mize the separation between the triphenylphosphine groups subject to the limitations set by the spatial extent of the anion, and of localized, directional electronic interactions. It should be noted that the adoption of this viewpoint in no way diminishes the validity of the arguments previously advanced for the opening up of the P–Cu–P angle but merely requires the explanation of smaller deviations from the "expected" value.[16]

Registry No. Bromobis(triphenylphosphine)copper(I) hemibenzenate, 36273-10-6.

Acknowledgment. This work was supported in part by the National Science Foundation, the University of Illinois Graduate Research Board, and the award of an NSF predoctoral fellowship to P. H. D. The authors wish to thank Dr. E. K. Barefield for helpful discussions.

(16) Subsequent to the submission of this article there appeared a preliminary communication of the structure of another monomeric, three-coordinate copper(I) complex, tris(2-picoline)copper(I) perchlorate: A. H. Lewin, R. J. Michl, P. Ganis, and U. Lepore, *J. Chem. Soc., Chem. Commun.*, 661 (1972). As in the present case the geometry of this cationic, three-coordinate copper(I) species deviates from the idealized trigonal planar. The extent of the deviation is obscured by an apparent error in reporting the bond angles about the Cu atom. As given, the sum of these angles is 370°. Geometric considerations require the sum to be $\leqslant 360°$.

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The Crystal and Molecular Structure of Tris(tetraisopropylmethylenediphosphonate)copper(II) Perchlorate with Comments on the Jahn-Teller Effect[1a]

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Received May 11, 1971

Tris(tetraisopropylmethylenediphosphonate)copper(II) perchlorate, $Cu[[(CH_3)_2CHO]_2P(O)CH_2P(O)[OCH(CH_3)_2]_2]_3(ClO_4)_2$, crystallizes in the monoclinic space group *C*2/*c* with eight molecules per unit cell. The unit cell dimensions are $a = 29.126$ (6) Å, $b = 23.399$ (4) Å, $c = 21.696$ (4) Å, and $\beta = 118.86$ (1)°. Intensity data were collected with a four-circle computer-controlled diffractometer using the θ–2θ scan technique. All 74 nonhydrogen atoms were refined anisotropically and the 90 hydrogen atoms were included as fixed atoms. Refinement by full-matrix least squares using 11,541 reflections gave a final *R* factor of 0.063. The CuO_6 group is a slightly distorted octahedron. Average bond distances and bond angles with rms deviations for the chelate rings are as follows: Cu–O, 2.089 Å (range 2.067–2.111 Å); P–O, 1.478 (5) Å; P–C–(P), 1.787 (8) Å; O–Cu–O, 90.1 (8)°; Cu–O–P, 131.0 (15)°; O–P–C, 112.3 (11)°; and P–C–P, 114.1 (14)°. Structural data for six-coordinate Cu(II) complexes with equivalent donor sites are compared with data for complexes where Jahn-Teller distortions are not expected. The results are interpreted in terms of a negligible static Jahn-Teller distortion in six-coordinate Cu(II) complexes with equivalent donor sites.

Introduction

The present paper describes the crystal and molecular structure of tris(tetraisopropylmethylenediphosphonate)copper(II) perchlorate, $Cu[[(CH_3)_2CHO]_2P(O)CH_2P(O)[OCH(CH_3)_2]_2]_3(ClO_4)_2$ (referred to as CuIPCP). Structural data are now available for seven complexes of six-coordinate Cu(II) which contain identical monodentate or bidentate ligands.[2] These data will be analyzed in terms of the Jahn-Teller effect.

Collection and Reduction of Data

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

The ligand IPCP was synthesized according to the procedure of Walmsley and Tyree[3]. Lannert[4] first synthesized the Cu complex by mixing hydrated copper(II) perchlorate and ligand in a 1:4 mole ratio in acetone. The compound was isolated by evaporating the acetone solution at room temperature in a desiccator. Well-formed hexagonal needles suitable for X-ray studies were obtained by using absolute ethanol rather than acetone in the above procedure. The data crystal was easily cleaved parallel to (101) to give a 0.64 × 0.94 × 0.64 mm hexagonal prism which was mounted with b^* parallel to the ϕ axis of the diffractometer. Like CuPCP, CuIPCP crystals are slightly sensitive to atmospheric moisture and X-radiation. However, special procedures were not required to protect the data crystal.

Precession photographs showed the crystals to be monoclinic with *hkl* reflections absent for $h + k$ odd and *h*0*l* reflections absent for *l* odd. The space group is therefore either *C*2/*c* or *Cc*.[5] The crystal density of 1.328 g/cm³, measured by flotation in a mixture of *n*-heptane and carbon tetrachloride, compares with the calculated value of 1.320 g/cm³ based on eight molecules per unit cell (volume 13037.8 Å³) and a molecular weight of 1295.42. Karle-Hauptman statistics indicated a center of symmetry,[6,7] so the space group *C*2/*c* was assumed. This choice was confirmed by the structure analysis.

Accurate cell parameters were determined at 21° from 26 high-angle reflections ($2\theta > 50°$) manually centered on an accurately aligned four-circle diffractometer using the Cu Kα_1 line of the resolved doublet (λ 1.54051 Å) and a 1.0° X-ray tube takeoff angle. Least-squares refinement with diffractometer angles of 2θ, ω, and χ as observations gave $a = 29.126$ (6) Å, $b = 23.399$ (4) Å, $c = 21.696$ (4) Å, and $\beta = 118.86$ (1)°.

Intensity data were collected with a four-circle computer-controlled Picker diffractometer (FACS-I system) using a Digital Equipment Corp. PDP-8/I with a DF-32 disk memory. The data set was measured with Mo Kα radiation complete to $2\theta = 50°$ in the *hkl* and $\bar{h}kl$ octants and included 11,541 reflections. A complete description of the experimental conditions and procedures for reduction of data are given in the previous paper of this series.[2]

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

(2) P. T. Miller, P. G. Lenhert, and M. D. Joesten, *Inorg. Chem.*, 11, 2221 (1972), and references therein.

(3) J. W. Walmsley and S. Y. Tyree, *Inorg. Chem.*, 2, 312 (1963).

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

(5) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965.

(6) H. Hauptman and J. Karle, "Solution of the Phase Problem. I. The Centrosymmetric Crystal," ACA Monograph No. 3, Polycrystal Book Service, Pittsburg, Pa., 1953, and references therein.

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

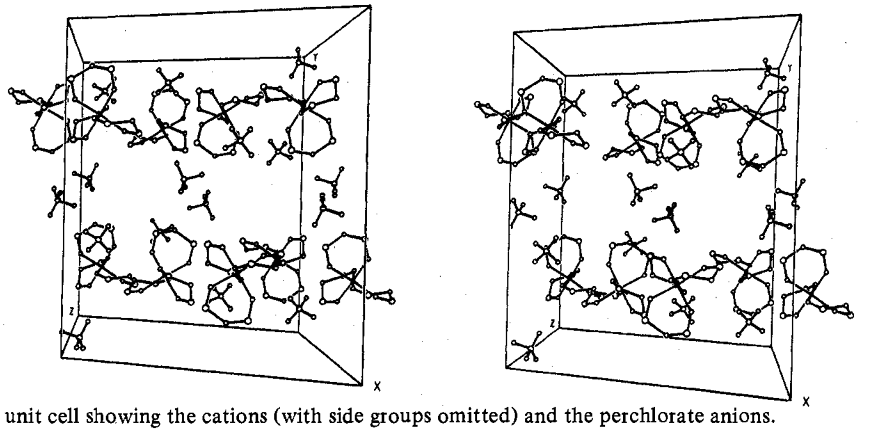

Figure 1. Stereogram of unit cell showing the cations (with side groups omitted) and the perchlorate anions.

Absorption corrections were made using a linear absorption coefficient of 6.5414 cm^{-1} calculated from mass absorption coefficients for Mo Kα.[8] The calculated absorption factors ranged from 0.645 to 0.769 with an average of 0.718.

Solution and Refinement of the Structure

The CuIPCP structure was solved by the heavy-atom method using the F^2 and F_o Fourier synthesis and the $F_o - F_c$ difference synthesis, with subsequent refinement of nonhydrogen atoms by full-matrix least squares.

A sharpened, origin-removed F^2 synthesis showed all Cu–Cu vectors and several P–P vectors. Subsequent F_o and $F_o - F_c$ syntheses alternating with least-squares refinement allowed assignment of the remaining nonhydrogen atoms. Several additional full-matrix least-squares calculations were carried out using various blocks of up to 200 parameters selected from the 667 heavy-atom parameters. At this point, R was 0.078.

Most of the 90 hydrogen atoms were located by a combination of difference synthesis and methyl group geometry as described previously.[2] The remaining 18 were fixed by the tetrahedral geometry of the adjacent carbon atoms. Attempts to refine hydrogen coordinates by least squares were unsuccessful.

In the final cycle of refinement the parameters of the 90 hydrogen atoms were fixed and all other atoms were refined anisotropically to a final R factor, $R = (\Sigma \| F_o | - | F_c \|)/\Sigma | F_o |$, of 0.063 and a weighted R', $R' = [[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w F_o^2]^{1/2}$, of 0.048. The final set of 11,541 data included reflections with $F_o = 0$ and allowed 17 observations for each of the 667 parameters refined.

Atomic scattering factors for Cu(II), P, Cl, O, N, and C were those tabulated by Cromer and Mann.[9] The Cu(II), Cl, and P scattering factors were corrected for the real part of anomalous dispersion. Hydrogen scattering factors were those of Stewart, Davidson, and Simpson.[10]

Structure factor, electron density, bond distance–angle, and least-squares calculations were carried out with the X-Ray 67 programs.[11]

The quantity minimized in the least-squares calculation was $\Sigma w(|F_o| - |F_c|)^2$ where the weights were $w = 1.0/\sigma^2(F)$ and ranged from 0.18 to 6.49. The atomic parameters and their standard deviations (calculated from the inverse matrix of the normal equations) are displayed in Table I. The values shown were used (before rounding) in the calculation of the final structure factors.[12] The large thermal parameters for the perchlorate oxygen atoms and some of the terminal methyl groups on the CuIPCP cation suggest local disorder. The average shift-to-error ratio for the final cycle was 0.18. The maximum ratio was 1.7 for a perchlorate coordinate and, in the IPCP ligands, 1.1 for B_{13} of C37. A final difference synthesis using all 11,541 reflections showed a maximum residual electron density of 0.76 e/Å^3 and a mimimum of −0.50 e/Å^3, both in the vicinity of the disordered perchlorate anions. No other residuals greater than 0.47 or less than −0.36 e/Å^3 appeared on the map.

Magnitudes and directions of thermal ellipsoid principal axes (Table II) are included to permit comparison with published values for other six-coordinate complexes of Cu(II) which have octahedral or trigonal symmetry.[2]

Description of the Structure

Figure 1 shows the orientation of the cations and anions in the unit cell. There is one C–H· · ·O interaction (C–O = 3.420 Å, H· · ·O = 2.536 Å) between two cations in adjacent layers; this is between a methylene hydrogen on C3 (H31) and the alkoxy oxygen O34 of the cation related by a twofold rotation (see Figure 2 for the numbering of the atoms). The nearest and next nearest copper atoms, related by a twofold rotation and inversion, respectively, lie in the sheets on either side of the original copper position (with copper-copper separations of 10.709 and 11.225 Å). These neighboring cations approach in the vicinity of the C1 and C3 methylene bridges of the original cation. In contrast to the packing of anions about the cation of CuPCP[2] (with anions near all methylene bridges), no anions are near the C1 and C3 bridges of CuIPCP so that the closest approach between cations involves atoms of rings A and B on neighboring cations. An examination of the interactions between cations gives an idea of the closeness of packing. In the CuPCP structure there were six intermolecular carbon-carbon distances less than 3.60 Å and 26 less than 4.00 Å. However, in the CuIPCP structure, there are only four carbon-carbon interactions less than 3.80 Å but 30 less than 4.00 Å.

Bond distances and bond angles are shown in Tables III and IV; Figure 2 shows the thermal motion. The geometry of the chelate rings (Figure 3) is similar to that of CuPCP.[2] Each chelate ring has a slightly twisted boat conformation with the bend in ring A opposite to that of rings B and C. The degree of twist in the rings is shown by the least-squares plane calculations given in Table V. The P_2O_2 combination is approximately planar and it makes dihedral angles of about 21° with the O–Cu–O plane and 43° with the P–C–P plane. These angles are very similar to those for CuPCP.[2] Apparently, the change from a dimethylamino substituent to an isopropoxy substituent has little influence on the conformation of the chelate ring.

The average bond distances and mean deviations for CuIPCP are as follows: phosphoryl P–O, 1.478 (5) Å; bridging P–C–(P), 1.787 (8) Å; alkoxy P–O, 1.554 (4) Å; O–C, 1.484 (19) Å; C–C, 1.484 (23) Å.

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(8) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(9) D. T. Cromer and I. B. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968)

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

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

(12) A listing of structure factors will appear immediately following this article in the microfilm edition of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-218.

Table I. Atomic Parameters for CuIPCP[a]

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
CU	.11780(1)	.27167(2)	.12095(2)	2.89(2)	3.02(2)	2.98(2)	.23(1)	1.42(1)	.15(1)
P(1)	.22628(3)	.26417(4)	.11203(4)	4.16(4)	3.71(4)	3.25(4)	.17(4)	1.83(3)	.18(3)
P(2)	.14675(3)	.34808(4)	.01874(4)	3.82(4)	3.83(4)	3.36(4)	.24(3)	1.72(4)	.24(3)
P(3)	.02414(3)	.30614(4)	.15180(4)	3.38(4)	4.15(5)	3.40(4)	.55(3)	1.55(3)	-.09(3)
P(4)	.13187(3)	.32964(4)	.26567(4)	3.42(4)	3.77(4)	3.17(4)	.35(3)	1.55(3)	.40(3)
P(5)	.08751(4)	.16634(4)	.01043(5)	4.28(5)	3.77(4)	5.29(5)	.07(4)	2.43(4)	.00(4)
P(6)	.11237(4)	.13633(4)	.15855(5)	4.20(5)	3.70(5)	5.14(5)	.53(4)	2.10(4)	.12(4)
O(1)	.19296(8)	.24483(9)	.14272(11)	5.01(12)	4.59(12)	3.52(10)	-.55(9)	2.19(9)	.43(9)
O(2)	.12501(8)	.34237(9)	.06758(11)	4.79(12)	4.44(11)	4.11(11)	.33(9)	2.75(10)	.00(9)
O(3)	.04276(8)	.28945(9)	.10207(10)	4.03(11)	4.87(12)	3.27(10)	1.02(9)	1.84(9)	.20(9)
O(4)	.14863(8)	.32160(9)	.21148(11)	3.78(10)	4.51(11)	4.07(11)	.12(9)	2.37(9)	.14(9)
O(5)	.08753(8)	.22775(9)	.02670(12)	4.62(11)	3.19(10)	5.78(13)	.31(9)	2.28(10)	.34(10)
O(6)	.11072(8)	.19795(9)	.17187(11)	4.94(12)	3.94(11)	4.94(13)	.87(10)	2.11(10)	-.41(10)
O(10)	.25910(9)	.21604(9)	.10166(11)	5.82(13)	4.56(12)	3.42(11)	1.86(10)	1.85(10)	.59(9)
O(14)	.26598(8)	.31177(9)	.15429(11)	4.13(11)	4.91(12)	3.75(11)	-.49(9)	2.10(9)	-.55(9)
O(20)	.18426(8)	.39978(8)	.03320(11)	4.35(11)	3.14(10)	4.99(12)	.17(9)	1.90(10)	.46(9)
O(24)	.10531(8)	.35377(10)	-.05913(11)	3.69(11)	6.05(14)	3.53(11)	.54(10)	1.19(9)	.43(10)
O(30)	.01053(8)	.37061(9)	.15034(11)	4.53(12)	4.25(11)	3.77(11)	1.46(9)	1.16(9)	-.08(9)
O(34)	-.02581(8)	.27395(10)	.14137(11)	3.81(11)	6.03(13)	5.07(12)	-.88(10)	2.21(10)	-1.94(11)
O(40)	.12693(8)	.39331(9)	.28200(11)	5.29(12)	3.76(11)	3.97(11)	.05(9)	2.39(10)	.04(9)
O(44)	.16676(8)	.30246(9)	.33802(11)	3.77(11)	4.87(12)	3.24(10)	-.12(9)	.65(9)	.81(9)
O(50)	.03260(8)	.13825(10)	-.02515(13)	4.28(12)	4.73(13)	6.29(14)	-.38(10)	1.51(11)	-.02(11)
O(54)	.11270(9)	.16096(10)	-.03862(13)	6.52(14)	5.06(13)	6.55(15)	.29(11)	4.13(13)	.27(11)
O(60)	.15389(9)	.10183(10)	.22074(13)	5.80(14)	4.74(13)	5.51(14)	1.16(11)	1.34(11)	1.00(11)
O(64)	.06033(9)	.10700(10)	.14305(13)	5.07(13)	5.74(14)	6.71(15)	-.53(11)	3.37(12)	-.13(12)
C(1)	.1884(1)	.2894(1)	.0245(2)	3.90(16)	3.22(15)	3.20(15)	.17(12)	1.79(13)	.09(12)
C(3)	.0709(1)	.2954(1)	.2406(2)	3.60(15)	3.79(15)	3.13(15)	.30(13)	1.83(13)	.31(12)
C(5)	.1246(1)	.1234(1)	.0862(2)	4.37(17)	2.88(15)	5.63(19)	.65(13)	2.71(16)	.15(14)
C(11)	.3007(2)	.1858(2)	.1634(2)	6.39(23)	6.71(24)	3.88(19)	2.73(19)	1.96(18)	1.55(17)
C(12)	.2959(2)	.1245(2)	.1437(2)	11.82(37)	5.52(25)	7.54(30)	3.70(25)	3.13(27)	1.91(22)
C(13)	.3515(2)	.2116(2)	.1791(2)	5.22(22)	11.56(36)	6.76(26)	2.32(23)	2.60(21)	.88(25)
C(15)	.2677(1)	.3449(2)	.2134(2)	4.31(18)	5.83(22)	4.44(19)	-.79(16)	2.20(15)	-1.39(16)
C(16)	.2951(2)	.3989(2)	.2160(2)	9.40(30)	6.38(25)	5.21(25)	-1.96(22)	3.49(23)	-1.57(21)
C(17)	.2939(2)	.3105(2)	.2778(2)	11.78(36)	8.42(30)	4.90(23)	-2.35(27)	3.97(25)	-.70(21)
C(21)	.1660(1)	.4600(2)	.0217(2)	5.43(20)	3.49(18)	6.15(23)	.84(15)	1.73(18)	.47(15)
C(22)	.1557(2)	.4779(2)	.0813(3)	9.98(34)	5.20(25)	12.83(41)	.47(23)	5.88(32)	-1.55(26)
C(23)	.2063(2)	.4932(2)	.0158(3)	10.51(35)	4.37(23)	14.92(45)	-.33(23)	7.08(34)	1.71(26)
C(25)	.0482(1)	.3483(2)	-.0868(2)	3.92(18)	6.91(25)	5.02(21)	.65(17)	1.34(16)	.29(19)
C(26)	.0250(2)	.4053(2)	-.1025(4)	6.45(29)	8.52(35)	19.26(59)	2.84(26)	4.18(35)	2.73(37)
C(27)	.0296(2)	.3091(3)	-.1473(3)	6.29(27)	13.49(44)	8.95(34)	-1.44(28)	1.42(25)	-4.21(32)
C(31)	-.0288(1)	.3953(2)	.0832(2)	5.32(21)	5.42(21)	4.39(20)	1.95(17)	1.22(17)	.93(16)
C(32)	-.0672(2)	.4241(2)	.0988(3)	7.75(29)	11.01(36)	10.18(35)	5.70(27)	4.47(27)	3.81(29)
C(33)	-.0018(2)	.4351(2)	.0581(2)	9.13(31)	9.28(32)	6.74(28)	.66(27)	3.10(25)	2.84(25)
C(35)	-.0485(2)	.2229(2)	.0978(2)	5.04(20)	7.24(26)	6.48(24)	-1.79(19)	2.82(19)	-3.19(21)
C(36)	-.0469(3)	.1766(2)	.1446(3)	18.21(58)	6.94(33)	14.78(52)	-3.67(35)	9.95(48)	-3.19(33)
C(37)	-.1008(2)	.2377(3)	.0450(3)	7.16(31)	13.25(46)	11.41(42)	-1.43(31)	-1.84(29)	-4.62(37)
C(41)	.1259(2)	.4432(2)	.2406(2)	6.12(22)	3.72(18)	5.22(20)	-.30(16)	2.51(18)	.30(15)
C(42)	.0908(2)	.4863(2)	.2484(3)	8.40(29)	4.54(22)	9.54(33)	1.13(20)	3.96(26)	.61(21)
C(43)	.1813(2)	.4639(2)	.2677(3)	7.71(27)	6.23(25)	10.27(34)	-1.92(22)	4.74(26)	-.17(24)
C(45)	.2185(1)	.3265(2)	.3868(2)	3.96(18)	6.76(24)	4.50(19)	.00(17)	1.17(16)	.70(18)
C(46)	.2128(2)	.3562(2)	.4448(2)	8.11(29)	9.19(33)	5.93(25)	-1.52(24)	1.47(23)	-1.06(23)
C(47)	.2552(2)	.2768(2)	.4123(2)	4.56(21)	11.58(37)	8.10(29)	2.00(24)	1.74(21)	3.46(28)
C(51)	-.0170(2)	.1722(2)	-.0671(3)	5.45(25)	8.32(30)	8.31(30)	-2.30(22)	.54(23)	1.36(25)
C(52)	-.0578(2)	.1430(3)	-.0593(3)	6.31(30)	17.29(57)	11.71(44)	.03(33)	3.21(31)	-.67(40)
C(53)	-.0289(3)	.1740(4)	-.1391(4)	10.94(46)	28.52(88)	11.01(48)	4.57(52)	4.05(41)	6.32(56)
C(55)	.1236(2)	.1074(2)	-.0645(3)	11.74(37)	6.11(25)	8.47(31)	1.16(25)	7.41(30)	.00(23)
C(56)	.1777(2)	.1111(3)	-.0531(3)	9.18(36)	18.91(57)	10.63(40)	5.99(38)	5.62(53)	-.38(39)
C(57)	.0865(3)	.0998(4)	-.1384(4)	12.51(48)	22.36(72)	15.37(56)	-1.29(43)	6.45(44)	-11.63(55)
C(61)	.2065(2)	.1202(2)	.2665(3)	6.98(27)	6.38(27)	8.92(33)	1.16(22)	.99(25)	1.49(24)
C(62)	.2104(3)	.1327(4)	.3333(4)	21.65(73)	19.47(71)	8.60(43)	2.70(56)	3.28(48)	-4.97(47)
C(63)	.2402(2)	.0707(3)	.2691(4)	7.87(34)	12.13(43)	15.72(53)	5.05(32)	2.30(34)	1.49(40)
C(65)	.0542(2)	.0443(2)	.1449(3)	8.38(29)	6.31(26)	9.49(33)	-2.05(22)	4.86(27)	.42(24)
C(66)	.0031(2)	.0304(2)	.0840(4)	11.59(42)	9.26(37)	14.79(53)	-4.69(33)	4.12(39)	-1.74(36)
C(67)	.0553(3)	.0305(3)	.2120(4)	22.51(72)	15.65(58)	11.56(48)	-8.50(52)	7.73(51)	2.75(42)
CL(1)	.38319(6)	.15122(7)	.37857(7)	8.85(9)	9.56(10)	6.65(7)	.49(8)	1.81(7)	1.35(7)
CL(2)	.33554(5)	.46115(6)	.44402(8)	6.57(7)	6.59(7)	11.52(10)	-1.28(6)	3.11(7)	-1.72(7)
O(70)	.3709(2)	.1292(2)	.4273(2)	18.75(41)	18.41(42)	9.23(28)	-6.75(34)	3.06(28)	2.32(28)
O(71)	.4295(2)	.1811(2)	.4132(3)	15.93(40)	17.40(42)	26.35(59)	-8.57(35)	11.50(43)	-5.87(41)
O(72)	.3867(2)	.1090(3)	.3400(3)	18.03(44)	19.80(50)	27.67(65)	-.92(38)	11.51(45)	-12.54(47)
O(73)	.3426(2)	.1850(2)	.3393(3)	21.75(50)	19.48(47)	15.93(42)	9.94(41)	4.66(38)	7.83(38)
O(80)	.3777(2)	.4860(2)	.4513(3)	11.13(29)	7.60(24)	38.11(74)	-.04(21)	13.07(40)	3.75(33)
O(81)	.3210(2)	.4126(2)	.4131(4)	20.64(47)	13.68(35)	33.35(71)	-9.18(34)	16.31(51)	-15.10(43)
O(82)	.2967(2)	.4991(2)	.4322(3)	8.98(26)	17.65(40)	27.06(58)	3.81(28)	3.97(32)	-7.15(41)
O(83)	.3540(3)	.4434(4)	.5117(4)	31.58(86)	31.50(86)	17.03(54)	-1.91(67)	4.74(56)	8.14(57)

	x/a	y/b	z/c	B, Å^2		x/a	y/b	z/c	B, Å^2
H(110)	.2932	.1925	.2042	6.71	H(331)	.0250	.4150	.0528	9.63
H(150)	.2281	.3562	.1972	5.87	H(332)	-.0188	.4488	.0125	9.63
H(210)	.1276	.4588	-.0319	6.30	H(333)	.0208	.4650	.0903	9.63
H(250)	.0417	.3300	-.0500	6.23	H(361)	-.0669	.1877	.1702	14.60
H(310)	-.0427	.3575	.0444	6.15	H(362)	-.0610	.1401	.1193	14.60
H(350)	-.0229	.2102	.0764	7.49	H(363)	-.0092	.1694	.1822	14.60
H(410)	.1104	.4287	.1889	5.95	H(371)	-.1013	.2718	.0171	11.79
H(450)	.2312	.3525	.3569	5.94	H(372)	-.1199	.2055	.0144	11.79
H(510)	-.0134	.2132	-.0481	8.57	H(373)	-.1213	.2425	.0764	11.79
H(550)	.1199	.0727	-.0378	10.81	H(421)	.1104	.4962	.2972	8.85
H(610)	.2156	.1563	.2437	8.44	H(422)	.0901	.5188	.2222	8.85
H(650)	.0885	.0263	.1389	9.59	H(423)	.0562	.4700	.2354	8.85
H(11)	.2125	.3025	.0042	4.18	H(431)	.2042	.4375	.2597	9.22
H(12)	.1667	.2563	-.0042	4.18	H(432)	.1776	.4975	.2375	9.22
H(31)	.0589	.3062	.2750	4.17	H(433)	.1948	.4750	.3194	9.22
H(32)	.0781	.2551	.2470	4.17	H(461)	.2010	.3275	.4708	8.90
H(51)	.1234	.0813	.0736	5.19	H(462)	.2469	.3675	.4667	8.90
H(52)	.1646	.1350	.1014	5.19	H(463)	.1917	.3925	.4167	8.90
H(121)	.2984	.1200	.1000	9.93	H(471)	.2583	.2575	.3680	8.86
H(122)	.3182	.0999	.1852	9.93	H(472)	.2906	.2900	.4403	8.86
H(123)	.2583	.1050	.1292	9.93	H(473)	.2401	.2487	.4403	8.86
H(131)	.3531	.2563	.1854	9.22	H(521)	-.0484	.1394	-.0064	12.98
H(132)	.3818	.1938	.2201	9.22	H(522)	-.0926	.1616	-.0828	12.98
H(133)	.3672	.2075	.1493	9.22	H(523)	-.0618	.1017	-.0762	12.98
H(161)	.2844	.4150	.1694	8.28	H(531)	-.0337	.1331	-.1587	17.44
H(162)	.3000	.4212	.2569	8.28	H(532)	-.0611	.1958	-.1696	17.44
H(163)	.3364	.3888	.2292	8.28	H(533)	.0011	.1911	-.1448	17.44
H(171)	.3318	.3075	.2792	9.40	H(561)	.2052	.1125	.0042	13.79
H(172)	.2969	.3375	.3153	9.40	H(562)	.1875	.0713	-.0667	13.79
H(173)	.2646	.2800	.2736	9.40	H(563)	.1724	.1450	-.0806	13.79
H(221)	.1969	.4775	.1180	10.86	H(571)	.0900	.1339	-.1662	16.63
H(222)	.1479	.5225	.0708	10.86	H(572)	.0896	.0675	-.1639	16.63
H(223)	.1281	.4526	.0824	10.86	H(573)	.0448	.1025	-.1486	16.63
H(231)	.2120	.4785	-.0241	11.45	H(621)	.2038	.0947	.3539	17.03
H(232)	.1943	.5325	.0153	11.45	H(622)	.2476	.1440	.3693	17.03
H(233)	.2406	.4912	.0653	11.45	H(623)	.1860	.1610	.3323	17.03
H(261)	.0312	.4248	-.1394	12.06	H(631)	.2342	.0618	.2184	13.98
H(262)	-.0145	.4024	-.1219	12.06	H(632)	.2784	.0790	.2972	13.98
H(263)	.0406	.4287	-.0611	12.06	H(633)	.2313	.0355	.2863	13.98
H(271)	.0500	.2713	-.1444	11.23	H(661)	.0125	.0325	.0458	12.34
H(272)	-.0063	.3025	-.1583	11.23	H(662)	-.0042	-.0175	.0771	12.34
H(273)	.0339	.3425	-.1805	11.23	H(663)	-.0256	.0501	.0883	12.34
H(321)	-.0552	.4500	.1403	11.14	H(671)	.0271	.0517	.2171	17.79
H(322)	-.0911	.4438	.0597	11.14	H(672)	.0520	-.0111	.2182	17.79
H(323)	-.0875	.3963	.1111	11.14	H(673)	.0901	.0439	.2529	17.79

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

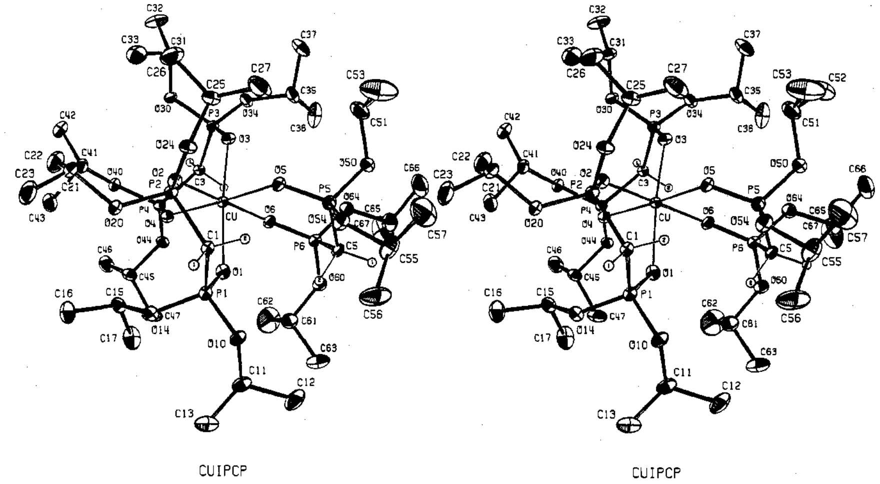

Figure 2. Stereogram of the cation. The thermal elipsoids are shown at the 12% probability level. Stereograms in this paper were drawn with C. K. Johnson's **ORTEP** program; see Oak Ridge National Laboratory Report ORNL-3794, 1965.

Table II. Thermal Ellipsoid Principal Axis Magnitudes (Å) and Directions for Selected Atoms

	Axis	$\sqrt{\overline{u^2}}$	Angle (deg) from *a*	*b*	*c*
Cu	1	0.202	67	40	75
	2	0.192	59	74	163
	3	0.185	41	126	96
O1	1	0.266	40	129	106
	2	0.236	63	50	71
	3	0.193	63	64	154
O2	1	0.254	48	67	76
	2	0.236	83	154	72
	3	0.197	137	78	23
O3	1	0.266	57	34	97
	2	0.207	58	118	69
	3	0.196	130	73	22
O4	1	0.241	79	28	73
	2	0.231	69	118	57
	3	0.192	24	90	142
O5	1	0.276	112	85	8
	2	0.243	24	79	97
	3	0.199	82	168	86
O6	1	0.278	38	60	133
	2	0.247	68	86	50
	3	0.201	120	31	70

The Cu–O bond distances range from 2.067 to 2.111 Å. However, the deviations do not resemble any of the distortions commonly attributed to the Jahn–Teller effect.

The Jahn–Teller Effect and the Geometry of Cu(II) Complexes

For many years distortions in six-coordinate complexes of Cu(II) have been attributed to the Jahn–Teller effect.[13] In the past 2 years several Cu(II) complexes have been found to have higher symmetry than the Jahn–Teller theorem allows. These include tris(octamethylpyrophosphoramide)copper(II) perchlorate,[14] tris(ethylenediamine)copper(II) sulfate,[15] potassium lead hexanitrocuprate(II),[16,17] and hexaaquocopper(II) hexafluorosilicate.[18]

Table III. Intramolecular Bond Distances and Standard Deviations for CuIPCP[a] (Å)

	Distances in Cation		
Cu–O1	2.106 (2)	O24–C25	1.484 (4)
Cu–O2	2.086 (2)	O30–C31	1.481 (4)
Cu–O3	2.067 (2)	O34–C35	1.472 (5)
Cu–O4	2.089 (2)	O40–C41	1.465 (5)
Cu–O5	2.077 (2)	O44–C45	1.484 (3)
Cu–O6	2.110 (2)	O50–C51	1.519 (5)
O1–P1	1.483 (3)	O54–C55	1.468 (6)
O2–P2	1.475 (3)	O60–C61	1.443 (5)
O3–P3	1.471 (3)	O64–C65	1.481 (5)
O4–P4	1.482 (3)	C11–C12	1.484 (7)
O5–P5	1.480 (2)	C11–C13	1.481 (8)
O6–P6	1.476 (2)	C15–C16	1.481 (7)
P1–C1	1.788 (4)	C15–C17	1.475 (6)
P2–C1	1.797 (3)	C21–C22	1.518 (9)
P3–C3	1.776 (3)	C21–C23	1.463 (7)
P4–C3	1.783 (3)	C25–C26	1.461 (6)
P5–C5	1.790 (3)	C25–C27	1.479 (8)
P6–C5	1.792 (5)	C31–C32	1.475 (8)
P1–O10	1.561 (3)	C31–C33	1.479 (7)
P1–O14	1.555 (2)	C35–C36	1.470 (8)
P2–O20	1.560 (2)	C35–C37	1.451 (6)
P2–O24	1.551 (2)	C41–C42	1.501 (8)
P3–O30	1.556 (2)	C41–C43	1.513 (8)
P3–O34	1.557 (3)	C45–C46	1.514 (7)
P4–O40	1.554 (2)	C45–C47	1.498 (6)
P4–O44	1.548 (2)	C51–C52	1.448 (9)
P5–O50	1.556 (2)	C51–C53	1.432 (11)
P5–O54	1.557 (4)	C55–C56	1.478 (9)
P6–O60	1.548 (2)	C55–C57	1.461 (9)
P6–O64	1.549 (3)	C61–C62	1.429 (12)
O10–C11	1.494 (4)	C61–C63	1.502 (9)
O14–C15	1.479 (5)	C65–C66	1.487 (7)
O20–C21	1.485 (5)	C65–C67	1.477 (12)
	Distances in Anions		
Cl1–O70	1.367 (6)	Cl2–O80	1.299 (6)
Cl1–O71	1.384 (5)	Cl2–O81	1.285 (5)
Cl1–O72	1.329 (7)	Cl2–O82	1.364 (6)
Cl1–O73	1.341 (5)	Cl2–O83	1.368 (8)

[a] The terminal C–C distances and the Cl–O distances are affected by the large apparent librational motion.

Room-temperature X-ray analysis does not eliminate the possibility of a dynamic Jahn–Teller effect. The epr spectra[19-22] of these high-symmetry compounds have been

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Table IV. Intramolecular Bond Angles and Standard Deviations for CuIPCP (deg)

Angles[a] about the Metal Ion		Other Angles in Chelate Rings	
Type I			
O1-Cu-O2	89.7 (1)	Cu-O1-P1	129.7 (1)
O3-Cu-O4	91.1 (1)	Cu-O2-P2	131.3 (2)
O5-Cu-O6	90.6 (1)	Cu-O3-P3	129.0 (1)
Type II		Cu-O4-P4	131.3 (2)
O1-Cu-O4	90.9 (1)	Cu-O5-P5	131.9 (2)
O1-Cu-O6	89.2 (1)	Cu-O6-P6	132.5 (2)
O2-Cu-O3	96.0 (1)	O1-P1-C1	111.8 (2)
O2-Cu-O5	87.3 (1)	O2-P2-C1	112.7 (2)
O3-Cu-O5	89.2 (1)	O3-P3-C3	113.5 (2)
O4-Cu-O6	94.0 (1)	O4-P4-C3	110.7 (2)
Type III		O5-P5-C5	113.2 (2)
		O6-P6-C5	112.0 (2)
O1-Cu-O5	89.3 (1)	P1-C1-P2	112.6 (3)
O2-Cu-O4	88.1 (1)	P3-C3-P4	114.3 (2)
O3-Cu-O6	85.0 (1)	P5-C5-P6	115.3 (2)

Other Angles in Cation			
O1-P1-O10	114.8 (2)	O10-C11-C12	105.8 (3)
O1-P1-O14	114.6 (2)	O10-C11-C13	108.2 (4)
O2-P2-O20	115.0 (2)	O14-C15-C16	106.1 (4)
O2-P2-O24	114.4 (2)	O14-C15-C17	109.0 (4)
O3-P3-O30	114.9 (2)	O20-C21-C22	108.5 (4)
O3-P3-O34	114.1 (2)	O20-C21-C23	106.3 (3)
O4-P4-O40	113.8 (2)	O24-C25-C26	108.8 (4)
O4-P4-O44	116.6 (2)	O24-C25-C27	106.5 (4)
O5-P5-O50	114.4 (2)	O30-C31-C32	105.7 (4)
O5-P5-O54	107.1 (2)	O30-C31-C33	108.0 (3)
O6-P6-O60	115.0 (1)	O34-C35-C36	107.2 (4)
O6-P6-O64	110.9 (2)	O34-C35-C37	107.4 (4)
O10-P1-O14	105.4 (2)	O40-C41-C42	106.5 (5)
O20-P2-O24	105.3 (2)	O40-C41-C43	107.9 (4)
O30-P3-O34	104.7 (2)	O44-C45-C46	107.1 (3)
O40-P4-O44	104.5 (1)	O44-C45-C47	106.1 (4)
O50-P5-O54	109.4 (2)	O50-C51-C52	106.5 (4)
O60-P6-O64	103.9 (2)	O50-C51-C53	110.0 (6)
C1-P1-O10	101.4 (2)	O54-C55-C56	107.0 (4)
C1-P1-O14	107.7 (1)	O54-C55-C57	110.0 (5)
C1-P2-O20	101.1 (1)	O60-C61-C62	108.0 (6)
C1-P2-O24	107.1 (2)	O60-C61-C63	105.0 (4)
C3-P3-O30	102.5 (1)	O64-C65-C66	106.0 (4)
C3-P3-O34	106.0 (2)	O64-C65-C67	107.3 (5)
C3-P4-O40	108.3 (2)	C12-C11-C13	114.1 (5)
C3-P4-O44	102.0 (2)	C16-C15-C17	113.6 (3)
C5-P5-O50	104.6 (2)	C22-C21-C23	114.7 (4)
C5-P5-O54	107.9 (2)	C26-C25-C27	115.1 (4)
C5-P6-O60	106.2 (2)	C32-C31-C33	112.9 (4)
C5-P6-O64	108.3 (2)	C36-C35-C37	113.6 (6)
P1-O10-C11	120.4 (3)	C42-C41-C43	113.5 (4)
P1-O14-C15	126.8 (3)	C46-C45-C47	112.9 (4)
P2-O20-C21	122.7 (2)	C52-C51-C53	110.6 (5)
P2-O24-C25	125.5 (3)	C56-C55-C57	111.7 (7)
P3-O30-C31	118.0 (2)	C62-C61-C63	112.4 (6)
P3-O34-C35	126.3 (3)	C66-C65-C67	112.0 (6)
P4-O40-C41	127.0 (3)		
P4-O44-C45	121.8 (3)		
P5-O50-C51	122.8 (3)		
P5-O54-C55	126.0 (3)		
P6-O60-C61	125.7 (3)		
P6-O64-C65	123.4 (3)		

[a] Types of angles: I, between bonds of the same ligand; II, between bonds related by a pseudo-threefold axis; III, between bonds in different ligands.

Table V. Least-Squares P_2O_2 Ligand Planes for CuIPCP

Ring A		Ring B		Ring C	
Atom	Dev, Å	Atom	Dev, Å	Atom	Dev, Å
Cu[a]	−0.50	Cu[a]	−0.57	Cu[a]	+0.51
O1	−0.12	O3	−0.05	O5	+0.01
P1	+0.12	P3	+0.05	P5	−0.01
C1[a]	−0.68	C3[a]	−0.67	C5[a]	+0.64
P2	−0.12	P4	−0.05	P6	+0.01
O2	+0.12	O4	+0.05	O6	−0.01

[a] Omitted from calculation of the plane.

interpreted in terms of a dynamic-static Jahn-Teller theory. This theory, developed by Abragam and Pryce[23,24] and expanded by Liehr and Ballhausen,[25] assumes that three mutually perpendicular tetragonal distortions of equal energy are present. Rapid oscillation among the three distortions gives an average structure with high symmetry at room temperature. The lack of static distortions at room temperature in six-coordinate Cu(II) complexes with equivalent ligands prompted us to investigate published structural results for six-coordinate Cu(II) complexes. Although the number of distorted species is much larger than the number of undistorted species,[26] most of the distortions attributed to the Jahn-Teller effect[27] can also be attributed to other causes. Some of these have been discussed by Hathaway and Billing.[28]

The most important consideration in determining the suitability of systems for study of the Jahn-Teller effect is the requirement that all six donor sites be equivalent. This requirement is necessary since the Jahn-Teller effect only applies to degenerate e_g orbitals. Nonequivalent ligands remove the degeneracy and any distortions which occur cannot be attributed to the Jahn-Teller effect. We have examined X-ray structural data for 77 representative six-coordinate Cu(II) complexes[26,29] and we find that *the requirement of six equivalent donor sites eliminates nearly all systems heretofore described as examples of Jahn-Teller distortion.* Unsuitable examples include $CsCuCl_5$[30] where ligands occupy both bridging and nonbridging positions, or bis(hexafluoroacetylacetonato)(bipyridine)copper(II), a CuO_4N_2 system.[31]

Structural data are now available for seven Cu(II) complexes which satisfy the requirements of donor site equivalence. Data for these complexes are given in Table VI. These results can be compared with results for complexes where Jahn-Teller distortions are not expected. Data for several complexes of Mg(II) and Ni(II) are included in Table VI for this purpose.

The tetragonality ratio, $T = R_S/R_L$, where R_S and R_L are the mean equatorial and axial bond distances, is used as a measure of tetragonal distortion.[32] We see that four of the seven Cu(II) complexes have higher site symmetry than that permitted by the Jahn-Teller theorem with all six Cu-O bond distances equal ($T = 1.00$). The complex $[Cu(H_2O)_6]SiF_6$ is an interesting case with one of the four copper cations at a $\bar{3}$ (C_{3i}) symmetry site while the other three are at $\bar{1}$ (C_i) sites. The tetragonality ratio for the $\bar{1}$ (C_i) sites is 0.83,

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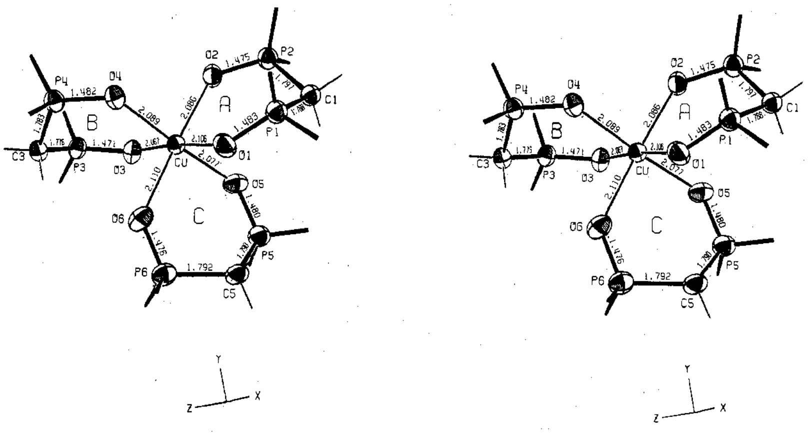

Figure 3. Stereogram of the CuIPCP backbone showing ligand rings A, B, and C.

Table VI. Six-Coordinate Metal Complexes with Chemically Equivalent Donor Sites

Ligand (L)[a]	Metal (M^{2+})	Site symmetry	M-L dist,[b] Å	L-M-L angle, deg	$T = R_S/R_L$	No. of cases	Ref
H_2O	Mg		2.056–2.077	85–95	0.99	15	26
H_2O	Ni		2.037–2.088	85–95	0.97	5	26
H_2O	Cu		1.966–2.229	85–95	0.88	6	26
H_2O	Cu[c]	$\bar{3}$ (C_{3i}) (1)	2.074	89.6–90.4	1.00	1	18
		$\bar{1}$ (C_i) (3)	1.970–2.367	87.6–92.4	0.83		
NO_2^-	Cu	m3 (T_h)	2.114	90	1.00	2	16, 17
NO_2^-	Ni[d]	m3 (T_h)	Equal		1.00	1	*d*
en	Ni	32 (D_3) (2) C_s (1)	2.115–2.128	82.3–94.6	0.99	3	*f*
en	Cu	32 (D_3)	2.150	80.9–94.2	1.00	1	15
OMPA	Mg	32 (D_3)	2.061	86.1–91.5	1.00	1	14
OMPA	Cu	32 (D_3)	2.065	88.4–90.6	1.00	1	14
NIPA	Cu[e]	32 (D_3)	Equal		1.00	1	2
PCP	Cu	C_s	2.023–2.134	87.2–93.7	0.95	1	2
IPCP	Cu	C_s	2.067–2.111	85.0–96.0	0.98	1	

[a] Abbreviations: en, ethylenediamine; OMPA, octamethylpyrophosphoramide; NIPA, nonamethylimidodiphosphoramide; PCP, octamethylmethylenediphosphonic diamide; IPCP, tetraisopropylmethylenediphosphonate. [b] M-L is the weighted average and standard deviation of the shortest and longest metal-to-ligand bond distance, respectively, for the number of cases reported. [c] In unit cell of $Cu(H_2O)_6SiF_6$ one Cu(II) is at a $\bar{3}$ (C_{3i}) symmetry site while the other three are at $\bar{1}$ (C_i) symmetry sites. [d] $K_2PbNi(NO_2)_6$ is isostructural with $K_2PbCu(NO_2)_6$: H. Elliott, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, **5**, 669 (1966). [e] $Cu(NIPA)_3(ClO_4)_2$ is isostructural with $Cu(OMPA)_3(ClO_4)_2$ but an independent structure determination has not been made.[2] [f] L. N. Swink and M. Atoji, *Acta Crystallogr.*, 13, 639 (1960); Mazhar-Ul-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, **9**, 2421 (1970); Y. I. Smolin, *Sov. Phys.–Crystallogr.*, **15**, 23 (1970).

the lowest in the table. The remaining two complexes have small deviations from octahedral symmetry with tetragonality ratios of 0.95 and 0.98. The L-M-L angles for the Cu(II) complexes are similar to those found in the corresponding Mg(II) and Ni(II) complexes.

In summary, six-coordinate complexes of Cu(II) with equivalent donor sites have either cubic, trigonal, octahedral, or slightly distorted octahedral geometry at room temperature. The distortions from octahedral geometry are small (maximum differences of 0.11 and 0.04 Å in Cu-O distances for CuPCP and CuIPCP). Where data for corresponding Mg(II) and Ni(II) complexes are available, the Cu(II) complex has a larger distortion in only one case, $[Cu(H_2O)_6{}^{2+}]$. Even in this case the difference in Cu-O distances is only 0.40 Å and the O-Cu-O angles are the same as the corresponding Mg(II) complex (90 ± 5°).

We conclude that static Jahn-Teller distortions are either small or not detectable at room temperature. Although the epr results[19-22] provide experimental support for a dynamic-static Jahn-Teller effect, the magnitude of the static distortion at low temperature is not known. X-Ray powder studies of potassium lead hexanitrocuprate(II)[21] indicate a change in the cubic structure as the temperature is lowered. However, no complete X-ray structure determinations have been made at low temperature on these high-symmetry systems so we have no data on the magnitude of the distortions seen in the epr work.

We have initiated a low-temperature X-ray diffraction study of tris(octamethylpyrophosphoramide)copper(II) perchlorate. The trigonal symmetry of the room-temperature diffraction pattern disappears at low temperature and several triclinic lattices appear.[33] Data are now being collected for these lattices to see if any change in the Cu(II) environment can be detected.

Although epr and X-ray results are in support of a dynamic-static Jahn-Teller effect, we feel that these distortions are quite small. The present survey of structural data indicates that most literature reports on distortions in six-coordinate Cu(II) complexes are incorrect in attributing these distortions to the Jahn-Teller effect.

Registry No. CuIPCP, 32161-99-2.

Acknowledgments. We are grateful for support of various stages of this research by the Public Health Service (Grants Gm-15451-03 and AM-09085), National Science Foundation (GP-28540), and Vanderbilt University. We thank Dr. S. Takagi for his assistance with the figures.

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