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The Crystal and Molecular Structure of μ-Diazido-tetrakis(triphenylphosphine)dicopper(I)

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The crystal and molecular structure of μ-diazido-tetrakis(triphenylphosphine)dicopper(I), $[Cu(N_3)(P(C_6H_5)_3)_2]_2$, has been determined from three-dimensional single-crystal X-ray data collected by counter techniques. The structure has been refined by full-matrix least-squares methods assuming anisotropic thermal motion and rigid phenyl groups to a conventional R factor of 0.065 for 2628 nonzero reflections. The compound crystallizes in space group $P2_1/c$ (C_{2h}^5) of the monoclinic system with unit cell dimensions a = 23.524 (15), b = 13.690 (8), c = 20.035 (15) Å, β = 106.3 (1)°, and V = 6193 Å^3. The measured and calculated densities are, respectively, 1.35 (1) and 1.36 g/cm^3 for four dimeric molecules per unit cell. The compound is a dimer in which two copper atoms are bridged by the two azide groups through terminal nitrogens to form an eight-membered ring. The structural results for this compound represent the first example of a complex possessing a diazido-bridged structure. Both azide ions possess an essentially linear structure with the N–N distances all equal and averaging 1.178 (12) Å. These N–N distances are in contrast to those observed in other transition metal–azido complexes but are approximately the same as those values observed in ionic azide compounds. The two azide ions are tilted by 38° with respect to each other and each of the $Cu–N_3–Cu$ bridges deviates quite significantly from planarity, in part because of the allenic nature of the middle nitrogen atom of the bridging azide ions. The copper(I) ion manifests its expected four-coordinate tetrahedral geometry with significant disortions as evidenced by the large P–Cu–P angle, 122.3 (1)°. Other structural features as related to other structurally known phosphine–copper(I) complexes are discussed and the nature of the complex in solution is considered.

Introduction

Tetiary phosphine and arsine complexes of copper(I) are known with metal to ligand ratios of 1:1, 1:2, 1:3, 1:4, and 2:3.[2] The tendency of copper(I) in these compounds to form four-coordinate tetrahedral complexes has been demonstrated by X-ray structural analyses of compounds of the 1:1,[3] 1:2,[4–6] and 2:3[7] types. In the case of the 1:2 type complex, L_2CuX, where L is $(C_6H_5)_3P$ and X^- is BH_4^-, NO_3^-, or $B_3H_8^-$, structural investigations have shown the anion to function as a bidentate ligand.

As part of our structural and photochemical studies of azido complexes of group Ib metals we have determined the structure of $Cu(N_3)(P(C_6H_5)_3)_2$. The complex was previously shown to undergo cycloaddition with CS_2 in a manner analogous to organic azides[8,9] and to give molecular weight values in $CHCl_3$ compatible with a monomeric species.[9,10] Although this evidence suggested that the complex contained three-coordinate copper(I), it was believed that the tendency of copper(I) to form four-coordinate tetrahedral complexes would be maintained in the solid state by formation of an azide-bridged dimer.

During the structural refinement of the azido complex, the structure of another copper(I) complex of the 1:2 type, $CuNCS(P(CH_3)(C_6H_5)_2)$, was determined.[11] The compound was found to be dimeric in the solid state with the two thiocyanate groups bridging the copper atoms. While structures containing bridging thiocyanates have been known for some time,[12,13] no structural evidence was known for end-to-end bridging azide groups in metal complexes prior to the study reported herein. The ability of the azide ion to bridge two transition metal ions through the terminal nitrogen atoms was first suggested by Snellgrove and King[14] and by Haim[15] from kinetic studies. However, the structural determinations of transition metal complexes containing the azide ion reported to date have found N_3^- to coordinate solely through one of the terminal nitrogen atoms.[16–19] In addition, significantly different N–N bond distances within each azide have been found in all of the coordinated species with the exception of the pentaazidoiron(III) complex.[19] The structural analysis of $Cu(N_3)(P(C_6H_5)_3)_2$ was carried out in order to determine the mode of coordination of the azide ligand and to provide further detailed structural data on phosphine complexes of group Ib metals. The structural results reported herein have appeared in preliminary form.[20]

Experimental Section

$Cu(N_3)(P(C_6H_5)_3)_2$ was synthesized as described previously[9] and single crystals suitable for X-ray diffraction studies were grown by slow evaporation of a chloroform–*n*-hexane solution containing the complex.

Unit Cell and Space Group.—Crystals of the complex were

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TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $[((C_6H_5)_3P)_2CuN_3]_2$[a,b]

Atom	x	y	z	β_{11}[c] or B, Å²	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu_1	0.1668 (1)	0.0147 (1)	−0.0776 (1)	0.0018 (0)	0.0056 (1)	0.0030 (1)	−0.0003 (0)	0.0003 (0)	−0.0000 (1)
Cu_2	0.3282 (1)	−0.1738 (1)	0.0831 (1)	0.0020 (0)	0.0064 (1)	0.0029 (1)	−0.0001 (0)	0.0002 (0)	−0.0004 (1)
P_1	0.1792 (1)	0.1789 (2)	−0.0817 (2)	0.0016 (1)	0.0053 (2)	0.0029 (1)	−0.0001 (1)	0.0004 (1)	0.0002 (1)
P_1'	0.3303 (1)	−0.3376 (2)	0.0666 (2)	0.0017 (1)	0.0048 (2)	0.0021 (1)	−0.0003 (1)	0.0003 (1)	0.0000 (1)
P_2	0.0837 (1)	−0.0608 (2)	−0.1393 (2)	0.0018 (1)	0.0062 (3)	0.0029 (1)	−0.0005 (1)	0.0005 (1)	−0.0003 (1)
P_2'	0.3948 (1)	−0.1009 (2)	0.1734 (2)	0.0016 (1)	0.0055 (2)	0.0025 (1)	0.0000 (1)	0.0002 (1)	−0.0001 (1)
N_1	0.1890 (4)	−0.0091 (8)	0.0302 (5)	4.9 (2)					
N_2	0.2150 (4)	−0.0785 (8)	0.0562 (5)	4.3 (2)					
N_3	0.2397 (4)	−0.1495 (8)	−0.0847 (6)	5.8 (2)					
N_4	0.2408 (5)	−0.0507 (7)	−0.0961 (6)	5.6 (2)					
N_5	0.2837 (5)	−0.0735 (7)	−0.0522 (6)	5.0 (2)					
N_6	0.3275 (5)	−0.0976 (8)	−0.0086 (6)	6.0 (3)					
Group	x_c[d]	y_c	z_c	δ	ϵ	η	B, Å²		
P_1R_1	0.3162 (3)	0.2297 (4)	−0.0177 (3)	−0.20 (2)	1.92 (1)	−2.74 (2)	2.3 (2)		
P_1R_2	0.1453 (2)	0.2668 (4)	−0.2361 (3)	−3.05 (1)	2.76 (1)	1.75 (1)	3.0 (3)		
P_1R_3	0.1094 (2)	0.3132 (4)	0.0015 (3)	2.37 (0)	−3.06 (0)	−2.44 (0)	2.0 (2)		
P_2R_1	0.0700 (2)	−0.2812 (4)	−0.0929 (2)	−1.36 (1)	−2.46 (0)	−2.74 (1)	2.1 (4)		
P_2R_2	0.0707 (2)	−0.0971 (3)	−0.3016 (2)	−1.63 (0)	3.08 (0)	1.76 ()	2.2 (3)		
P_2R_3	−0.0340 (2)	0.0540 (4)	−0.1341 (3)	2.90 (1)	−2.31 (0)	−2.71 (0)	2.1 (4)		
$P_1'R_1$	0.2607 (2)	−0.3999 (4)	−0.0907 (3)	−2.57 (0)	3.05 (1)	2.12 (0)	3.0 (2)		
$P_1'R_2$	0.4607 (2)	−0.4198 (4)	0.0785 (3)	−0.22 (0)	2.72 (0)	2.88 (0)	3.1 (2)		
$P_1'R_3$	0.2839 (2)	−0.4640 (4)	0.1758 (3)	2.91 (0)	2.52 (0)	−1.73 (0)	2.9 (4)		
$P_2'R_1$	0.4165 (2)	−0.2307 (4)	0.3125 (3)	−2.30 (0)	2.61 (0)	−1.92 (0)	3.2 (2)		
$P_2'R_2$	0.3561 (2)	0.1060 (4)	0.2239 (3)	1.84 (0)	3.00 (0)	−2.70 (0)	3.0 (3)		
$P_2'R_3$	0.5235 (2)	−0.0718 (3)	0.1495 (3)	−1.63 (1)	−2.02 (0)	1.41 (1)	2.9 (2)		

[a] See Figures 1 and 2 for the atom-labeling scheme in this and in subsequent tables. For the sake of clarity in Figure 1, only two of the three rings (R_1, R_2, and R_3) of each triphenylphosphine group are labeled. [b] The estimated standard deviations in the least significant figure(s) as derived from the inverse matrix of the final least-squares refinement cycle are given in parentheses in this and in subsequent tables. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [d] x_c, y_c, and z_c are fractional coordinates of the ring center. The angles δ, ϵ, and η (in radians) are as defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

studied by optical goniometry and by standard film techniques. On the basis of Weissenberg and precession photographs, the complex was found to crystallize in the space group $P2_1/c$ (C_{2h}^5) of the monoclinic system in a cell of refined (*vide infra*) dimensions $a = 23.524$ (15), $b = 13.690$ (8), $c = 20.035$ (15) Å, $\beta = 106.3$ (1)°, and $V = 6193$ Å³. The only systematic extinctions observed from the photographs were for $0k0$ reflections with $k = 2n + 1$ and $h0l$ reflections with $l = 2n + 1$. An experimental density of 1.35 (1) g/cm³ obtained by the flotation method using benzene–carbon tetrachloride solutions is in agreement with a calculated value of 1.36 g/cm³ for eight monomeric molecules of formula $CuP_2N_3C_{36}H_{30}$ or four dimers per unit cell. Hence, no crystallographic symmetry was required of either the monomer or dimer species.

Collection and Reduction of the Data.—The set of independent intensity data was collected from a single crystal at ambient room temperature using a Picker four-circle automated diffractometer. The crystal employed for the data collection had approximate dimensions of 0.41 × 0.38 × 0.31 mm and was mounted along the b axis. The mosaic spread of the crystal was determined from open-counter, narrow-source ω scans[21] and was found to have an average value of 0.30°. Twenty-one reflections of both general and special classes were then centered in the counter aperture by varying 2θ, χ, and ϕ in conjunction with the left–right and top–bottom balancing features of the variable receiving aperture. The settings for these reflections formed the basis for a least-squares refinement of the unit cell parameters and the orientation angles using our PICKLST program.[22]

The intensity data were collected by the θ–2θ scan technique using Zr-filtered Mo Kα radiation. A takeoff angle of 3° was used for the data collection with a counter opening of approximately 6 × 6 mm. The scan range was from −0.60 to +0.80° of the calculated 2θ value of the reflection plus an allowance for the Mo Kα_1–Kα_2 separation at higher 2θ angles. A scan rate of 1°/min was employed with stationary-crystal, stationary-background counts of 10-sec duration collected at both ends of the 2θ scan range. The intensities were measured with a scintillation detector and pulse height analysis. Attenuators of a factor of ~3 each were automatically inserted into the diffracted beam when the counting rate exceeded 8000 counts/sec. The set of intensity data was gathered in two distinct but contiguous segments (owing to a minor change in the variable receiving aperture during data collection) and each was assigned its own variable scale factor in the refinements. The intensities of four standard reflections were measured after every 100 reflections and showed no significant change during the data collection. The greatest single deviation of any of the standard reflections from its respective mean was 3%.

The intensities of a total of 3200 independent reflections were measured, of which 2637 reflections were observed to be greater than their estimated standard deviations (*vide infra*). The intensities were then corrected for the usual Lorentz and polarization effects but not for absorption owing to the smallness of the linear absorption coefficient (8.74 cm⁻¹) and the uniformity of crystal dimensions (*vide supra*). These calculations yielded a set of F_o^2 values where $|F_o|$ is the observed structure factor amplitude.

Solution and Refinement of the Structure

The structure was solved by the usual heavy-atom methods. With the set of F_o^2 values, a three-dimensional Patterson function was calculated, and from it, two copper and two phosphorus atom positions were located. The relatively short Cu–Cu vector within the asymmetric unit (5.1 Å), together with the positions of the phosphorus atoms, indicated that the complex was dimeric in the solid state. The positional parameters of the located copper and phosphorus atoms together with individual isotropic thermal parameters and the two scale factors were refined through several cycles of least squares. A difference Fourier based on phases obtained from these heavy-atom positions revealed the positions of the remaining phosphorus atoms as well as those of the bridging azide groups. All of the phenyl ring carbon atoms were located by a succession of difference Fourier maps which were based on contributions from the previously located atoms.

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(21) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(22) In addition to the PICKLST setting program, the main programs used in this work were local versions of the Busing–Levy ORFLS least-squares program, the Zalkin FORDAP Fourier program, the Busing–Martin–Levy ORFFE function and error program, and the Johnson ORTEP plotting program. Various other local programs were also used. All computing was performed on Brown's IBM 360/67 computer and on Temple's CDC 6400 computer.

TABLE II

DERIVED POSITIONAL PARAMETERS FOR GROUP ATOMS[a,b]

Atom	x	y	z	Atom	x	y	z
$P_1R_1C_1$	0.2561 (4)	0.2119 (21)	−0.0469 (4)	$P_1'R_1C_1$	0.2905 (3)	−0.3779 (6)	−0.0219 (3)
$P_1R_1C_2$	0.2824 (5)	0.1911 (12)	0.0229 (4)	$P_1'R_1C_2$	0.2469 (4)	−0.3152 (5)	−0.0601 (5)
$P_1R_1C_3$	0.3426 (4)	0.2089 (11)	0.0521 (4)	$P_1'R_1C_3$	0.2171 (3)	−0.3371 (6)	−0.1289 (4)
$P_1R_1C_4$	0.3763 (4)	0.2475 (21)	0.0115 (5)	$P_1'R_1C_4$	0.2309 (4)	−0.4218 (7)	−0.1594 (3)
$P_1R_1C_5$	0.3500 (4)	0.2683 (12)	−0.0584 (4)	$P_1'R_1C_5$	0.2745 (4)	−0.4846 (5)	−0.1212 (5)
$P_1R_1C_6$	0.2899 (3)	0.2505 (11)	−0.0876 (4)	$P_1'R_1C_6$	0.3044 (3)	−0.4626 (5)	−0.0525 (4)
$P_1R_2C_1$	0.1582 (4)	0.2315 (6)	−0.1684 (3)	$P_1'R_2C_1$	0.4041 (3)	−0.3875 (7)	0.0764 (4)
$P_1R_2C_2$	0.1470 (3)	0.3306 (5)	−0.1815 (4)	$P_1'R_2C_2$	0.4216 (3)	−0.4820 (6)	0.0986 (4)
$P_1R_2C_3$	0.1342 (4)	0.3658 (4)	−0.2492 (4)	$P_1'R_2C_3$	0.4783 (4)	−0.5143 (5)	0.1007 (5)
$P_1R_2C_4$	0.1324 (4)	0.3021 (6)	−0.3039 (3)	$P_1'R_2C_4$	0.5173 (3)	−0.4521 (7)	0.0807 (5)
$P_1R_2C_5$	0.1435 (3)	0.2031 (6)	−0.2908 (4)	$P_1'R_2C_5$	0.4998 (3)	−0.3577 (6)	0.0585 (5)
$P_1R_2C_6$	0.1564 (4)	0.1678 (4)	−0.2230 (4)	$P_1'R_2C_6$	0.4432 (4)	−0.3253 (5)	0.0564 (5)
$P_1R_3C_1$	0.1410 (3)	0.2554 (5)	−0.0328 (4)	$P_1'R_3C_1$	0.3012 (4)	−0.4104 (6)	0.1258 (4)
$P_1R_3C_2$	0.1623 (3)	0.3472 (6)	−0.0081 (4)	$P_1'R_3C_2$	0.3023 (4)	−0.3676 (5)	0.1892 (4)
$P_1R_3C_3$	0.1307 (4)	0.4050 (4)	0.0262 (4)	$P_1'R_3C_3$	0.2850 (3)	−0.4212 (6)	0.2392 (3)
$P_1R_3C_4$	0.0778 (3)	0.3710 (5)	0.0358 (4)	$P_1'R_3C_4$	0.2666 (4)	−0.5176 (6)	0.2258 (4)
$P_1R_3C_5$	0.0565 (3)	0.2792 (6)	0.0111 (4)	$P_1'R_3C_5$	0.2654 (4)	−0.5604 (5)	0.1624 (4)
$P_1R_3C_6$	0.0881 (3)	0.2214 (4)	−0.0232 (4)	$P_1'R_3C_6$	0.2828 (3)	−0.5067 (6)	0.1124 (3)
$P_2R_1C_1$	0.0728 (5)	−0.1844 (4)	−0.1129 (4)	$P_2'R_1C_1$	0.4088 (4)	−0.1723 (6)	0.2538 (3)
$P_2R_1C_2$	0.0306 (3)	−0.2470 (6)	−0.1539 (3)	$P_2'R_1C_2$	0.3785 (4)	−0.1508 (6)	0.3025 (4)
$P_2R_1C_3$	0.0278 (4)	−0.3438 (6)	−0.1339 (4)	$P_2'R_1C_3$	0.3863 (3)	−0.2091 (6)	0.3612 (4)
$P_2R_1C_4$	0.0672 (5)	−0.3780 (4)	−0.0728 (4)	$P_2'R_1C_4$	0.4243 (4)	−0.2891 (6)	0.3713 (4)
$P_2R_1C_5$	0.1094 (3)	−0.3154 (6)	−0.0319 (3)	$P_2'R_1C_5$	0.4545 (4)	−0.3106 (6)	0.3226 (5)
$P_2R_1C_6$	0.1122 (3)	−0.2186 (6)	−0.0519 (4)	$P_2'R_1C_6$	0.4468 (3)	−0.2522 (6)	0.2638 (4)
$P_2R_2C_1$	0.0750 (3)	−0.0785 (6)	−0.2321 (3)	$P_2'R_2C_1$	0.3743 (4)	0.0188 (5)	0.2006 (4)
$P_2R_2C_2$	0.0197 (3)	−0.0823 (6)	−0.2808 (4)	$P_2'R_2C_2$	0.4162 (3)	0.0853 (6)	0.2374 (4)
$P_2R_2C_3$	0.0154 (3)	−0.1009 (6)	−0.3503 (4)	$P_2'R_2C_3$	0.3980 (3)	0.1725 (5)	0.2607 (4)
$P_2R_2C_4$	0.0664 (4)	−0.1156 (6)	−0.3712 (3)	$P_2'R_2C_4$	0.3379 (4)	0.1932 (5)	0.2472 (4)
$P_2R_2C_5$	0.1217 (3)	−0.1118 (6)	−0.3225 (4)	$P_2'R_2C_5$	0.2960 (2)	0.1267 (6)	0.2103 (4)
$P_2R_2C_6$	0.1260 (2)	−0.0933 (6)	−0.2529 (4)	$P_2'R_2C_6$	0.3142 (3)	0.0395 (5)	0.1870 (4)
$P_2R_3C_1$	0.0159 (4)	0.0016 (8)	−0.1373 (4)	$P_2'R_3C_1$	0.4682 (3)	−0.0824 (16)	0.1613 (4)
$P_2R_3C_2$	−0.0006 (3)	0.0853 (7)	−0.1775 (4)	$P_2'R_3C_2$	0.4726 (3)	−0.0748 (12)	0.0937 (3)
$P_2R_3C_3$	−0.0505 (4)	0.1377 (5)	−0.1743 (6)	$P_2'R_3C_3$	0.5278 (4)	−0.0643 (7)	0.0818 (3)
$P_2R_3C_4$	−0.0838 (4)	0.1064 (8)	−0.1309 (5)	$P_2'R_3C_4$	0.5787 (3)	−0.0613 (16)	0.1377 (4)
$P_2R_3C_5$	−0.0673 (3)	0.0227 (7)	−0.0907 (4)	$P_2'R_3C_5$	0.5744 (3)	−0.0688 (12)	0.2054 (4)
$P_2R_3C_6$	−0.0174 (4)	−0.0296 (5)	−0.0939 (4)	$P_2'R_3C_6$	0.5192 (4)	−0.0793 (6)	0.2172 (3)

[a] See footnotes a and b of Table I. [b] In Figure 1 the carbon atoms attached to the phosphorus atom of each triphenylphosphine group are defined as C_1. The carbon atom numbers thereafter follow sequentially from 2 to 6 with carbon atom 2 or 6 labeled.

The complete trial structure was refined using a least-squares procedure in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weights w were assigned as $4F_o^2/\sigma^2$ and the standard deviations σ were estimated from counting statistics according to the formula[23]

$$\sigma(F^2) = \frac{1}{TLp}\left(C + \left(\frac{t_c}{2t_b}\right)^2 (B_1 + B_2) + (0.03I)^2\right)^{1/2}$$

in which Lp is the Lorentz–polarization factor, T is the transmission coefficient, C is the total integrated count obtained in time t_c, B_1 and B_2 are the background counts, each obtained in time t_b, and I is the net integrated count. Throughout the refinement, the neutral atom scattering factors as tabulated by Ibers[24] were used. The effects of anomalous dispersion for the Cu and P atoms, obtained from Templeton's tabulation,[25] were included in the calculated structure factors.[26]

In the refinement, the phenyl rings were treated as rigid groups (D_{6h} symmetry, C–C bond length 1.392 Å, C–H bond length 1.08 Å) in which each phenyl ring is described by three positional and three orientational parameters and each carbon atom is assigned its own variable isotropic thermal parameter.[27] Three cycles of least-squares refinement in which the nongroup atoms were assumed to vibrate according to an isotropic thermal model converged to a conventional R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.092 and a weighted R factor R' ($R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$) of 0.114 for 134 positional, scale, and isotropic thermal parameters. A difference Fourier map based on this refinement revealed evidence for anisotropic thermal motion of the heavy atoms.

In the next round of calculations, the Cu and P atoms were assumed to vibrate according to an anisotropic thermal model while the light atoms remained limited to isotropic thermal motion. Five cycles of refinement converged to discrepancy indices R and R' of 0.077 and 0.089, respectively. The hydrogen atom contributions to the calculated structure factors were then computed and subsequently included as fixed contributions in all further calculations. After the elimination of several reflections because of punching or positioning errors, three more cycles of least squares were carried out in which R and R' converged to their final values of 0.065 and 0.072, respectively, for 2628 reflections above σ. The largest parameter shifts in the final cycle of refinement were less than 0.10 of their estimated standard deviations. A final difference Fourier map showed its highest peak to be 0.44 e⁻/Å³ as compared with a value of 2.0 e⁻/Å³ for a typical carbon atom in this structure. The parameters obtained in this refinement are taken as the final parameters of the structure and are given in Table I along with their estimated standard deviations

(23) P. W. P. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(24) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1.

(25) D. H. Templeton, ref 24, Table 3.3.2.

(26) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

(27) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS) FOR $[Cu(N_3)(P(C_6H_5)_3)_2]_2$[a]

H	K	L	FO	FC
3	0	0	95	91
4	0	0	130	135
3	0	2	34	33
4	0	2	266	231
5	0	2	95	92
6	0	2	184	176
7	0	2	171	152
8	0	2	33	25
9	0	2	37	35
10	0	2	266	211
11	0	2	25	26
12	0	2	177	180
13	0	2	20	22
14	0	2	71	70
15	0	2	23	24
16	0	2	102	101
17	0	2	22	21
18	0	2	71	62
-19	0	4	32	25
-18	0	4	70	65
-16	0	4	154	150
-15	0	4	67	61
-13	0	4	61	58
-12	0	4	130	130
-11	0	4	119	117
-10	0	4	187	187
-9	0	4	32	29
-8	0	4	139	151
-6	0	4	109	112
-5	0	4	17	16
-4	0	4	146	154
-3	0	4	32	31
-2	0	4	284	291
-1	0	4	182	164
0	0	4	168	125
5	0	4	88	84
-19	0	6	13	12
-18	0	6	64	55
-17	0	6	34	38
-16	0	6	83	82
-14	0	6	55	57
-13	0	6	32	34
-12	0	6	163	171
-11	0	6	65	50
-10	0	6	142	159
-9	0	6	120	142
-7	0	6	13	13
-6	0	6	35	47
-5	0	6	71	76
-4	0	6	26	32
-3	0	6	72	76
-2	0	6	94	92
-1	0	6	217	198
0	0	6	295	271
7	0	6	31	29
8	0	6	119	130
-18	0	8	45	38
-17	0	8	19	17
-16	0	8	88	88
-15	0	8	38	38
-14	0	8	113	111
-13	0	8	37	40
-12	0	8	37	43
-10	0	8	164	122
-9	0	8	23	26
-8	0	8	67	76
-7	0	8	16	18
-6	0	8	118	135
-5	0	8	16	19
-4	0	8	166	173
-3	0	8	55	52
-2	0	8	237	222
-1	0	8	38	37
0	0	8	155	146
10	0	8	164	160
11	0	8	26	24
12	0	8	52	43
14	0	8	60	69
-15	0	10	20	24
-14	0	10	25	33
-12	0	10	48	60
-11	0	10	27	29
-10	0	10	163	167
-9	0	10	10	12
-8	0	10	63	77
-7	0	10	49	61
-6	0	10	88	84
-5	0	10	45	28
-4	0	10	134	136
-3	0	10	96	93
-2	0	10	148	139
-1	0	10	77	71
0	0	10	42	33
12	0	10	47	48
-17	0	12	66	69
-16	0	12	40	51
-14	0	12	87	101
-13	0	12	32	33
-12	0	12	68	75
-11	0	12	17	19
-10	0	12	102	115
-9	0	12	32	35
-7	0	12	11	7
-6	0	12	157	157
-5	0	12	76	78
-4	0	12	62	62
-3	0	12	35	41
0	0	12	142	138
-15	0	14	34	40
-14	0	14	82	89
-13	0	14	26	30
-12	0	14	99	106
-11	0	14	39	41
-10	0	14	17	18
-9	0	14	12	17
-8	0	14	61	79
-7	0	14	79	84
-6	0	14	97	93
-5	0	14	53	54
-4	0	14	62	56
-3	0	14	27	23
-2	0	14	105	92
-1	0	14	30	24
0	0	14	72	64
-11	0	16	45	40
-10	0	16	57	79
-9	0	16	29	34
-8	0	16	59	59
-6	0	16	42	38
-5	0	16	11	12
-4	0	16	42	33
-2	0	16	70	58
-1	0	16	39	36
-19	1	0	44	45
-17	1	0	38	34
-16	1	0	79	79
-15	1	0	59	55
4	1	0	208	202
5	1	0	237	220
6	1	0	58	57
7	1	0	20	22
8	1	0	178	174
9	1	0	105	99
10	1	0	169	168
11	1	0	33	37
12	1	0	45	42
13	1	0	72	70
15	1	0	58	55
16	1	0	76	79
17	1	0	36	34
18	1	0	44	45
-19	1	1	18	17
-18	1	1	24	17
-17	1	1	16	16
-16	1	1	8	3
-15	1	1	68	67
-14	1	1	101	102
-13	1	1	29	26
-12	1	1	29	34
-11	1	1	145	142
-10	1	1	55	47
-9	1	1	12	6
-8	1	1	155	149
-7	1	1	94	98
-6	1	1	224	219
-5	1	1	65	63
-4	1	1	41	36
-3	1	1	82	84
2	1	1	124	129
3	1	1	86	86
4	1	1	60	59
5	1	1	181	174
6	1	1	30	24
7	1	1	8	10
8	1	1	24	31
9	1	1	23	28
10	1	1	85	83
11	1	1	9	5
12	1	1	173	175
13	1	1	79	77
14	1	1	39	33
15	1	1	32	28
16	1	1	52	52
17	1	1	28	31
18	1	1	30	33
-19	1	2	18	16
-18	1	2	85	81
-17	1	2	12	18
-16	1	2	26	23
-15	1	2	48	47
-14	1	2	28	28
-13	1	2	37	36
-12	1	2	155	143
-11	1	2	4	2
-10	1	2	152	147
-9	1	2	23	24
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-6	1	2	315	313
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-2	1	2	29	30
-19	1	3	11	7
-17	1	3	40	39
-16	1	3	63	62
-15	1	3	7	12
-14	1	3	57	53
-13	1	3	128	126
-12	1	3	46	48
-11	1	3	77	79
-10	1	3	46	50
-9	1	3	56	53
-8	1	3	106	107
-7	1	3	28	26
-6	1	3	59	60
-5	1	3	136	135
-4	1	3	281	284
-3	1	3	112	112
-1	1	3	56	56
1	1	3	113	106
2	1	3	206	189
3	1	3	90	85
4	1	3	54	58
5	1	3	85	85
6	1	3	60	55
7	1	3	38	41
8	1	3	135	136
9	1	3	44	41
10	1	3	100	107
11	1	3	55	58
12	1	3	40	33
14	1	3	50	50
15	1	3	19	14
16	1	3	52	50
17	1	3	25	26
-19	1	4	16	15
-17	1	4	47	47
-16	1	4	66	62
-15	1	4	54	54
-14	1	4	44	59
-13	1	4	7	4
-12	1	4	8	7
-11	1	4	64	66
-10	1	4	25	23
-9	1	4	102	104
-8	1	4	112	113
-7	1	4	57	56
-6	1	4	214	219
-5	1	4	6	5
-4	1	4	107	105
-2	1	4	91	94
-1	1	4	45	40
1	1	4	310	318
3	1	4	118	114
4	1	4	98	100
5	1	4	37	35
6	1	4	59	67
7	1	4	51	54
8	1	4	51	56
9	1	4	64	66
10	1	4	98	64
12	1	4	124	127
13	1	4	72	63
14	1	4	44	46
16	1	4	37	40
17	1	4	49	43
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-17	1	5	57	52
-16	1	5	38	35
-15	1	5	72	72
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-13	1	5	60	64
-12	1	5	51	55
-11	1	5	31	27
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-9	1	5	77	75
-7	1	5	36	35
-6	1	5	49	53
-5	1	5	39	43
-2	1	5	37	41
-1	1	5	234	230
1	1	5	140	142
4	1	5	57	55
5	1	5	71	69
6	1	5	83	87
7	1	5	14	12
8	1	5	72	79
9	1	5	50	55
11	1	5	55	53
12	1	5	78	70
14	1	5	36	34
16	1	5	33	10
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-17	1	6	49	48
-15	1	6	39	34
-14	1	6	32	34
-13	1	6	9	9
-12	1	6	9	5
-11	1	6	142	145
-10	1	6	74	79
-8	1	6	79	84
-7	1	6	26	27
-6	1	6	21	24
-4	1	6	121	121
-2	1	6	14	14
-1	1	6	41	43
1	1	6	89	88
5	1	6	91	87
6	1	6	72	71
7	1	6	39	41
8	1	6	47	58
9	1	6	15	13
10	1	6	85	89
11	1	6	69	68
12	1	6	79	81
13	1	6	10	16
14	1	6	17	17
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-18	1	7	43	44
-17	1	7	63	59
-16	1	7	25	27
-15	1	7	47	46
-14	1	7	65	65
-13	1	7	24	21
-12	1	7	49	49
-11	1	7	15	19
-9	1	7	35	34
-8	1	7	77	74
-7	1	7	53	52
-5	1	7	63	63
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-3	1	7	78	80
-2	1	7	134	141
-1	1	7	42	42
1	1	7	133	130
6	1	7	133	140
7	1	7	42	42
9	1	7	75	77
10	1	7	108	105
11	1	7	30	32
13	1	7	20	18
15	1	7	54	48
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-15	1	8	51	55
-14	1	8	33	33
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-12	1	8	66	70
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-1	1	8	61	66
7	1	8	17	14
8	1	8	80	84
9	1	8	30	33
10	1	8	55	59
14	1	8	87	88
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-17	1	9	65	70
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-15	1	9	21	20
-14	1	9	11	12
-13	1	9	35	36
-11	1	9	61	61
-10	1	9	68	69
-9	1	9	88	85
-7	1	9	7	4
-6	1	9	21	19
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-3	1	9	56	52
-2	1	9	64	73
-1	1	9	32	28
1	1	9	19	20
8	1	9	72	75
9	1	9	48	45
10	1	9	11	15
13	1	9	24	26
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-16	1	10	14	17
-15	1	10	31	32
-14	1	10	73	75
-12	1	10	27	27
-11	1	10	87	89
-10	1	10	32	31
-8	1	10	109	107
-7	1	10	9	9
-6	1	10	88	88
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1	1	10	77	73
9	1	10	8	8
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-3	1	12	22	19
-2	1	12	91	94
0	1	12	20	17
1	1	12	51	51
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-14	1	13	22	20
-13	1	13	76	79
-11	1	13	19	15
-10	1	13	24	22
-9	1	13	64	58
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-4	1	13	16	13
-2	1	13	46	49
-1	1	13	41	47
0	1	13	73	74
-14	1	14	31	33
-12	1	14	41	37
-11	1	14	39	30
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-9	1	14	4	7
-8	1	14	36	33
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-6	1	14	36	38
-5	1	14	21	19
-4	1	14	103	98
-1	1	14	19	18
0	1	14	49	57
1	1	14	26	22
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-12	1	15	16	17
-11	1	15	49	47
-10	1	15	28	27
-8	1	15	47	43
-7	1	15	15	15
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-2	1	15	51	50
0	1	15	12	12
1	1	15	56	53
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-9	1	16	68	67
-8	1	16	66	64
-7	1	16	8	6
-6	1	16	53	51
-5	1	16	35	31
-4	1	16	9	8
-2	1	16	33	30
-1	1	16	16	36
0	1	16	18	17
-18	2	0	26	20
-17	2	0	68	61
-16	2	0	26	28
-15	2	0	47	49
-14	2	0	29	32
-13	2	0	53	55
-12	2	0	33	32
-11	2	0	97	86
-10	2	0	108	104
-9	2	0	148	144
-7	2	0	55	52
-6	2	0	33	29
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-4	2	0	245	233
-3	2	0	108	99
-2	2	0	47	48
-19	2	1	28	32
-18	2	1	44	65
-17	2	1	8	10
-16	2	1	81	78
-15	2	1	8	1
-14	2	1	45	47
-13	2	1	7	2
-12	2	1	166	162
-11	2	1	32	32
-10	2	1	40	39
-9	2	1	85	80
-8	2	1	130	120
-7	2	1	75	68
-6	2	1	16	13
-5	2	1	182	176
-4	2	1	10	8
-2	2	1	39	30
-1	2	1	87	77
5	2	1	159	157
6	2	1	9	5
7	2	1	[illegible]	88
8	2	1	86	82
9	2	1	31	34
10	2	1	6	3
12	2	1	31	30
13	2	1	28	25
16	2	1	40	40
17	2	1	11	14
18	2	1	12	11
-19	2	2	35	31
-18	2	2	21	22
-17	2	2	57	58
-16	2	2	25	28
-15	2	2	19	39
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-13	2	2	11	14
-12	2	2	14	13
-11	2	2	161	165
-10	2	2	48	43
-9	2	2	29	33
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-2	2	2	142	137
-1	2	2	209	206
2	2	2	34	35
3	2	2	117	118
4	2	2	13	3
5	2	2	91	19
6	2	2	8	6
7	2	2	247	237
10	2	2	18	12
11	2	2	29	36
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-12	2	3	16	13
-11	2	3	85	64
-10	2	3	52	49
-9	2	3	12	10
-8	2	3	44	48
-7	2	3	117	111
-6	2	3	28	24
-5	2	3	88	81
-4	2	3	79	75
-3	2	3	20	24
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-1	2	3	17	8
2	2	3	63	64
3	2	3	163	152
4	2	3	22	21
5	2	3	47	44
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-16	2	4	18	22
-15	2	4	73	74
-14	2	4	129	127
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-11	2	4	39	39
-10	2	4	11	13
-9	2	4	84	102
-8	2	4	105	108
-7	2	4	74	77
-6	2	4	149	147
-5	2	4	6	5
-4	2	4	78	74
-3	2	4	81	79
-2	2	4	136	134
-1	2	4	8	4
2	2	4	68	74
3	2	4	98	86
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6	2	4	58	50
7	2	4	11	8
10	2	4	91	84
11	2	4	88	65
12	2	4	27	23
13	2	4	28	21
14	2	4	18	19
-19	2	5	24	27
-18	2	5	44	48
-17	2	5	34	35
-16	2	5	15	17
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-13	2	5	44	42
-12	2	5	34	37
-11	2	5	57	60
-10	2	5	38	40
-9	2	5	13	14
-8	2	5	165	172
-7	2	5	68	70
-6	2	5	89	89
-5	2	5	45	47
-4	2	5	105	111
-2	2	5	118	119
-1	2	5	148	145
2	2	5	34	31
3	2	5	7	5
4	2	5	111	110
5	2	5	81	74
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-8	8	5	49	40
-7	8	5	12	10
-6	8	5	19	23
2	8	5	51	45
4	8	5	16	13
7	8	5	64	66
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9	8	5	27	25
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-3	8	6	41	38
-2	8	6	49	48
1	8	6	16	18
2	8	6	19	19
6	8	6	39	40
7	8	6	39	38
8	8	6	33	38
9	8	6	13	12
10	8	6	12	11
-13	8	7	28	26
-12	8	7	37	39
-11	8	7	38	36
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-8	8	7	17	10
-7	8	7	48	46
-6	8	7	9	7
-5	8	7	48	50
-4	8	7	56	52
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-1	8	7	24	21
1	8	7	46	48
2	8	7	83	86
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-11	8	8	28	28
-8	8	8	10	10
-7	8	8	30	32
-6	8	8	33	36
-5	8	8	47	46
-4	8	8	83	78
-3	8	8	43	38
-2	8	8	15	14
1	8	8	65	65
2	8	8	25	23
4	8	8	12	12
5	8	8	17	21
6	8	8	33	31
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-9	8	9	40	39
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-5	8	9	14	12
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-3	8	9	26	31
-2	8	9	68	61
-1	8	9	83	83
1	8	9	8	7
3	8	9	41	36
4	8	9	24	24
-11	8	10	34	31
-9	8	10	49	53
-8	8	10	30	36
-7	8	10	22	23
-6	8	10	46	48
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-4	8	10	30	32
-3	8	10	34	38
-1	8	10	36	38
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1	8	10	52	53
2	8	10	32	32
3	8	10	11	5
4	8	10	29	32
-8	8	11	49	50
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-5	9	0	40	33
-3	9	0	16	17
-2	9	0	17	14
10	9	0	23	26
12	9	0	24	23
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-11	9	1	13	8
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-9	9	1	45	40
-8	9	1	10	6
-7	9	1	11	13
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-2	9	1	12	10
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-1	9	2	52	49
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-4	9	3	12	6
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2	9	8	22	21
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-7	10	0	36	30
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-1	10	1	108	90
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3	10	1	8	7
4	10	1	39	36
5	10	1	17	13
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-2	10	2	29	23
-1	10	2	31	29
1	10	2	19	11
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3	10	2	42	43
4	10	2	12	8
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0	10	7	16	11
2	10	7	19	18
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-5	10	8	61	65
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-1	10	8	8	0
-5	11	0	22	17
-4	11	0	35	37
-3	11	0	20	23
-2	11	0	16	15
-6	11	1	71	72
-5	11	1	15	19
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-3	11	1	19	11
-2	11	1	66	67
2	11	1	21	19
3	11	1	13	13
4	11	1	17	14
5	11	1	17	19
-6	11	2	38	41
-5	11	2	10	18
-4	11	2	30	37
-3	11	2	41	45
-1	11	2	87	88
1	11	2	31	38
2	11	2	17	15
3	11	2	20	17
1	11	3	27	27
-5	11	4	58	58
-2	11	4	29	29
0	11	4	25	25
1	11	4	26	25
2	11	4	17	18
-2	11	5	12	8
-1	11	5	42	42
0	11	5	22	17
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0

[a] The calculated value of $F(000)$ is 2608.

as obtained from the inverse matrix. The derived position parameters for the group atoms are reported in Table II, and observed and calculated structure factor amplitudes (in electrons) are presented in Table III. The root-mean-square amplitudes of vibration of the six heavy atoms refined anisotropically are listed in Table IV.

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION ALONG PRINCIPAL ELLIPSOID AXES (Å)[a,b]

Atom	Min	Intermed	Max
Cu_1	0.204 (3)	0.231 (2)	0.252 (2)
Cu_2	0.209 (3)	0.244 (2)	0.260 (2)
P_1	0.197 (6)	0.218 (5)	0.238 (5)
P_2	0.187 (6)	0.203 (5)	0.225 (5)
P_1'	0.202 (6)	0.236 (5)	0.246 (5)
P_2'	0.193 (6)	0.223 (5)	0.233 (5)

[a] See footnotes *a* and *b* in Table I. [b] The orientation of these axes relative to those of the unit cell may be determined from atomic positional and unit cell parameters. Their relative orientation may be seen in Figure 2.

Description of the Structure and Discussion

The complex $Cu(N_3)(P(C_6H_5)_3)_2$ exists as a diazido-bridged dimer in the solid state with four such dimers per unit cell. A stereoscopic view of the binuclear complex is given in Figure 1. The dimerization occurs *via* the end-to-end bridging of two azide groups to the two copper atoms. The nonplanar eight-membered heteroatom ring thus formed is stereoscopically illustrated in Figure 2, which also shows the coordination geometry around the copper atoms. The inner coordination of the dimer possesses essentially D_2 symmetry although no crystallographic symmetry is required of the molecule. All important intramolecular distances and angles within the coordination sphere are presented in Table V and selected dihedral angles between significant planes in the inner coordination geometry are given in Table VI.

TABLE V

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG) FOR THE COPPER, PHOSPHORUS, AND NITROGEN ATOMS[a]

Atoms	Distance	Atoms	Angle
Cu_1–N_1	2.102 (10)	N_1–Cu_1–N_4	97.9 (4)
Cu_1–N_4	2.085 (10)	N_1–Cu_1–P_1	101.2 (3)
Cu_2–N_6	2.109 (11)	N_1–Cu_1–P_2	114.8 (3)
Cu_2–N_3	2.116 (10)	N_4–Cu_1–P_1	107.3 (3)
Cu_1–P_1	2.271 (4)	N_4–Cu_1–P_2	110.3 (3)
Cu_1–P_2	2.250 (3)	P_1–Cu_1–P_2	122.3 (1)
Cu_2–P_1'	2.269 (4)	N_3–Cu_2–N_6	99.7 (4)
Cu_2–P_2'	2.266 (3)	N_6–Cu_2–P_1'	111.0 (3)
N_1–N_2	1.169 (11)	N_6–Cu_2–P_2'	108.2 (3)
N_2–N_3	1.193 (12)	N_3–Cu_2–P_1'	102.7 (3)
N_4–N_5	1.179 (13)	N_3–Cu_2–P_2'	112.4 (3)
N_5–N_6	1.194 (12)	P_1'–Cu_2–P_2'	120.8 (1)
Cu_1–Cu_2	4.956 (2)	N_1–N_2–N_3	177.0 (1.0)
N_1–N_4	3.155 (1)	N_4–N_5–N_6	178.6 (1.1)
N_2–N_5	3.052 (1)	Cu_1–N_1–N_2	122.1 (8)
N_3–N_6	3.229 (1)	Cu_2–N_3–N_2	118.1 (8)
		Cu_1–N_4–N_5	124.4 (9)
		Cu_2–N_6–N_5	124.6 (8)

[a] See footnotes *a* and *b* of Table I.

TABLE VI

SELECTED DIHEDRAL ANGLES (DEG) BETWEEN PLANES EACH DEFINED BY THREE ATOMS[a]

Planes	Angle
P_1–Cu_1–P_2 and P_1'–Cu_2–P_2'	20.7 (1)
P_1–Cu_1–P_2 and N_1–Cu_1–N_4	94.0 (3)
P_1'–Cu_2–P_2' and N_3–Cu_2–N_6	85.4 (3)
N_1–N_6–N_3 and N_4–N_2–N_6	38.8 (5)

[a] See footnotes *a* and *b* of Table I.

Each copper atom in the structure is bonded to two nitrogen and two phosphorus atoms and thus possesses its anticipated coordination number of 4. The coordination geometry around the copper atoms is best described as a distorted tetrahedron with large P–Cu–P bond angles of 122.3 (1) and 120.8 (1)°. These values compare favorably with those found in borohydridobis(triphenylphosphine)copper(I) (123.25 (6)°)[4] and octahydrotriboratobis(triphenylphosphine)copper(I) (119.98 (7)°),[6] respectively. The dihedral angles between the planes defined by P–Cu–P and N–Cu–N average 94.3 (3)° as compared with a value of 90° expected for an undistorted tetrahedral environment.

The bond distances around the Cu atoms appear normal. The Cu–P bond distances range from 2.250

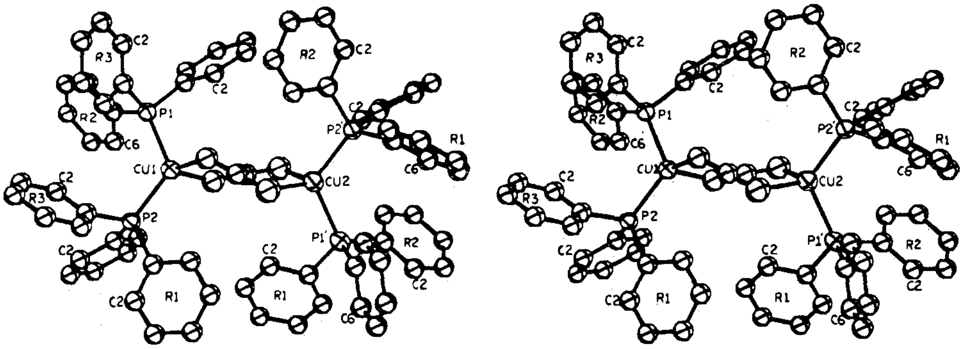

Figure 1.—A stereoscopic view of the dimeric molecule $[Cu(N_3)(P(C_6H_5)_3)_2]_2$.

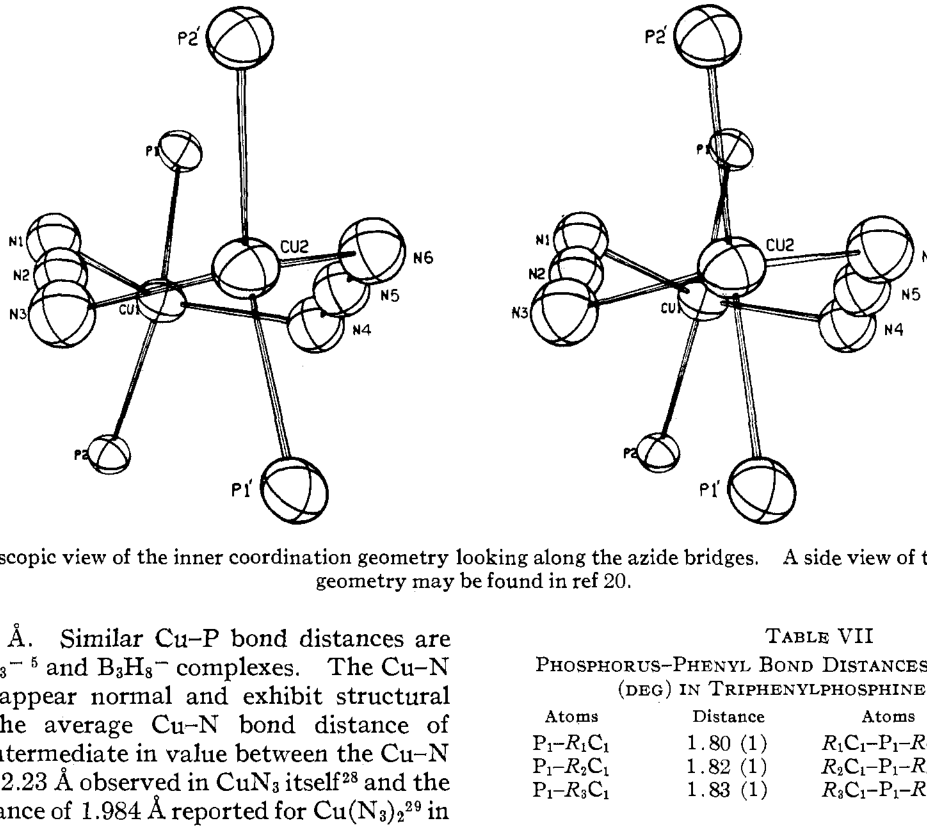

Figure 2.—A stereoscopic view of the inner coordination geometry looking along the azide bridges. A side view of the inner coordination geometry may be found in ref 20.

(3) to 2.271 (4) Å. Similar Cu–P bond distances are found in the NO_3^- [5] and $B_3H_8^-$ complexes. The Cu–N bond distances appear normal and exhibit structural equivalency. The average Cu–N bond distance of 2.102 (10) Å is intermediate in value between the Cu–N bond distance of 2.23 Å observed in CuN_3 itself[28] and the Cu–N bond distance of 1.984 Å reported for $Cu(N_3)_2$[29] in which the two azide ions bridge two copper atoms through the same nitrogen atom. The Cu–N distance in the present structure does, however, appear long relative to the Cu–P distance (*vide infra*).

Table VII summarizes the dimensions about the phosphorus atoms of the triphenylphosphine ligands. The average P–C bond distance of 1.83 (1) Å and the C–P–C bond angles are consistent with values previously observed for coordinated,[5,6] as well as uncoordinated,[30] triphenylphosphine. As in most cases involving the structure of triphenylphosphine, the phenyl rings adopt a configuration in which the $(C_6H_5)_3P$ group possesses no symmetry. The relative orientation of the phenyl rings is shown in Figure 1. We note that the volume of the triphenylphosphine in the present structure is only slightly greater (<5%) than the volume of free triphenylphosphine (364 Å^3).[30]

TABLE VII

PHOSPHORUS–PHENYL BOND DISTANCES (Å) AND ANGLES (DEG) IN TRIPHENYLPHOSPHINE GROUPS[a]

Atoms	Distance	Atoms	Angle
$P_1–R_1C_1$	1.80 (1)	$R_1C_1–P_1–R_2C_1$	104.1 (5)
$P_1–R_2C_1$	1.82 (1)	$R_2C_1–P_1–R_3C_1$	104.0 (4)
$P_1–R_3C_1$	1.83 (1)	$R_3C_1–P_1–R_1C_1$	103.8 (5)
$P_2–R_1C_1$	1.81 (1)	$R_1C_1–P_2–R_2C_1$	100.9 (4)
$P_2–R_2C_1$	1.83 (1)	$R_2C_1–P_2–R_3C_1$	103.6 (4)
$P_2–R_3C_1$	1.82 (1)	$R_3C_1–P_2–R_1C_1$	103.7 (4)
$P_1'–R_1C_1$	1.84 (1)	$R_1C_1–P_1'–R_2C_1$	101.6 (4)
$P_1'–R_2C_1$	1.83 (1)	$R_2C_1–P_1'–R_3C_1$	104.2 (4)
$P_1'–R_3C_1$	1.82 (1)	$R_3C_1–P_1'–R_1C_1$	106.3 (4)
$P_2'–R_1C_1$	1.82 (1)	$R_1C_1–P_2'–R_2C_1$	100.8 (4)
$P_2'–R_2C_1$	1.83 (1)	$R_2C_1–P_2'–R_3C_1$	104.6 (4)
$P_2'–R_3C_1$	1.83 (1)	$R_3C_1–P_2'–R_1C_1$	104.8 (6)

[a] See footnotes *a* and *b* of Table I and footnote *b* of Table II.

Of particular importance in this investigation are the bridging function and structure of the azide ion. Each azide group is essentially linear with an average N–N–N bond angle of 177.8 (1.0)°. The four independent N–N distances do not differ significantly and average 1.178 (12) Å. This average value compares favorably with the corresponding N–N distance of 1.17 Å observed in ionic azides such as NaN_3[31] and CuN_3. These results, however, are in sharp contrast with those of previous X-ray structure determinations of complexed metal azides in which the N–N distances within the azide ligand differ significantly in a manner analogous to that observed for covalent organic azide molecules such as

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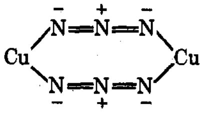
[28] H. Wilsdorf, *Acta Crystallogr.*, **1**, 115 (1948).

[29] I. Agrell, *Acta Chem. Scand.*, **21**, 2647 (1967).

[30] J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

[31] S. B. Hendricks and L. Pauling, *J. Amer. Chem. Soc.*, **47**, 2904 (1925).

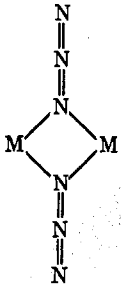
cyanuric triazide (1.26 and 1.11 Å)[32] and methyl azide (1.24 and 1.10 Å)[33a] and for hydrazoic acid (1.24 and 1.13 Å).[33b] We therefore conclude that the predominant canonical form in a description of the bonding in this diazido-bridged structure may be written as I.



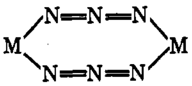
I

The eight-membered heteroatom ring composed of the two copper atoms and the two azide groups is distinctly nonplanar as is evident from Figure 2. The two azide groups are tilted at an angle of 38.8 (5)° with respect to one another and each Cu–N_3–Cu bridge is significantly nonplanar. This result is in contrast with that found for $[CuNCS(P(CH_3)(C_6H_5)_2)_2]_2$ in which the two linear bridging groups are essentially parallel. Two factors which may contribute to the unusual geometry in the present structure are, first, packing effects which optimize the efficiency of the packing and minimize the nonbonded repulsions between the phenyl rings and, second, the allenic nature of the middle nitrogen and the trigonal hybridization of the terminal nitrogens which oppose the planarity of the Cu–N_3–Cu bridge.

The factors influencing the mode of bridging for the azide ion in binuclear transition metal complexes, that is, whether the azide coordinates as a one-end bridge forming a four-membered ring (A) or as an end-to-end bridge forming an eight-membered ring (B), are as yet still unknown.[34] However, a structure of type A with a relatively short M–M distance will, in the present case, undoubtedly increase the nonbonded repulsions due to crowding of the coordination sphere, and, thus, on steric grounds it seems that a structure of type B is preferable.



A



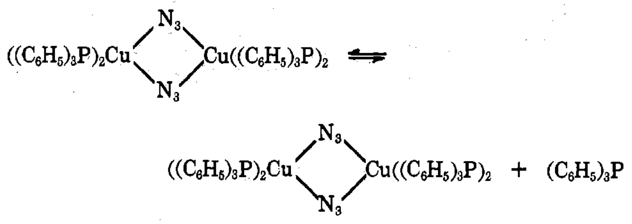
B

Mode B is uniquely exemplified in the present structure while structural results of Dahl and Fehlhammer[35] for $Pd_2(N_3)_6^{2-}$ indicate that the azide groups in that complex bridge as depicted in A. The one-end mode of bridging in $Pd_2(N_3)_6^{2-}$ was predicted by Beck, *et al.*,[36] from infrared studies. Two other azide-bridged binuclear complexes $[Au(CH_3)_2N_3]_2$ and $[Pd(N_3)_2(P(C_6H_5)_3)]_2$ have been isolated but the mode of bridging could not be unequivocally established from either infrared or nmr studies.[37] Further structural work in this area for the elucidation of the factors which prefer one type of bridging network over the other is clearly warranted.

Previously, it was shown that observed molecular weight measurements for $Cu(N_3)(P(C_6H_5)_3)_2$ in chloroform solution were suggestive of a monomer species.[9,10] Two other complexes, the NCS^--bridged dimer (*vide supra*) and the tetraazolato complex $[Ag(C_2N_4F_3)(P(C_6H_5)_3)_2]_2$, which was also found to have a solid-state dimeric structure,[38] behaved similarly in solution in that molecular weight measurements for each complex indicated considerable dissociation of the dimer. In these three complexes, we find that the M–N distance appears relatively long when compared to the M–P distance. If one assumes that the metal atom radii are the same for the two types of bonds in each complex, then the difference in the (M–P)–(M–N) bond distance should equal the differences in the covalent radii of the phosphorus and nitrogen atoms which is 0.36 Å.[39] The MP–MN bond difference for each complex is given below.

Complex	Δ(MP–MN), Å
$[Cu(N_3)(P(C_6H_5)_3)_2]_2$	0.16
$[CuNCS(P(CH_3)(C_6H_5)_2)_2]_2$	0.23
$[Ag(C_2N_4F_3)(P(C_6H_5)_3)_2]_2$	0.07

These values are considerably lower than might be expected and may be indicative of a weak M–N bond. It is not unreasonable then to suggest that for $[Cu(N_3)(P(C_6H_5)_3)_2]_2$ in solution dissociation *via* bridge splitting through the M–N bonds occurs to give the observed molecular weight values. More recently, however, it has been demonstrated that in solution, complexes of the type $Cu_nX_nL_m$ ($L = R_3P$) undergo extensive ligand dissociation and rapid ligand exchange even at low temperatures and in nonpolar solvents.[40] In view of these facts and of the recently determined solid-state structure of $Cu_2Cl_2(P(C_6H_5)_3)_3$[7] and its detection in solution for L = tri-*p*-tolylphosphine,[40] we cannot rule out the possibility that in solution the following dissociation occurs to give the 3,4-coordinate binuclear complex



Such a dissociation would indeed give molecular weight values compatible with the monomer. The observation that the ir-active asymmetric N–N stretch of the N_3^- ligand is at 2053 cm^{-1} both in the solid state and in $CHCl_3$ solution may lend support to the existence of the 3,4-coordinate complex in solution. However, in this situation the ir data for discerning changes in the azide group must be questioned. We note that for the solid-state complex $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$, in which the

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(32) I. E. Knaggs, *Proc. Roy. Soc., Ser. A*, **150**, 576 (1935).

(33) (a) L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.*, **59**, 13 (1937); (b) E. Amble and B. P. Dailey, *J. Chem. Phys.*, **18**, 1422 (1950).

(34) That the azide ion could function as a coordinated bridge in both modes was demonstrated by Agrell[29] in $Cu(N_3)_2$.

(35) W. Beck, private communication.

(36) W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schuierer, and K. Feldl, *Chem. Ber.*, **100**, 2335 (1967).

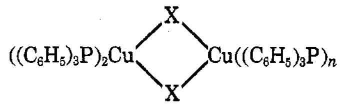
(37) W. Beck, W. P. Fehlhammer, P. Pöllmann, and R. S. Tobias, *Inorg. Chim. Acta*, **2**, 467 (1968).

(38) C. G. Pierpont, R. Eisenberg, R. F. Ziolo, A. P. Gaughan, and Z. Dori, in preparation.

(39) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1967.

(40) E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, **92**, 4114 (1970).

azide ions are nonbridging,[41] the N–N asymmetric stretching frequency differs by about 20 cm^{-1} from that of $[Cu(N_3)(P(C_6H_5)_3)_2]_2$.[42] It is interesting to note also that for compounds of the type



n = 1 or 2 and X^- = Cl^-, Br^-, and I^-, the 4,4-coordinate complex (*i.e.*, $n = 2$) is relatively rare in the solid state and that attempted isolation usually results in the formation of the 3,4-coordinate complex. When $X^- = N_3^-$ or NCS^-, only the 4,4-coordinate complex has been isolated. The dissociation of a triphenylphosphine in the present system in order to explain the solution molecular weight and the constancy of the infrared spectrum in going from the solid to the solution state thus remains as a distinct possibility. The recent work of Muetterties and Alegranti[40] involving temperature-dependent ^{31}P nmr data on coinage metal–phosphine complexes should prove fruitful in this area.

Acknowledgments.—We wish to thank the National Science Foundation, the Advanced Research Projects Agency, and the Brown University and Temple University Computing Centers for support of this work.

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[41] A. P. Gaughan and Z. Dori, *Inorg. Chem.*, in press.

[42] W. Beck, W. P. Fehlhammer, P. Pöllman, and H. Schächl, *Chem. Ber.*, **102**, 1976 (1969).

Notes

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Determination of the H_2SO_4:HSO_4^- and $HClO_4$:ClO_4^- Ratios in Graphite Lamellar Compounds[1]

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Graphite reacts with concentrated sulfuric and perchloric acid either by electrolysis or in the presence of oxidizing agents to form layer compounds.[2,3] In these compounds, layers of bisulfate or perchlorate ions are sandwiched between layers of aromatic carbon atoms. In addition to the ions, the corresponding acid molecules are also incorporated into the adduct layers.

The formulas for the most concentrated compounds, in which layers of acid adduct alternate with carbon layers, can be written $C_{24}^+ \cdot HSO_4^- \cdot xH_2SO_4$ and $C_{24}^+ \cdot ClO_4^- \cdot yHClO_4$. The next most concentrated compounds, in which two layers of carbon are interposed between nearest-neighbor adduct layers, have the compositions $C_{48}^+ \cdot HSO_4^- \cdot x'H_2SO_4$ and $C_{48}^+ \cdot ClO_4^- \cdot y'HClO_4$. Because of the instability of these compounds in air and water, chemical analysis is difficult and values for x', y, and y' have not been reported. The value of x generally consigned to $C_{24}^+ \cdot HSO_4^- \cdot xH_2SO_4$ is 2.[2-4]

In connection with an electrochemical study of the graphite–bisulfate compounds, it was of interest to determine accurately the H_2SO_4:HSO_4^- ratios in the bisulfate lamellar compounds. A gravimetric method of analysis in which graphite compounds formed by electrolysis were weighed in sulfuric acid was used. The method was extended to the graphite–perchloric acid system.

Experimental Section

Procedure for the Determination of the H_2SO_4:HSO_4^- Ratio.—A schematic diagram of the apparatus used to prepare $C_{48}^+ \cdot HSO_4^- \cdot x'H_2SO_4$ and $C_{24}^+ \cdot HSO_4^- \cdot HSO_4^- \cdot xH_2SO_4$ is shown in Figure 1. Similar procedures have been used by a number of investigators.[2-6] The cathode in the electrolysis was a platinum wire. The anode, C_1, was a thin piece (about 0.03 cm thick) of annealed (3200°) pyrolitic graphite with a surface area of about 1 cm^2. This piece was cut from a slab obtained several years ago from the General Electric Metallurgical Products Department, Detroit, Mich. The electrolyte was Baker and Adamson reagent grade concentrated (95.5–96.5 wt %) sulfuric acid obtained from the Allied Chemical Co., Morristown, N. J. The voltage was supplied by two 1.5-V batteries in series. The current was kept constant by manually adjusting the resistance in a resistance box, R_1. The current was measured using a Keithley 602 electrometer which monitored the voltage across a precision resistor, R_2, having a resistance of 100.1 ± 0.1 ohms. The voltage drop between the anode, C_1, and an electrode consisting of another piece of annealed pyrolitic graphite, C_2, was continuously recorded with a Honeywell Electronik 19 voltage recorder.

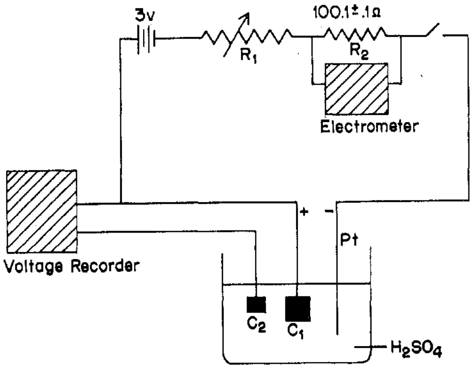

Figure 1.—Schematic of apparatus used for the preparation of graphite layer compounds.

Figure 2 shows data for a typical electrolysis run transcribed from the recorder paper. As bisulfate ions are incorporated into the graphite sample, C_1, the voltage builds up. The break at 54.5 min is in fairly good agreement with the calculated value of 55.6 min for complete formation of the compound $C_{48}^+ \cdot HSO_4^- \cdot x'H_2SO_4$ on the assumption that the electrolysis is 100% efficient and that 1 HSO_4^- ion is present for every 48 carbon atoms. Sample C_1 was weighed three times. It was initially weighed in air as pure graphite. It was weighed in sulfuric acid at the calculated midpoint of the electrolysis (55.6 min) when the for-

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[1] This work was supported by a grant from the National Science Foundation.

[2] W. Rudorff, *Advan. Inorg. Chem. Radiochem.*, **1**, 223 (1959).

[3] G. R. Hennig, *Progr. Inorg. Chem.*, **1**, 125 (1959).

[4] W. Rudorff and U. Hofmann, *Z. Anorg. Allg. Chem.*, **238**, 1 (1938).

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[6] G. R. Hennig, *J. Chem. Phys.*, **19**, 922 (1951).