The Crystal and Molecular Structure of Diazido-μ-1,2-bis(diphenylphosphino)ethane-bis(1,2-bis(diphenylphosphino)ethane)-dicopper(I), $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$

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The crystal and molecular structure of $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$ has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter techniques. The structure has been refined by least-squares methods to a conventional R factor of 0.065 for 1136 nonzero reflections. The structure has been refined in space group *Pbca* of the orthorhombic system in a unit cell of dimensions $a = 18.06$ (2), $b = 18.63$ (2), $c = 21.02$ (2) Å, and $V = 7077$ Å³. The experimental density of 1.33 ± 0.01 g/cm³ is in good agreement with a calculated density of 1.32 g/cm³ for four molecules in the unit cell. The complex is centrosymmetric with the center of symmetry located between the methylene carbons of a bridging diphos (1,2-bis(diphenylphosphino)ethane) ligand. The coordination sphere around each copper atom is completed by a bidentate diphos ligand and an azide moiety, resulting in a distorted tetrahedral geometry. The coordinated azide shows the expected configuration of two nonequivalent N–N distances of 1.196 and 1.076 Å, the longer distance being between the middle nitrogen atom and the nitrogen which is attached to the metal.

Introduction

The chemistry of coordinated azide has received some attention in the last several years.[1] In particular, it was established that several azido complexes of transition metals undergo cycloaddition reactions with dipolarophiles such as CS_2 in a manner analogous to that of organic azides.[2,3]

As part of our structural, chemical, and photochemical studies of azido complexes of group Ib metals we have determined the structure of $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$. This complex was of particular interest to us because solution measurements indicated that the azide moiety is bound through only one nitrogen in contrast to $[Cu(N_3)(P(C_6H_5)_3)_2]_2$ in which the azide ion was shown to bridge two copper atoms through the terminal nitrogens.[4]

With the exception of a pentaazidoiron(III) complex[5a] and an azidoruthenium(II) complex,[5b] all complexes containing nonbridging azides (or azides which bridge through the same nitrogen atom) show significant differences between the two $N–N$ distances.[6-8] Invariably, the longer distance occurs between the middle nitrogen and the nitrogen which is attached to the metal. The structural results reported here indicate this to be the case.

Experimental Section

A 0.5-g sample (5 mmol) of freshly prepared CuCl was added to 50 ml of a chloroform solution containing 4.0 g (10 mmol) of diphos (1,2-bis(diphenylphosphino)ethane) and stirred for 1 hr at room temperature. The addition of 100 ml of hexane resulted in the precipitation of a colorless complex. A solution of 0.07 g (1 mmol) of NaN_3 in 25 ml of absolute ethanol was added slowly to 100 ml of chloroform containing 0.45 g of the chloro complex. The resulting solution was refluxed for 1 hr and filtered. The addition of 100 ml of hexane to the filtrate followed by cooling caused the precipitation of a faintly yellow complex. An analytically pure sample was obtained by recrystallization from a chloroform–hexane solution. *Anal.* Calcd for $Cu_2(N_3)_2$-$((CH_2P(C_6H_5)_2)_2)_3$: C, 66.62; H, 5.12; P, 13.24. Found: C, 66.12; H, 5.28; P, 12.82. Crystals suitable for the X-ray analysis were obtained by slow evaporation of a methylene chloride–diethyl ether solution.

Preliminary precession and Weissenberg photographs taken with Cu Kα radiation indicated the crystals to be orthorhombic. The systematic absences $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$, and $hk0$, $h = 2n + 1$, establish the centrosymmetric space group *Pbca* (D_{2h}^{15}, no. 61).

A tiny crystal ($0.30 \times 0.25 \times 0.30$ mm) in the form of a capped pyramid was selected and mounted with its c^* axis coincident with the ϕ axis of a GE quarter-circle orienter incorporated into a GE XRD-6 diffractometer system. Cell parameters were obtained by a least-squares refinement[9] of 31 reflections which were carefully centered in the counter aperture. The measurements were made at 25° using a takeoff angle of 2° and Zr-filtered Mo Kα radiation (λ 0.7107 Å). The refined cell constants are $a = 18.06$ (2), $b = 18.63$ (2), $c = 21.02$ (2) Å, and a cell volume of 7077 Å³. A calculated density of 1.32 g/cm³ based on four molecules of $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$ in the unit cell agrees well with the experimental value of 1.33 ± 0.01 g/cm³ obtained by flotation in carbon tetrachloride–hexane solution.

Intensity data were collected on a manually operated GE XRD-6 diffractometer. Zr-filtered Mo Kα radiation was used to collect 2644 independent reflections ($2\theta_{max} = 45°$) at a takeoff angle of 3°. Intensities were measured by a scintillation counter with a pulse height selector set to receive 90% of the Mo Kα line. A coupled θ–2θ scan technique was employed with a scan range of 2° centered on the calculated 2θ value and a scan speed of 2°/min. Background counts of 20-sec duration with the crystal and the counter stationary were taken at the limits of the scan for each reflection. Four reflections in different regions of reciprocal space were checked periodically to monitor any decomposition of the crystal. In addition, the crystal alignment was checked twice a day. None of the standard reflections deviated from its mean value by more than 3%.

After the data had been corrected for background, the usual Lorentz and polarization factors were applied to the observed intensities to yield a set of $|F_o|^2$ values, where $|F_o|$ is the observed structure factor amplitude. Of the 2644 independent reflections measured, only 1140 had values above 3σ (*vide infra*). Because of the uniformity of the crystal, the small linear absorption coefficient ($\mu = 8.10$ cm⁻¹), and the fact that at $\chi = 90°$ the intensi-

(1) (a) W. P. Fehlhammer, W. Beck, and P. Pollmann, *Chem. Ber.*, **102**, 3903 (1969); (b) W. Beck, W. P. Fehlhammer, P. Pollmann, and H. Schachl, *ibid.*, **102**, 1976 (1969); (c) W. Beck and M. Bander, *ibid.*, **103**, 583 (1970).

(2) W. Beck, M. Bander, W. P. Fehlhammer, P. Pollmann, and H. Schachl, *Inorg. Nucl. Chem. Lett.*, **4**, 143 (1968).

(3) R. F. Ziolo and Z. Dori, *J. Amer. Chem. Soc.*, **90**, 6560 (1968).

(4) R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *ibid.*, **92**, 738 (1970).

(5) (a) J. Drummond and J. S. Wood, *Chem. Commun.*, 1373 (1969); (b) B. R. Davis and J. A. Ibers, *Inorg. Chem.*, **9**, 2768 (1970).

(6) G. J. Palenik, *Acta Crystallogr.*, **17**, 360 (1964).

(7) Z. Dori, *Chem. Commun.*, 714 (1968).

(8) I. Agrell, *Acta Chem. Scand.*, **20**, 1281 (1966).

(9) In addition to our GEXRD1.1 setting program, the main programs used in this work were local modifications 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 the Temple University CDC6400 computer.

TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$

Atom	x	y	z	B, Å²
Cu^a	0.0566 (1)	0.1051 (1)	0.1385 (1)	
P_1	0.0744 (3)	−0.0024 (3)	0.0853 (2)	
P_2	0.1213 (3)	0.2054 (3)	0.1081 (2)	
P_3	0.1104 (3)	0.1110 (3)	0.2385 (2)	
N_1	−0.0562 (7)	0.1106 (7)	0.1364 (6)	4.2 (3)
N_2	−0.1013 (9)	0.1483 (8)	0.1613 (7)	6.1 (5)
N_3	−0.1419 (10)	0.1823 (8)	0.1836 (7)	8.8 (5)
C_1	0.0008 (9)	−0.0287 (7)	0.0257 (6)	3.9 (4)
C_2	0.1973 (9)	0.2135 (9)	0.1751 (8)	5.3 (5)
C_3	0.1594 (9)	0.2003 (8)	0.2359 (8)	5.4 (5)
$P_1R_1C_1{}^b$	0.2218 (6)	0.0257 (6)	0.0634 (5)	3.8^c
$P_1R_1C_2$	0.2870 (6)	0.0267 (8)	0.0280 (7)	4.9
$P_1R_1C_3$	0.2921 (5)	−0.0129 (11)	−0.0279 (6)	5.5
$P_1R_1C_4$	0.2320 (7)	−0.0535 (7)	−0.0485 (5)	6.3
$P_1R_1C_5$	0.1668 (7)	−0.0544 (8)	−0.0132 (6)	5.1
$P_1R_1C_6$	0.1617 (5)	−0.0148 (10)	0.0427 (5)	1.6
$P_1R_2C_1$	0.1164 (5)	−0.1357 (7)	0.1383 (5)	5.3
$P_1R_2C_2$	0.1057 (7)	−0.1939 (6)	0.1788 (6)	5.7
$P_1R_2C_3$	0.0444 (8)	−0.1957 (5)	0.2189 (5)	5.5
$P_1R_2C_4$	−0.0062 (5)	−0.1394 (7)	0.2185 (5)	5.5
$P_1R_2C_5$	0.0045 (6)	−0.0812 (6)	0.1780 (6)	3.6
$P_1R_2C_6$	0.0658 (8)	−0.0794 (4)	0.1379 (4)	2.1
$P_2R_1C_1$	−0.0403 (4)	0.3602 (8)	0.0999 (4)	4.3
$P_2R_1C_2$	−0.0007 (8)	0.4329 (5)	0.1058 (5)	4.6
$P_2R_1C_3$	0.0759 (8)	0.4221 (5)	0.1132 (5)	6.4
$P_2R_1C_4$	0.1127 (4)	0.3565 (8)	0.1147 (5)	5.0
$P_2R_1C_5$	−0.0034 (7)	0.2946 (5)	0.1014 (4)	2.6
$P_2R_1C_6$	0.0731 (7)	0.2928 (5)	0.1088 (4)	2.1
$P_2R_2C_1$	0.2452 (9)	0.2387 (6)	0.0317 (6)	4.1
$P_2R_2C_2$	0.2822 (5)	0.2428 (7)	−0.0263 (10)	6.3
$P_2R_2C_3$	0.2473 (10)	0.2203 (8)	−0.0818 (6)	3.9
$P_2R_2C_4$	0.1754 (9)	0.1936 (6)	−0.0793 (6)	6.7
$P_2R_2C_5$	0.1284 (5)	0.1894 (7)	−0.0214 (9)	4.6
$P_2R_2C_6$	0.1733 (9)	0.2120 (8)	0.0341 (6)	1.5
$P_3R_1C_1$	−0.0200 (8)	0.1096 (4)	0.3066 (5)	3.9
$P_3R_1C_2$	−0.0637 (4)	0.1191 (7)	0.3605 (7)	4.5
$P_3R_1C_3$	−0.0309 (8)	0.1363 (7)	0.4184 (5)	5.8
$P_3R_1C_4$	0.0455 (8)	0.1440 (5)	0.4224 (5)	6.7
$P_3R_1C_5$	0.0892 (4)	0.1345 (6)	0.3685 (7)	5.7
$P_3R_1C_6$	0.0564 (7)	0.1173 (7)	0.3106 (5)	3.7
$P_3R_2C_1$	0.2561 (8)	0.0575 (5)	0.2548 (6)	4.7
$P_3R_2C_2$	0.3066 (4)	0.0025 (8)	0.2660 (6)	5.1
$P_3R_2C_3$	0.2816 (7)	−0.0658 (7)	0.2817 (5)	4.8
$P_3R_2C_4$	0.2060 (8)	−0.0792 (4)	0.2863 (5)	3.8
$P_3R_2C_5$	0.1554 (4)	−0.0243 (8)	0.2751 (5)	3.3
$P_3R_2C_6$	0.1805 (7)	0.0441 (6)	0.2594 (5)	1.9

Group	$x_0{}^d$	y_0	z_0	ϕ^e	θ	ρ	B, Å²
P_1R_1	0.2269 (4)	−0.0139 (4)	0.0074 (4)	−0.586 (12)	−2.410 (9)	2.342 (10)	2.5 (2)
P_1R_2	0.0551 (4)	−0.1376 (4)	0.1784 (3)	−2.036 (9)	2.788 (8)	−2.431 (7)	1.8 (2)
P_2R_1	0.0362 (4)	0.3583 (4)	0.1073 (2)	1.021 (9)	3.064 (6)	−3.052 (6)	2.0 (2)
P_2R_2	0.2103 (5)	0.2161 (3)	−0.0238 (4)	−1.127 (8)	−2.660 (13)	1.727 (8)	4.1 (3)
P_3R_1	0.0128 (4)	0.1268 (3)	0.3645 (4)	1.802 (7)	2.571 (10)	1.827 (7)	1.3 (2)
P_3R_2	0.2310 (4)	−0.0109 (4)	0.2705 (3)	−0.873 (10)	2.964 (7)	−2.970 (7)	2.5 (2)

	$\beta_{11}{}^{f,g}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	42.0 (9)	32.9 (8)	23.0 (7)	−1.8 (10)	−1.4 (8)	0.0 (8)
P_1	42 (2)	33 (2)	22 (2)	0 (2)	0 (2)	0 (2)
P_2	43 (2)	33 (2)	24 (2)	1 (2)	4 (2)	4 (2)
P_3	42 (2)	30 (2)	19 (2)	−2 (2)	−2 (2)	−1 (2)

^{a} Estimated standard deviations in the least significant figure(s) in this and all subsequent tables are given in parentheses. ^{b} Estimated standard deviations in the rigid-group carbon atoms are derived from an analysis of the rigid-group positional and orientational parameters. ^{c} The thermal parameters of the rigid-group carbon atoms should be regarded as estimates only since they were varied early in the refinement only and fixed throughout the final stages of refinement. The quantity refined was the group thermal parameter. ^{d} x_0, y_0, and z_0 are the fractional coordinates of the origin of the rigid-group coordinate system. In this case the origin is chosen as the center of gravity of the ring. ^{e} The rigid-group *orientational* parameters, ϕ, θ, and ρ are given in radians. ϕ, θ, ρ correspond to δ, ϵ, and η, respectively, as defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965). ^{f} The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^{g} The quantities given in the table are the thermal coefficients × 10^4.

ties of several 00*l* reflections as a function of ϕ varied by less than 1% no absorption correction was applied. The resulting $|F_o|^2$ values were then brought to an approximately absolute scale through a modification of Wilson's procedure.

Solution and Refinement of the Structure[10]

From a sharpened, origin-removed three-dimensional Patterson function, the positions of the copper and three phosphorus

atoms were determined. An isotropic thermal parameter was then assigned to each of the four atoms and three cycles of least-
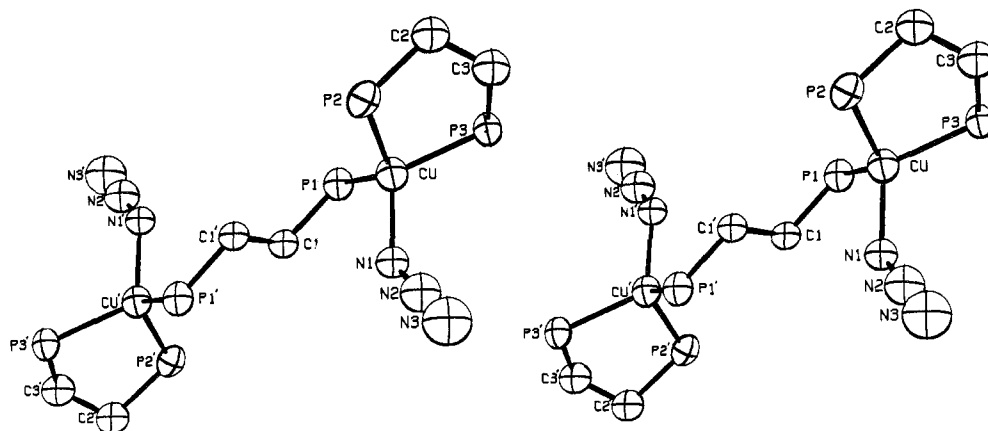
Figure 1.—Stereoscopic view of the coordination geometry of $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$. The phenyl rings are omitted for clarity. In Figures 1 and 2 the primed symbols refer to the centrosymmetrically equivalent atoms.

squares refinement were performed in which the individual positional and isotropic thermal parameters were refined. The positions of all nonhydrogen atoms were determined from a number of difference Fourier maps based on phases obtained from the refined positions of the previously located atoms.

The complete trial structure was refined by a least-squares procedure. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weights were taken as $3F_o^2/\sigma^2(F_o)^2$ and the standard deviations were estimated according to the formula[11]

$$\sigma(F_o^2) = \frac{1}{Lp}(C + B + (0.02P)^2)^{1/2}$$

in which Lp is the Lorentz–polarization factor, C is the count accumulated during the scan, B is the total background count, and P is the net count for the reflection. The neutral Cu, P, N, and C scattering factors were obtained from Ibers' tabulation[12a] while the anomalous parts of the Cu and P scattering factors were obtained from Templeton's tabulation[12b] and included in the calculated structure factors. Only those reflections with $F_o^2 > 3\sigma(F_o^2)$ were included in the refinement and in the calculation of the discrepancy indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

In the first round of calculations, the Cu, P, N, and nonring carbon atoms were assigned an individual isotropic thermal parameter. 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. Three cycles of isotropic refinement converged to $R = 0.12$, $R' = 0.10$.

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. In addition, the overall temperature factor of each group was refined rather than the individual temperature factor of each carbon atom. This refinement converged to discrepancy indices R and R' of 0.087 and 0.065, respectively. The hydrogen atom contributions to the calculated structure factors (including the methylene hydrogens which were located from a difference Fourier map) were then computed and subsequently included as fixed contributions in all further calculations. Examination of the structure factor table showed four reflections with large discrepancies between $|F_o|$ and $|F_c|$. These reflections were found to be affected by streaking and thus omitted. Three additional cycles of refinement with 1136 reflections above 3σ converged to the final values of 0.065 and 0.045 for R and R', respectively.[13] The largest parameter shifts in the final cycle of

(11) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, 1968, Appendix H.

(12) (a) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1; (b) D. N. Templeton, ref 12a, Table 3.3.2.

(13) Three cycles of refinement in which the nitrogen atoms were also allowed to vibrate according to an anisotropic thermal model refined to R and R' values of 0.064 and 0.042, respectively. This slight improvement is insignificant according to Hamilton test (W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965)) and because of the relatively small number of observed reflections we have rejected this model.

refinement were less than 0.1 of their estimated standard deviations and the estimated standard deviation of an observation of unit weight was 1.02. A final difference Fourier map showed no peaks higher then $0.4\ e^-/Å^3$ whereas the average electron density of a carbon atom in this structure was approximately $3.0\ e^-/Å^3$. 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 as obtained from the inverse matrix. The derived positional parameters for the group atoms are also reported in Table I, and an analysis of the agreement between observed and calculated structure factor amplitudes is presented in Table II. Significant interatomic distances and

TABLE II

ANALYSIS OF THE AGREEMENT BETWEEN OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES[a]

Range of $(\sin\theta)/\lambda$	No. within range	R	R'
0.00–0.12	35	0.027	0.024
0.12–0.18	93	0.041	0.036
0.18–0.24	160	0.049	0.041
0.24–0.30	223	0.055	0.052
0.30–0.36	289	0.075	0.066
0.36–0.42	231	0.101	0.102
0.42–0.48	105	0.116	0.121
All	1136	0.065	0.045

[a] The calculated value of $F(000)$ is 2920. See the listing of structure factor amplitudes following this article in the microfilm edition of this volume of the journal.[10]

angles will be found in Table III. The root-mean-square amplitude of vibration of the four heavy atoms refined anisotropically and the dihedral angle between planes about the copper are listed in Table IV.

Description of the Structure and Discussion

As can be seen from Figures 1 and 2, each copper atom is bound to one nitrogen and three phosphorus atoms and thus possesses the anticipated coordination number of 4. There are two types of diphos ligands in the molecule, two crystallographically equivalent bidentate species and, one monodentate diphos which bridges the two copper atoms. The molecule as a whole is centrosymmetric with the center of symmetry located between the methylene carbons of the bridging diphos ligand.

The coordination geometry around each copper atom is best described as a distorted tetrahedron. Since the distortion is at least partially imposed by the bite of the bidentate diphos ligand, meaningful comparison with other phosphine complexes of copper(I) is impossible. However, it is of interest to note that unlike the $(Cu-(N_3)(P(C_6H_5)_3)_2)_2$ structure[4] the distance of the Cu atom

TABLE III
SIGNIFICANT INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG) FOR $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$

Atoms	Distance	Atoms	Angle	Atoms	Angle
$Cu-P_1$	2.317 (6)	P_1-Cu-P_2	119.9 (2)	$Cu-P_2-P_2R_2C_6$	123.7 (5)
$Cu-P_2$	2.295 (6)	P_1-Cu-P_3	114.8 (2)	$P_2R_1C_6-P_2-P_2R_2C_6$	101.1 (4)
$Cu-P_3$	2.319 (5)	P_1-Cu-N_1	99.9 (4)	$P_2R_1C_6-P_2-C_2$	104.8 (4)
$Cu-N_1$	2.040 (13)	P_2-Cu-P_3	90.0 (2)	$P_2R_2C_6-P_2-C_2$	104.3 (2)
N_1-N_2	1.196 (8)	P_2-Cu-N_1	117.5 (4)	$P_2-C_2-C_3$	107 (1)
N_2-N_3	1.076 (18)	P_3-Cu-N_1	115.8 (4)	$Cu-P_3-C_3$	102.2 (6)
P_1-C_1	1.892 (15)	$Cu-N_1-N_2$	132. (1)	$Cu-P_3-P_3R_1C_6$	122.5 (4)
$P_1-P_1R_1C_6$	1.827 (12)	$N_1-N_2-N_3$	179. (1)	$Cu-P_3-P_3R_2C_6$	118.5 (5)
$P_1-P_1R_2C_6$	1.818 (13)	$Cu-P_1-C_1$	116.4 (5)	$P_3R_1C_6-P_3-P_3R_2C_6$	102.5 (3)
C_1-C_1'	1.519 (23)	$Cu-P_1-P_1R_1C_6$	117.8 (2)	$P_3R_1C_6-P_3-C_3$	102.7 (2)
P_2-C_2	1.973 (17)	$Cu-P_1-P_1R_2C_6$	112.1 (3)	$P_3R_2C_6-P_3-C_3$	106.4 (3)
$P_2-P_2R_1C_6$	1.846 (16)	$P_1R_1C_6-P_1-P_1R_2C_6$	105.8 (2)	$P_3-C_3-C_2$	113 (1)
$P_2-P_2R_2C_6$	1.820 (12)	$P_1R_1C_6-P_1-C_1$	104.5 (3)		
P_3-C_3	1.886 (15)	$P_1R_2C_6-P_1-C_1$	98.0 (3)		
$P_3-P_3R_1C_6$	1.807 (14)	$P_1-C_1-C_1'$	108. (1)		
$P_3-P_3R_2C_6$	1.830 (12)	$Cu-P_2-C_2$	102.5 (5)		
C_2-C_3	1.469 (20)	$Cu-P_2-P_2R_1C_6$	118.4 (5)		

TABLE IV
Root-Mean-Square Amplitudes of Vibration along Principal Ellipsoid Axes, Å

Atom	Min	Intermediate	Max
Cu	0.226 (3)	0.239 (3)	0.266 (3)
P_1	0.222 (9)	0.240 (8)	0.264 (8)
P_2	0.217 (10)	0.247 (8)	0.276 (8)
P_3	0.204 (10)	0.231 (8)	0.265 (7)

Dihedral Angle between Planes of Three Atoms about Copper, Deg

Plane 1	Plane 2	Angle
Cu, P_1, P_2	Cu, P_3, N_1	75.6 (2)
Cu, P_2, P_3	Cu, P_1, N_1	88.6 (3)
Cu, P_2, N_1	Cu, P_1, P_3	74.4 (2)

from the four bounding faces of the tetrahedron is approximately the same[14] (0.79 Å from the $P_1P_2P_3$ plane, 0.62 Å from the $P_1P_2N_1$ plane, 0.70 Å from the $P_1P_3N_1$ plane, 0.77 Å from the $P_2P_3N_1$ plane). In addition, the
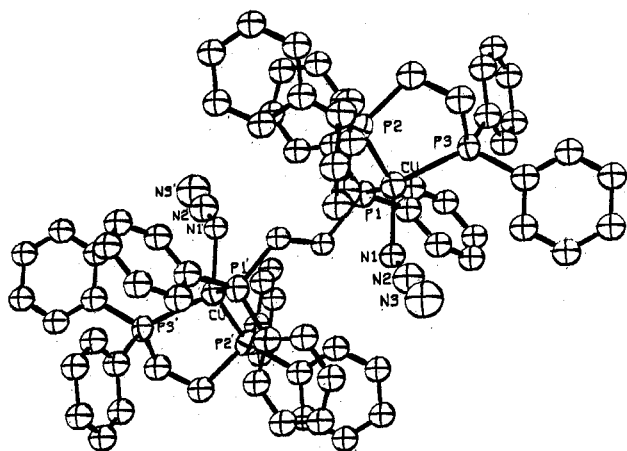
Figure 2.—Perspective view of the molecular structure of $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$.

two planes P_2CuP_3 and P_1CuN_1 are nearly perpendicular to one another (dihedral angle 88.6 (3)°) and the angles between the P_2CuP_3 plane and the $Cu-N_1$ and $Cu-P_1$ vectors are approximately the same. Thus, unlike Cu(I) complexes containing monodentate phosphine ligands, the overall geometry of the present molecule is pretty much dictated by the bidentate diphos ligand.

The three Cu-P bond lengths found in the structure (see Table III) are the longest yet observed in phosphine complexes of Cu(I). Although several explanations are plausible,[15] we do not feel that these are adequate for discussing this structure because of the distortion imposed on the tetrahedral geometry by the bidentate ligand. The Cu-N distance of 2.04 (1) Å is shorter than that observed in the structure of [Cu(N₃)(P(C₆H₅)₃)₂]₂, mean (of four) 2.103 Å, and reflects the stronger σ-donor properties of the monodentate azide ion relative to the bidentate configuration observed in the diazidocopper(I) complex.[4]

The Monodentate diphos Ligand.—The presence of a crystallographically imposed center of symmetry between the two methylene carbon atoms of the bridging diphos ligand constrains the C_1-C_1', C_1-P_1, and $C_1'-P_1'$ vectors to be coplanar and the $P_1-C_1-C_1'-P_1'$ chain to adopt the trans configuration. The C_1-C_1' bond length, 1.519 (23) Å, agrees, within experimental error, with the expected C-C single-bond distance of 1.537 (5) Å.[16] The P_1-phenyl carbon distances, mean 1.822 Å, are in excellent agreement with phosphorus–phenyl carbon distances of 1.81 Å (mean of four) in [CuNCS(PCH₃(C₆H₅)₂)₂]₂,[14] 1.82 Å (mean of twelve) in [Cu(N₃)(P(C₆H₅)₃)₂]₂,[17] and 1.828 Å (mean of three) in P(C₆H₅)₃.[18] The P_1-C_1 bond distance is 1.892 (15) Å. The C–P₁–C bond angles range from 98.0 (3) to 105.8 (2)°, mean 102.8°, and are significantly lower than the tetrahedral value of 109.5°. The contraction of the C-P-C bond angles was observed in the structures of [Cu(N₃)(P(C₆H₅)₃)₂]₂[17] and P(C₆H₅)₃[18] and has been noted for other transition metal complexes of P(C₆H₅)₃[19] and diphos,[20–22] in which the diphos ligand was acting as a bidentate chelating agent. As expected, the Cu–P₁–C bond angles (mean 115.4°) show an expansion, the magnitude of which is

(14) A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chim. Acta*, **4**, 640 (1970).

(15) (a) A decrease in the "s" contribution to the copper hybrid orbitals used by the phosphorus donor atoms can lead to a lengthening of the Cu-P bond: H. A. Bent, *Chem. Rev.*, **61**, 275 (1961). (b) Weakening of the Cu-P, dπ-dπ back-bonding resulting from the increased number of phosphorus atoms about the copper may lead to a lengthening of the Cu-P bond(s).

(16) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 18**, S14s (1965).

(17) R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, **10**, 1289 (1971).

(18) J. J. Daly, *J. Chem. Soc.*, 3799 (1964).

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approximately equal to the magnitude of the contraction observed in the C–P$_1$–C bond angles. The P$_1$–C$_1$–C$_1$' bond angle, 108 (1)°, is very close to the expected tetrahedral value.

One of the features dominating the structure is the conformation of the Cu–diphos–Cu chain. Although the conformation of the P$_1$'–C$_1$'–C$_1$–P$_1$ chain is fixed by symmetry (*vide supra*), centrosymmetric rotations about the C$_1$–P$_1$ bonds lead to a large variety of conformations and consequent variation in the Cu–Cu' distance. Three possible conformations as a function of the angular rotation, δ (−δ), about the C$_1$–P$_1$ bonds are illustrated in I (where the smallest circles are C, the medium-sized ones are P, and the largest are Cu).


Ia (δ = 0?)

Ib (δ = 90°)   Ic (δ = 180°)
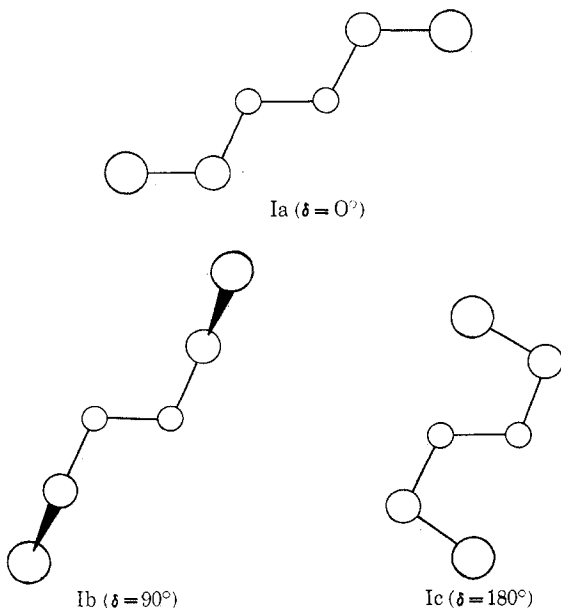
For a hypothetical structure in which all bond angles are 109.5° and bond distances are 1.54, 1.90, and 2.30 Å for the C–C, C–P, and P–Cu bond lengths, respectively, the Cu–Cu' distances are 8.23, 7.53, and 6.52 Å for conformations a, b, and c. In conformations a and c, the copper atoms lie in the plane formed by P$_1$', C$_1$', C$_1$, P$_1$. Conformation b results in the displacement of the copper atoms by 2.17 Å above and below the P$_1$'–C$_1$'–C$_1$–P$_1$ plane and a dihedral angle of 90° between the P$_1$'–C$_1$'–C$_1$–P$_1$ and C$_1$–P$_1$–Cu planes. The Cu–Cu' distance in the molecule is found to be 7.31 Å with the copper atoms displaced by 1.83 Å above and below the P$_1$'–C$_1$'–C$_1$–P$_1$ plane and a dihedral angle of 62° between the P$_1$'–C$_1$'–C$_1$–P$_1$ and C$_1$–P$_1$–Cu planes. This indicates that conformation b most closely represents the conformation of the chain in this molecule. The observed dihedral angle of 62° represents a δ rotation of 62° from conformation c toward b.

Inspection of a molecular model shows that conformation c can be rejected on steric grounds. Conformation b is conditionally acceptable. Severe steric interactions will occur between the phenyl rings of the bidentate and monodentate ligands for various values of the rotation angle about the P$_1$–Cu bond. Conformation a is acceptable on steric grounds for all values of the rotation angle about the P$_1$–Cu bond. The conformation adopted by the molecule is therefore a trade-off between the optimization of packing efficiency (con-

formation c) and minimization of intramolecular non-bonding interactions (conformations b, a).

The Bidentate diphos Ligand.—The five-membered chelate ring formed by Cu, P$_2$, C$_2$, C$_3$, P$_3$ is nonplanar. The deviation from planarity is manifested in the displacement of C$_2$ and C$_3$ by 0.50 and 0.30 Å, respectively, above and below the plane defined by P$_2$, Cu, P$_3$. The phosphorus–phenyl carbon distances, mean 1.825 Å, are similar to those observed for the monodentate diphos ligand in this structure, *vide supra*, and to those found in other transition metal complexes containing a bidentate diphos moiety.[20–22] Similarly, the C–P–C bond angles (mean 103.7°) show the expected contraction relative to the tetrahedral value. With the exception of the Cu–P$_2$–C$_2$ and Cu–P$_3$–C$_3$ bond angles, the Cu–P–C angles, mean (of four) 120.8°, show values which are slightly higher than those of the monodentate diphos in this structure but are within the range of those observed in structures containing diphos chelate rings.[20–22] The internal angles of the chelate ring are in qualitative agreement with reported values.[20–22] Evidence for the presence of considerable strain in the ring, other than that afforded by the deformation of the ring from planarity, is found in the distortion of several of the bond distances within the ring. The P$_2$–C$_2$ bond length, 1.973 (17) Å, is considerably longer than the P$_3$–C$_3$ bond length, 1.886 (15) Å, and longer than any phosphorus–alkyl carbon distance observed in similar structures.[20–22] The C$_2$–C$_3$ bond length, 1.469 (20) Å, is shorter than the value expected for a C–C single bond (*vide supra*). A more detailed consideration of the conformation of the diphos chelate ring will be presented in the report on the structure of the trifluoroacetonitrile adduct of Cu$_2$(N$_3$)$_2$-((CH$_2$P(C$_6$H$_5$)$_2$)$_2$)$_3$.[23]

As expected, the azide ion is essentially linear with an N–N–N bond angle of 179.2 (1.0)°. The two N–N distances are significantly different being 1.196 (18) and 1.076 (18) Å with the longer bond between the middle nitrogen and the nitrogen which is attached to the metal. We, therefore, conclude that the predominant canonical form in a description of the bonding of azide to the copper may be written as II.

$$\overset{-}{N}\!\!-\!\!\overset{+}{N}\!\!\equiv\!\!N$$
$$\diagup$$
$$Cu$$

II
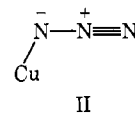
The crystal structure consists of the packing of discrete units of Cu$_2$(N$_3$)$_2$((CH$_2$P(C$_6$H$_5$)$_2$)$_2$)$_3$ oriented about the four (a) positions of $\bar{1}$ symmetry. The Cu–Cu' vector (see Figure 1) exhibits angles of 73.75, 57.60, and 37.17° with respect to the crystallographic a, b, and c directions. All intermolecular contacts appear normal. The shortest intermolecular contact is 2.3 Å between the calculated positions of two of the phenyl hydrogens. The average "contact" is 3.5 Å. The spatial arrangement of the phenyl rings (both intra- and intermolecular) is such that it creates an approximately spherical hole in which the azide ion is accommodated. The relatively large empty space around the azide moiety is undoubtedly responsible for the somewhat high thermal parameters observed for the middle and terminal nitro-

(23) A. P. Gaughan and Z. Dori, *Inorg. Chem.*, in press.

gen atoms. In fact, the hole size (the approximate radius is 3.5 Å taking phenyl hydrogens into account) seems large enough to accommodate larger anions. Thus, the structure of the trifluoroacetonitrile adduct of $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$,[23] which is currently under investigation, might be expected to have a similar overall geometry.

Polyatomic Cations of Sulfur. II. The Crystal Structure of Octasulfur Bis(hexafluoroarsenate), S₈(AsF₆)₂

BY C. G. DAVIES, R. J. GILLESPIE,* J. J. PARK, AND J. PASSMORE

The structure of $S_8(AsF_6)_2$ has been determined from three-dimensional X-ray diffraction data by a direct sign determination procedure. The crystals are monoclinic, mol wt 634.3, $a = 15.005 \pm 0.005$ Å, $b = 13.401 \pm 0.005$ Å, $c = 16.489 \pm 0.005$ Å, $\beta = 107.96 \pm 0.01°$, $V = 3154$ Å³, $Z = 8$, $d_m = 2.6 \pm 0.1$ g cm⁻³, $d_c = 2.66$ g cm⁻³, space group $P2_1/c$. The least-squares refinement of this structure gave a conventional R index of 0.067 for 1975 reflections. The configuration of the $S_8{}^{2+}$ cation is that of a folded ring with approximate C_s symmetry having an endo–exo conformation. The average S–S bond distance around the ring is 2.04 Å, and the S–S–S bond angles average 102° excluding the two end angles which average 93°. The cross-ring S–S distances between atoms related by the pseudo mirror plane range between 2.83 and 3.05 Å. The average As–F bond length in the approximately octahedral $AsF_6{}^-$ ion is 1.67 Å.

Introduction

Sulfur, selenium, and tellurium can be oxidized by various oxidizing agents such as SO_3, $S_2O_6F_2$, AsF_5, and SbF_5 to colored cations containing the element in low oxidation states of 1+ or less. For example sulfur can be oxidized with arsenic pentafluoride to the two compounds $S_{16}{}^{2+}(AsF_6{}^-)_2$ and $S_8{}^{2+}(AsF_6{}^-)_2$[1,2] and with antimony pentafluoride to $S_{16}{}^{2+}(SbF_6{}^-)_2$ and $S_8{}^{2+}(Sb_2F_{11}{}^-)_2$.[2] Stable solutions of these cations as well as $S_4{}^{2+}$ have been obtained by oxidizing sulfur with SO_3 in solution in oleum or with $S_2O_6F_2$ in solution in fluorosulfuric acid.[2,3] The white crystalline material $S_4{}^{2+}(SO_3F^-)_2$ has been obtained by oxidizing sulfur with $S_2O_6F_2$ in solution in SO_2.[2,3] The oxidation state and molecular weight of the cations have been established by chemical analysis of their compounds, by cryoscopic and conductometric measurements on their solutions, and by magnetic and spectroscopic measurements on the solids and the solutions. Similar studies have shown that selenium can be oxidized to $Se_4{}^{2+}$ and $Se_8{}^{2+}$ and tellurium to $Te_4{}^{2+}$ and $Te_n{}^{n+}$.[4] These ions thus constitute a new class of homopolyatomic cations which contain the elements sulfur, selenium, and tellurium in hitherto unknown oxidation states. Their structures are of obvious interest. The first structure to be determined was that of $Se_4{}^{2+}$. A single-crystal X-ray crystallographic study of the orange crystalline compound $Se_4{}^{2+}(HS_2O_7^-)_2$ has shown that $Se_4{}^{2+}$ has a square-planar structure.[5,6] Comparison of the absorp-

tion spectra, the infrared and Raman spectra, and the magnetic circular dichroism of $S_4{}^{2+}$ and $Te_4{}^{2+}$ with those of $Se_4{}^{2+}$ lead to the conclusion that these ions also have a square-planar structure.[4] Very recently this conclusion has been confirmed for $Te_4{}^{2+}$ by an X-ray crystallographic study of $Te_4(AlCl_4)_2$ and $Te_4(Al_2Cl_7)_2$.[7]

The present paper reports a single-crystal X-ray crystallographic investigation of the structure of $S_8{}^{2+}(AsF_6{}^-)_2$. While our investigation was in progress, a preliminary communication on the structure $Se_8(AlCl_4)_2$ was published[8] which showed that $Se_8{}^{2+}$ has the structure of a folded ring with an endo–exo conformation and a long cross-ring bond giving a bicyclic structure reminiscent of bicyclo[3.3.0]octane. The results of this work on $Se_8{}^{2+}$ are compared with our own in the discussion.

Experimental Section

The preparation of the compound $S_8(AsF_6)_2$ from arsenic pentafluoride and sulfur has been described previously.[1,2] Slow recrystallization from hydrofluoric acid yielded dark blue crystals. These were pumped dry on a vacuum line and subsequently handled in a drybox. The crystals were mounted in 0.3-mm thin-walled quartz capillary tubes for the subsequent X-ray examination.

Precession photographs of the $0kl$, $1kl$, $2kl$, and $hk0$, $hk1$, $hk2$ planes using Cu Kα radiation showed the systematic absences characteristic of the space group $P2_1/c$ (no. 14, $C_{2h}{}^5$). The crystals are monoclinic, mol wt 634.3, $a = 15.005 \pm 0.005$ Å, $b = 13.401 \pm 0.005$ Å, $c = 16.489 \pm 0.005$ Å, $\beta = 107.96 \pm 0.01°$, $V = 3153.9$ Å³, $Z = 8$, $d_m = 2.6$ (1) g cm⁻³, $d_c = 2.66$ g cm⁻³. The density was determined by the standard displacement method using Fluorolube oil as the inert liquid. All weighings were performed in a drybox. The unit cell parameters were found by least-squares refinement of the Bragg angle and crystal

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