure 5. Linewidth variation as a function of angle of rotation.

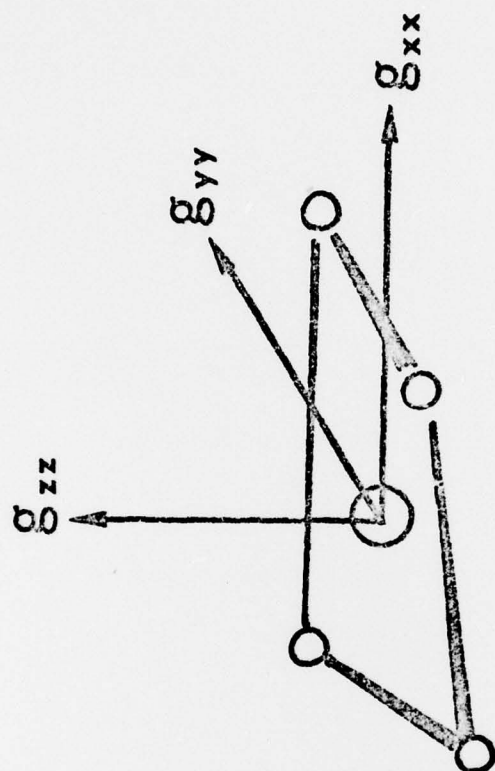


FIG. 1

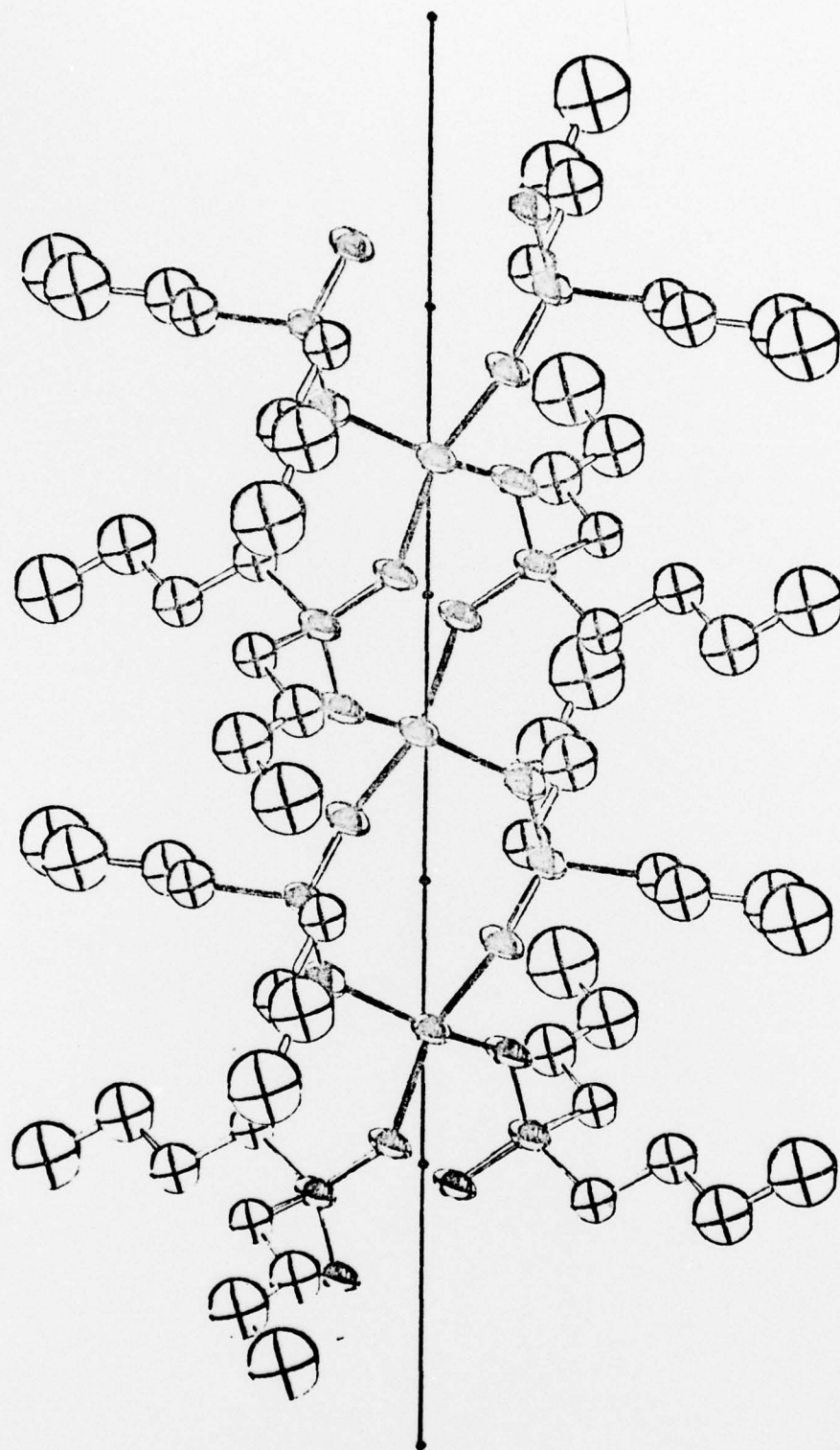


FIG. 2

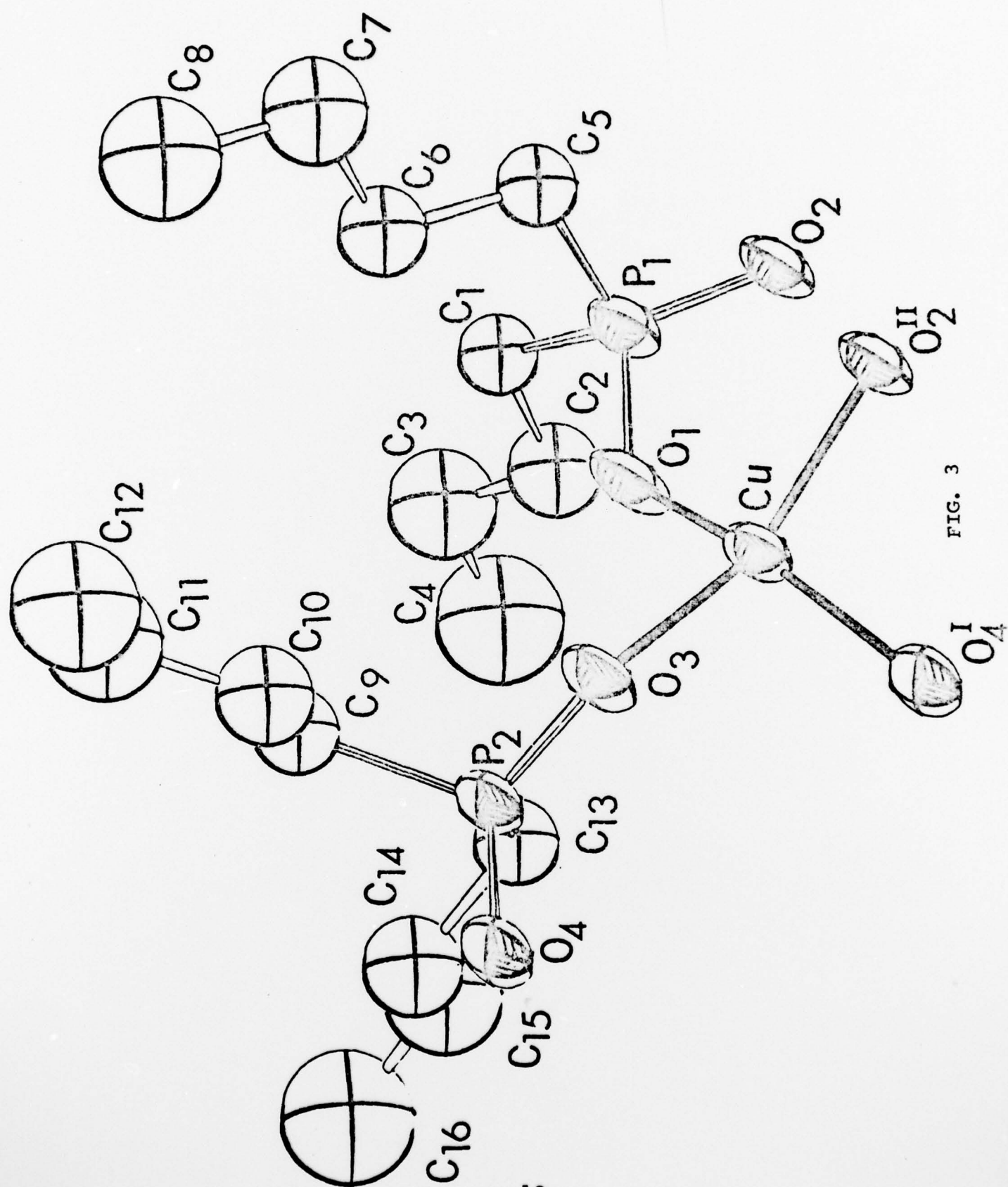


FIG. 3

FIG. 4

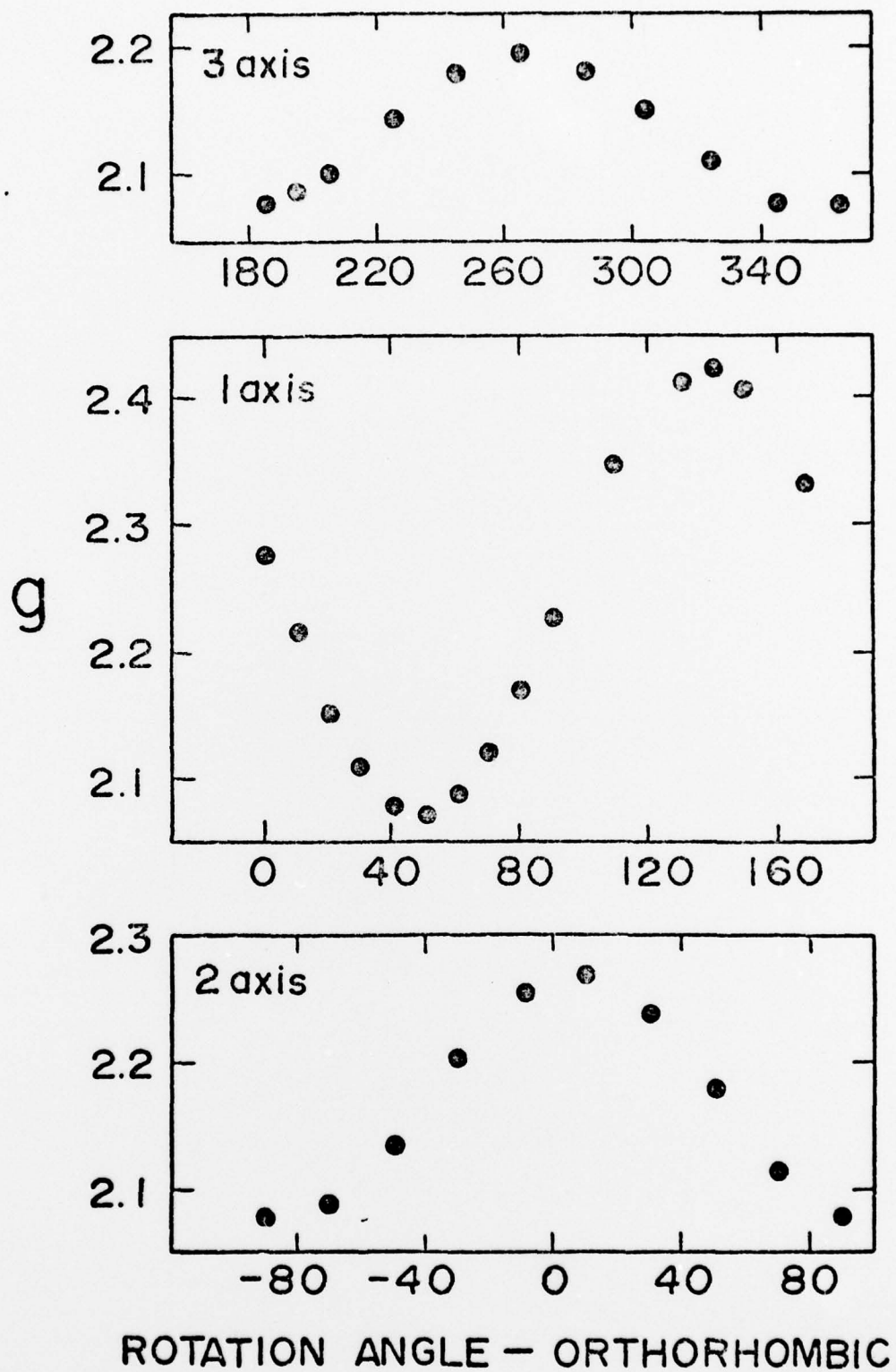
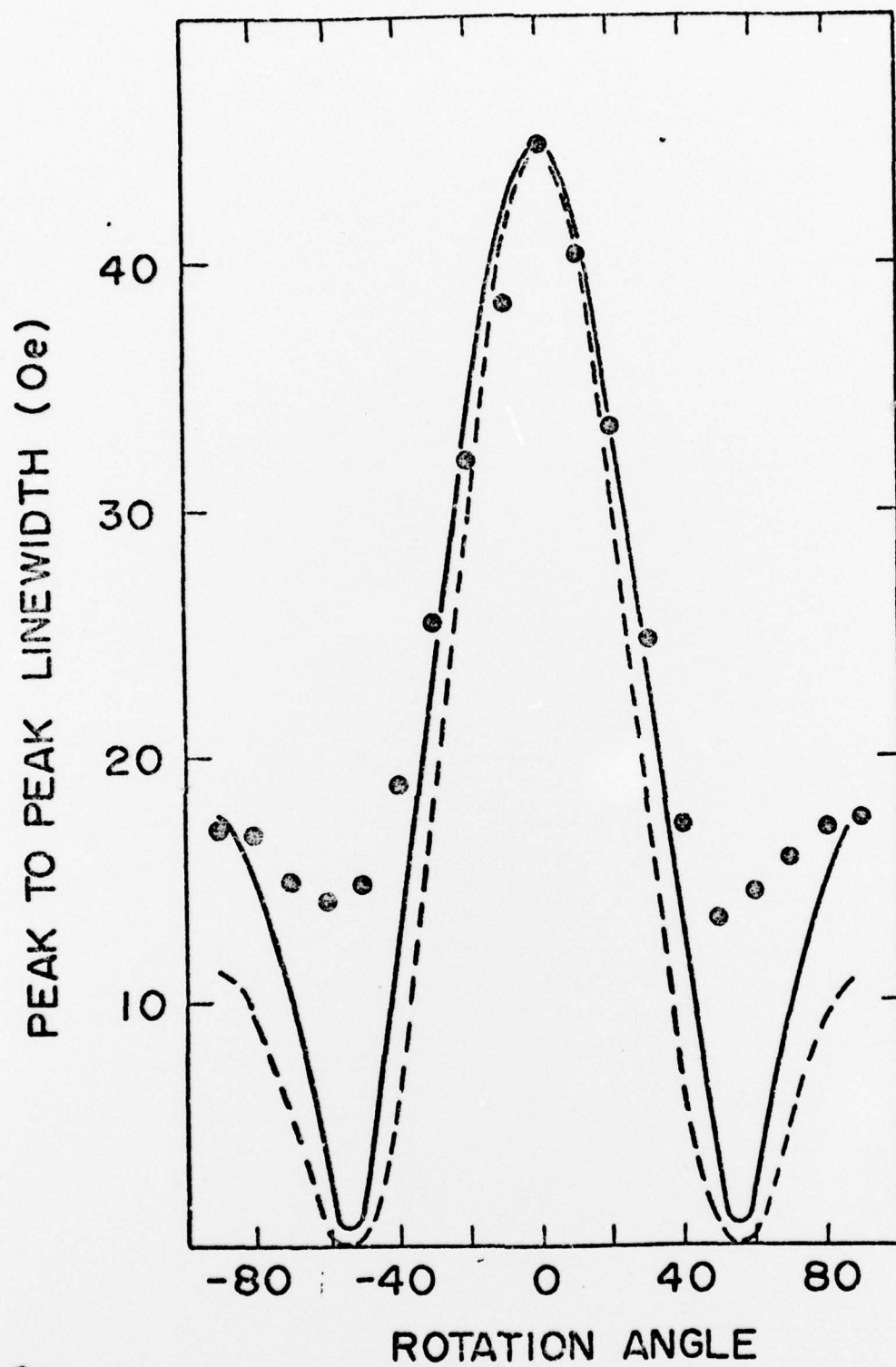


FIG. 5



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TABLE 1

POSITIONAL PARAMETERS ( X 10<sup>4</sup> ), THERMAL PARAMETERS ( ANGSTRÖM<sup>2</sup> X 10<sup>3</sup> ) AND ESTIMATED STANDARD DEVIATIONS FOR THE ATOMS OF BIS(DIBUTYLPHOSPHINATO)COPPER(II).

| ATOM | X/A     | Y/B       | Z/C      | U11    | U22   | U33     | U12       | J13       | J23    |
|------|---------|-----------|----------|--------|-------|---------|-----------|-----------|--------|
| CJ   | 113(1)  | 257(1)    | 2588(1)  | 46(0)  | 51(0) | 24(0)   | 15(0)     | 19(0)     | 12(0)  |
| P(1) | 1389(1) | -938(2)   | 5235(2)  | 51(1)  | 51(1) | 27(1)   | 21(1)     | 20(1)     | 13(1)  |
| P(2) | 1598(1) | -480(2)   | 381(2)   | 43(1)  | 65(1) | 27(1)   | 15(1)     | 18(1)     | 16(1)  |
| S(1) | 1097(3) | -858(4)   | 3647(4)  | 66(3)  | 78(3) | 28(2)   | 41(2)     | 28(2)     | 20(2)  |
| S(2) | 378(3)  | -1164(4)  | 5799(4)  | 54(3)  | 56(3) | 29(2)   | 18(2)     | 25(2)     | 9(2)   |
| S(3) | 1058(3) | 452(4)    | 1350(4)  | 54(3)  | 62(3) | 32(2)   | 12(2)     | 28(2)     | 17(2)  |
| S(4) | 1307(3) | -319(4)   | -1184(4) | 49(3)  | 94(3) | 32(2)   | 19(2)     | 21(2)     | 24(2)  |
| ATOM | X/A     | Y/B       | Z/C      | J      | AT9M  | X/A     | Y/B       | Z/C       | U      |
| C(1) | 2180(5) | -2399(6)  | 5388(6)  | 51(2)  | C(9)  | 3133(6) | -42(7)    | 1097(7)   | 60(2)  |
| C(2) | 1522(6) | -3740(7)  | 4512(7)  | 70(2)  | C(10) | 3490(7) | 1458(8)   | 1104(8)   | 79(2)  |
| C(3) | 2221(7) | -4985(9)  | 4540(9)  | 96(3)  | C(11) | 4771(8) | 1901(10)  | 1636(10)  | 115(3) |
| C(4) | 1555(9) | -6289(11) | 3660(11) | 133(4) | C(12) | 5094(9) | 3395(11)  | 1639(11)  | 133(4) |
| C(5) | 2318(5) | 582(6)    | 6328(6)  | 52(2)  | C(13) | 1255(5) | -2268(7)  | 400(7)    | 59(2)  |
| C(6) | 3373(6) | 962(7)    | 5870(7)  | 64(2)  | C(14) | 1749(6) | -3316(8)  | -561(8)   | 81(2)  |
| C(7) | 4113(7) | 2236(8)   | 6797(9)  | 90(3)  | C(15) | 1417(8) | -4788(10) | -503(10)  | 114(3) |
| C(8) | 5170(8) | 2611(10)  | 6323(10) | 120(3) | C(16) | 1855(9) | -5867(11) | -1442(12) | 146(4) |

( CONTINUED OVER )

(CONTINUED TABLE 1)

| ATOM  | X/A  | Y/B   | Z/C  | U   | AT9M  | X/A  | Y/B   | Z/C   | U   |
|-------|------|-------|------|-----|-------|------|-------|-------|-----|
| H(1)  | 2521 | -2361 | 5448 | 51  | H(19) | 3305 | -172  | 2150  | 60  |
| H(2)  | 2899 | -2195 | 5119 | 51  | H(20) | 3468 | -676  | 532   | 60  |
| H(3)  | 974  | -3825 | 3573 | 70  | H(21) | 3303 | 1586  | 0     | 79  |
| H(4)  | 826  | -4027 | 4835 | 70  | H(22) | 3323 | 2555  | 1710  | 79  |
| H(5)  | 2884 | -4586 | 4153 | 96  | H(23) | 4847 | 1507  | 2513  | 115 |
| H(6)  | 2513 | -5077 | 5733 | 96  | H(24) | 5151 | 1316  | 1005  | 115 |
| H(7)  | 717  | -6367 | 3173 | 133 | H(25) | 4656 | 3861  | 2355  | 133 |
| H(8)  | 1945 | -6617 | 2911 | 133 | H(26) | 4969 | 3592  | 743   | 133 |
| H(9)  | 1693 | -6995 | 4266 | 133 | H(27) | 6180 | 3703  | 2082  | 133 |
| H(10) | 1834 | 1223  | 6203 | 52  | H(28) | 528  | -2310 | 0     | 59  |
| H(11) | 2621 | 548   | 7358 | 52  | H(29) | 1583 | -2366 | 1400  | 59  |
| H(12) | 3723 | 0     | 5761 | 64  | H(30) | 1424 | -3124 | -1522 | 81  |
| H(13) | 3223 | 712   | 4800 | 64  | H(31) | 2503 | -3216 | -135  | 81  |
| H(14) | 3861 | 3061  | 7370 | 90  | H(32) | 587  | -4936 | -739  | 114 |
| H(15) | 4508 | 1826  | 7519 | 90  | H(33) | 1716 | -4926 | 476   | 114 |
| H(16) | 4774 | 2931  | 5587 | 120 | H(34) | 2627 | -5573 | -1086 | 146 |
| H(17) | 5601 | 1753  | 6343 | 120 | H(35) | 1280 | -5816 | -2553 | 146 |
| H(18) | 5656 | 3395  | 7077 | 120 | H(36) | 1636 | -6812 | -1343 | 146 |

\* ANISOTROPIC THERMAL FACTORS ARE OF THE FORM :

$$\exp(-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 h_i h_j a_i^* a_j^* U_{ij})$$

TABLE 2

Bond lengths ( Å ) and angles ( ° ) with estimated standard deviations in parentheses .

|                       |          |                                           |          |
|-----------------------|----------|-------------------------------------------|----------|
| Cu-O(1)               | 1.919(4) | O(1)-Cu-O(2) <sup>II</sup>                | 95.7(2)  |
| Cu-O(2) <sup>II</sup> | 1.926(4) | O(1)-Cu-O(3)                              | 93.7(2)  |
| Cu-O(3)               | 1.919(4) | O(1)-Cu-O(4) <sup>I</sup>                 | 147.2(2) |
| Cu-O(4) <sup>I</sup>  | 1.916(4) | O(2) <sup>II</sup> -Cu-O(3)               | 145.8(2) |
|                       |          | O(2) <sup>II</sup> -Cu-O(4) <sup>I</sup>  | 93.7(2)  |
|                       |          | O(3)-Cu-O(4) <sup>I</sup>                 | 96.0(2)  |
|                       |          | Cu-O(1)-P(1)                              | 130.8(3) |
|                       |          | Cu-O(2) <sup>II</sup> -P(1) <sup>II</sup> | 135.8(2) |
|                       |          | Cu-O(3)-P(2)                              | 137.9(3) |
|                       |          | Cu-O(4) <sup>I</sup> -P(2) <sup>I</sup>   | 132.4(3) |
| P(1)-O(1)             | 1.521(4) | O(1)-P(1)-O(2)                            | 115.4(2) |
| P(1)-O(2)             | 1.508(5) | O(1)-P(1)-O(3)                            | 105.8(3) |
| P(1)-O(3)             | 1.780(7) | O(1)-P(1)-O(5)                            | 109.6(3) |
| P(1)-O(5)             | 1.783(5) | O(2)-P(1)-O(3)                            | 107.9(3) |
|                       |          | O(2)-P(1)-O(5)                            | 110.3(3) |
|                       |          | O(3)-P(1)-O(5)                            | 107.5(3) |
| P(2)-O(3)             | 1.507(4) | O(3)-P(2)-O(4)                            | 115.7(2) |
| P(2)-O(4)             | 1.522(4) | O(3)-P(2)-O(9)                            | 107.8(2) |
| P(2)-O(9)             | 1.809(6) | O(3)-P(2)-O(13)                           | 110.5(3) |
| P(2)-O(13)            | 1.790(7) | O(4)-P(2)-O(9)                            | 105.4(3) |
|                       |          | O(4)-P(2)-O(13)                           | 109.2(3) |
|                       |          | O(9)-P(2)-O(13)                           | 108.0(3) |

( Continued over )

( continued table 2 )

|             |         |                   |          |
|-------------|---------|-------------------|----------|
| C(1)-C(2)   | 1.48(1) | P(1)-C(1)-C(2)    | 113.6(4) |
| C(2)-C(3)   | 1.54(1) | C(1)-C(2)-C(3)    | 114.1(5) |
| C(3)-C(4)   | 1.45(1) | C(2)-C(3)-C(4)    | 112.9(7) |
| C(5)-C(6)   | 1.53(1) | P(1)-C(5)-C(6)    | 116.3(4) |
| C(6)-C(7)   | 1.48(1) | C(5)-C(6)-C(7)    | 114.5(6) |
| C(7)-C(8)   | 1.54(1) | C(6)-C(7)-C(8)    | 114.1(7) |
| C(9)-C(10)  | 1.51(1) | P(2)-C(9)-C(10)   | 111.0(5) |
| C(10)-C(11) | 1.52(1) | C(9)-C(10)-C(11)  | 114.6(7) |
| C(11)-C(12) | 1.50(2) | C(10)-C(11)-C(12) | 113.1(8) |
| C(13)-C(14) | 1.53(1) | P(2)-C(13)-C(14)  | 115.1(6) |
| C(14)-C(15) | 1.50(1) | C(13)-C(14)-C(15) | 112.1(7) |
| C(15)-C(16) | 1.50(2) | C(14)-C(15)-C(16) | 114.8(9) |

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