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The Crystal and Molecular Structure of Di-2-(5-perfluoromethyltetrazolato)-μ-1,2-bis(diphenylphosphino)ethane-bis(1,2-bis(diphenylphosphino)-ethane)dicopper(I), $Cu_2(CF_3CN_4)_2((CH_2P(C_6H_5)_2)_2)_3$

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The crystal and molecular structure of di-2-(5-perfluoromethyltetrazolato)-μ-1,2-bis(diphenylphosphino)ethane-bis(1,2-bis(diphenylphosphino)ethane)dicopper(I), $Cu_2(CF_3CN_4)_2((CH_2P(C_6H_5)_2)_2)_3$, has been determined from three-dimensional X-ray diffraction data collected by counter techniques. The structure was refined by full-matrix least-squares techniques to a conventional R factor of 0.068 for 1436 nonzero reflections. The material crystallizes in space group C_2/c (C_{2h}^6, no. 15) of the monoclinic system. Unit cell data are $a = 23.619$ (20) Å, $b = 18.368$ (18) Å, $c = 17.897$ (18) Å, $\beta = 92.28$ (5)°, $V = 7758$ Å^3, $Z = 4$; $d_{\text{measd}} = 1.38 \pm 0.02$ g/cm^3, $d_{\text{calcd}} = 1.365$ g/cm^3. The complex is centrosymmetric with the center of symmetry located midway between the methylene carbons of a bridging diphos (1,2-bis(diphenylphosphino)ethane) ligand. The coordination sphere about the copper atom is completed by a bidentate diphos ligand and a nitrogen atom in the 2(3) position of the 5-perfluoromethyltetrazolate ion. The resulting geometry about the copper atom can be described as a distorted tetrahedron. The independent Cu–P bonds range from 2.277 (5) to 2.338 (5) Å. The internal angles in the tetrazole ring range from 97 (2) to 119 (2)°. The N–N distances vary from 1.119 (17) to 1.482 (20) Å and the C–N distances are 1.372 (24) and 1.413 (22) Å.

Introduction

The formation of a number of 5-substituted tetrazoles *via* an addition reaction involving a nitrile function and an azide moiety coordinated to a transition metal has recently been reported.[1,2] The reaction appears to proceed by a mechanism similar to the 1,3 dipolar cycloaddition proposed for the addition of organic and ionic azides to dipolarophiles such as acetylenes and nitriles.[3]

Recently, Nelson, *et al.*,[4] reported a series of nmr studies on the products of oxidative addition and substitution reactions of a number of 5-substituted tetrazoles to phosphine complexes of zero and divalent palladium and platinum. Their results indicated the presence of both N_1- and N_2-bonded tetrazoles.[5] A structural study performed in this laboratory on the product of the cycloaddition reaction between trifluoroacetonitrile and azidobis(triphenylphosphine)silver(I)[6] has shown the complex to be binuclear with two tetrazolate ions, each functioning as a bridging ligand utilizing the 2 and 3 positions on the ring. This novel mode of coordination is apparently the result of the tendency of phosphine complexes of silver(I) to attain four-coordination. The approximate dimensions of the tetrazole ring were taken to indicate the presence of a localized double bond between the 2 and 3 positions and a delocalization of electron density over the N–C–N part of the ring.

A recent report on the structure of $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$[7] showed the azide moiety to be bound through only one nitrogen in contrast to $[Cu(N_3)(P(C_6H_5)_3)_2]_2$[8] (and presumably the analogous silver complex).[9] In order to provide further information concerning the electronic structure of coordinated tetrazoles and the details of their bonding to the metal ion, the structure determination of the cycloaddition product of trifluoroacetonitrile and $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$ was undertaken.

Experimental Section

The complex is obtained as the product of a cycloaddition reaction between a chloroform solution of $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$ and trifluoroacetonitrile. The preparation of $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$ has been described previously.[7] Trifluoroacetonitrile (CF_3CN) was obtained from Peninsular Chem. Research Inc.

Gaseous trifluoroacetonitrile was bubbled (with the aid of a gas dispersion device) through 100 ml of a chloroform solution containing 1.4 g (1 mmol) of the azido complex for a period of 10 min. The solution was purged of excess trifluoroacetonitrile with nitrogen and the addition of 100 ml of hexane caused the precipitation of a colorless complex. The formation of the tetrazole ring was confirmed by the absence of the asymmetric azide stretch at 2035 (2) cm^{-1} [10] which is characteristic of the azide moiety in $Cu_2(N_3)_2$(diphos)$_3$ (diphos is 1,2-bis(diphenylphosphino)ethane) and by the appearance of several bands in the region 1100–1250 cm^{-1} which are characteristic of the tetrazolate anion[4] and the CF_3 group. Crystals suitable for the X-ray analysis were obtained by the slow evaporation of a methylene chloride–hexane solution.

Precession and Weissenberg photographs taken with Cu Kα radiation showed the crystal to belong to the monoclinic system. The systematic absences hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, indicate the space group to be Cc (C_s^4, no. 9) or $C2/c$ (C_{2h}^6, no. 15). A tiny crystal (0.27 × 0.31 × 0.24 mm) was selected and mounted with its b^* 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[11] of 27 reflections which were carefully centered in the counter aperture. The measurements were made at ambient temperature using a takeoff angle of 2° and Zr-filtered

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[1] W. Beck and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl.*, **6**, 169 (1967).

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

[3] G. L'Abbé, *Chem. Rev.*, **69**, 345 (1969), and references therein.

[4] J. H. Nelson, D. L. Schmitt, R. A. Henry, D. W. Moore, and H. B. Jonassen, *Inorg. Chem.*, **9**, 2678 (1970).

[5] The numbering of atoms in the ring starts with the nitrogen atom adjacent to the carbon and proceeds counterclockwise around the ring: A. I. Popov, *Coord. Chem. Rev.*, **4**, 463 (1969).

[6] C. G. Pierpont, R. Eisenberg, A. P. Gaughan, and Z. Dori, to be submitted for publication.

[7] A. P. Gaughan, R. F. Ziolo, and Zvi Dori, *Inorg. Chem.*, **10**, 2776 (1971). The molecule was found to be oriented about the 4(a) positions of $\bar{1}$ symmetry in space group $Pbca$ in a cell of dimensions $a = 18.06$ Å, $b = 18.63$ Å, and $c = 21.02$ Å.

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

[9] Unit cell and space group determination indicate that $Ag(N_3)(P(C_6H_5)_3)_2$ is isomorphous with $Cu(N_3)(P(C_6H_5)_3)_2$ (see ref 8).

[10] A. P. Gaughan, unpublished results.

[11] In addition to our GEXRD 1.1 setting program, the main programs used in this work were local modifications of the Busing–Levy–Martin ORFLS and ORFFE, Iber's GROUP 1, Zalkin's FORDAP, AND Johnson's ORTEP. Various other programs were also used. All computing was performed on the Temple University CDC 6400 and the University of Pennsylvania IBM 360/75 computers.

Mo Kα radiation (λ 0.7107 Å). The refined cell constants are $a = 23.619$ (20) Å, $b = 18.368$ (18) Å, $C = 17.897$ (18) Å, $\beta = 92.28$ (5)°, and a cell volume of 7758 Å^3. A calculated density of 1.365 g/cm^3 based on four molecules of $Cu_2(CF_3CN_4)_2((CH_2P(C_6H_5)_2)_2)_3$ in the unit cell agrees with the experimental value of 1.38 (2) g/cm^3 obtained by flotation in a carbon tetrachloride–hexane mixture.

Intensity data were collected on a manually operated GE XRD-6 diffractometer. Zr-filtered Mo Kα radiation was employed. A total of 3644 independent reflections ($2\theta_{\max} = 40°$) were measured 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. The θ–2θ scan technique[12a] was used with a scan range of 2°[12b] centered on the calculated 2θ value and a scan speed of 2°/min. Background counts of 20-sec duration with crystal and counter stationary were taken at the limits of the scan for each reflection.

The crystal alignment was checked at 6-hr intervals and four reflections (two each in the zones hkl, $hk\bar{l}$) were checked periodically to monitor any decomposition of the crystal. No systematic trends were noted in the intensities of the standard reflections and none deviated from its mean value by more than 3.5%.

The data were corrected for background to yield a set of raw intensities to which were applied the usual Lorentz and polarization factors. No absorption correction was applied. Consideration of the maximum and minimum path lengths for the crystal and the linear absorption coefficient for the complex ($\mu = 7.7$ cm^{-1}) shows the transmission coefficients to vary from about 0.79 to 0.83. The fact that the intensity of several of the $0k0$ reflections ($\chi = 90°$) as a function of ϕ were found to vary by less than 1.5% indicates that the effect of absorption is indeed minimal. The resulting F_o^2 ($|F_o|$ is the observed structure factor amplitude) were then brought to an approximately absolute scale through a modification of Wilson's procedure. In addition to the 3644 observations, the reflections within the range $0° < 2\theta < 40°$ which were systematically absent were included in the scaling.

Standard deviations were estimated according to the formula[13]

$$\sigma(F_o^2) = \frac{1}{Lp}\left(C + \frac{3}{2}B + (0.02P)^2\right)^{1/2}$$

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. Using the arbitrary criterion $F_o^2 < 2\sigma(F_o^2)$, all but 1445 reflections were rejected as being statistically insignificant.

Solution and Refinement of the Structure

From a sharpened, origin removed three-dimensional Patterson function, a trial position for the copper atom was derived using the $0, v, {}^1/_2$ $({}^1/_2, v, {}^1/_2)$ and $u, 0, w$ $(u, {}^1/_2, w)$ Harker vectors consistent with space group $C2/c$. The choice of space group is supported by the presence of a concentration of vectors in the Harker section $u, 0, w$, $(u, {}^1/_2, w)$.[14] The agreement ultimately attained between observed and calculated structure amplitudes confirms $C2/c$ as the correct choice. Further analysis of the Patterson function led to trial positions for the three phosphorus atoms. The arrangement of the heavy atoms indicated that the molecule was oriented about the 4(c) positions of $\bar{1}$ symmetry[15] and the presence of a short Cu–Cu vector (7.29 Å) which is almost identical with the centrosymmetric Cu–Cu vector (7.31 Å) observed in the structure of $Cu_2(N_3)_2(diphos)_3$[7] strongly suggests that the two complexes are isostructural except for one coordination position.

The y coordinate of each of the four atomic positions (Cu_1, P_1, P_2, P_3) derived from the Patterson function was found to lie sufficiently close to ${}^1/_4$ to suggest that a false-mirror operation would be present in the electron density function based on phases (signs) derived from these atomic positions. This anticipation proved correct and it was found to be impossible to locate a sufficient number of the phenyl carbon atoms belonging to the correct image to destroy the false mirror operation.[16]

It was apparent that a large number of the atoms belonging to the correct image would have to be located before the refinement could proceed. Based on the isostructural asssumption (*vide supra*), a series of transformations was made which took the complete set of atomic positions (exclusive of the azide nitrogens) for $Cu_2(N_3)_2(diphos)_3$[7] through an internal coordinate system based on the known geometry about the copper atom and into the unit cell of $Cu_2(CF_3CN_4)_2(diphos)_3$ where the copper atoms were made coincident[17] and the rest of the molecule oriented so as to superimpose the corresponding phosphorus atoms.[18] These transformations were performed for the two mirror-image solutions of $Cu_2(CF_3CN_4)_2(diphos)_3$ yielding a set of trial positions for each. Each of the trial structures was used as the basis for a least-squares refinement. One refinement resulted in divergence; the other converged to a conventional agreement factor of 0.27. The positions of the remaining nonhydrogen atoms were determined from a subsequent difference Fourier map.

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 $3F_o^2/\sigma^2(F_o^2)$. The neutral Cu, P, F, N, and C scattering factors were those of Cromer and Waber[19] and the anomalous parts of the Cu and P scattering factors were obtained from Cromer's tabulation[20] and were included in the calculated structure factors. Only those reflections with $F_o^2 > 2\sigma(F_o^2)$ were included in the refinement and in the calculation of the discrepancy indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

Initially, the Cu, P, F, 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 refinement converged to $R = 0.14$, $R' = 0.11$ During the refinement, the thermal parameters for the atoms of the tetrazole moiety with the exception of the nitrogen atom coordinated to the copper were observed to rise to a relatively high value (B = 8–14). Previous work[7] had led us to expect a high degree of thermal agitation for the atoms in this coordination position, and, further, we anticipated the possibility of a disorder problem involving the fluorine atoms of the CF_3 group. A subsequent difference Fourier map revealed three regions of high electron density (1.2 e/Å^3) lying approximately in the plane of the three fluorines and symmetrically distributed about the fluorine positions. Several other regions of high electron density in the vicinity of the heavy atoms were attributed to anisotropic thermal motion of these 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. The CF_3 moiety was treated as a rigid group involving a static twofold disorder of the fluorine positions (C_{6v} symmetry, C–F bond length 1.33 Å, F–C–F bond angle 108°).[21] Each of the disordered positions for the fluorine atoms was assigned an occupancy factor of 0.5. In addition, the overall temperature factor of each phenyl group was refined rather than the individual temperature factor of each carbon atom. The refinement converged to discrepancy indices R and R' of 0.081 and 0.064, respectively. It was noted that the isotropic thermal coefficients for the original three fluorine positions were systematically lower (B = 3–5) than those of the remaining three positions (B = 9–13). This was taken to indicate that the occupancy factors

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(12) (a) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957. (b) The possibility of the occurrence of overlap at the counter window was examined in our setting program using established criteria [J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **6**, 1575 (1967)], and the results indicated that the problem was of a minor nature.

(13) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, Appendix H.

(14) M. J. Buerger, "Vector Space," Wiley, New York, N. Y., 1959.

(15) The 4(c) and 4(d) positions are equivalent in $C2/c$ and an equally good solution based on the 4(d) positions could have been derived from the Patterson function.

(16) As expected, a least-squares refinement based on each of the images for Cu, P_1, P_2, P_3 resulted in the same agreement factor ($R = 0.37$). A least-squares refinement based on Cu, 3 P, and 15 C belonging to what proved to be the correct image resulted in an R factor of 0.33.

(17) The y coordinate of the copper atom derived from the Patterson function was 0.25 and therefore there was only one copper atom position for both images.

(18) The mathematical details of these transformations will be found in the Appendix.

(19) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(20) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(21) *Chem. Soc., Spec. Publ.*, **No. 11**, M120 (1958).

TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $Cu_2(CF_3CN_4)_2((CH_2P(C_6H_5)_2)_2)_3$

Atom	x	y	z	B, Å^2
Cu[a]	0.23023 (9)	0.23831 (11)	0.19731 (11)	...
P_1	0.2077 (2)	0.1812 (3)	0.0872 (2)	...
P_2	0.3216 (2)	0.2232 (3)	0.2436 (2)	...
P_3	0.1963 (2)	0.1906 (3)	0.3081 (2)	...
N_1	0.1470 (8)	0.3463 (11)	0.1450 (9)	10.4 (6)
N_2	0.2028 (6)	0.3403 (8)	0.1776 (7)	3.7 (4)
N_3	0.2139 (7)	0.3941 (10)	0.2037 (9)	7.3 (5)
N_4	0.1748 (8)	0.4565 (10)	0.1916 (10)	10.1 (6)
C_1	0.2172 (5)	0.2384 (9)	−0.0006 (7)	3.0 (4)
C_2	0.3102 (6)	0.1531 (8)	0.3183 (7)	2.9 (4)
C_3	0.2632 (6)	0.1761 (8)	0.3708 (7)	2.6 (4)
C_4	0.1305 (9)	0.4172 (14)	0.1548 (12)	8.5 (6)
C_5[b]	0.0810 (3)	0.4557 (5)	0.1328 (5)	9.5[c]
F_1	0.0485 (6)	0.4568 (9)	0.1927 (5)	8.4
F_2	0.0518 (5)	0.4192 (7)	0.0792 (8)	6.0
F_3	0.0863 (6)	0.5239 (6)	0.1098 (9)	5.4
F_4[d]	0.0381 (6)	0.4094 (6)	0.1446 (10)	1.2
F_5[d]	0.0759 (6)	0.4765 (9)	0.0616 (5)	4.7
F_6[d]	0.0726 (5)	0.5141 (7)	0.1752 (7)	6.5
$P_1R_1C_1$	0.2859 (4)	0.0067 (8)	−0.0100 (6)	4.1
$P_1R_1C_2$	0.2942 (5)	−0.0394 (5)	0.0513 (9)	3.1
$P_1R_1C_3$	0.2789 (6)	−0.0167 (7)	0.1219 (7)	3.9
$P_1R_1C_4$	0.2554 (4)	0.0520 (8)	0.1312 (5)	3.2
$P_1R_1C_5$	0.2424 (6)	0.0754 (7)	−0.0006 (6)	2.2
$P_1R_1C_6$	0.2472 (5)	0.0980 (5)	0.0700 (8)	1.1
$P_1R_2C_1$	0.1170 (5)	0.1035 (8)	0.0207 (5)	2.0
$P_1R_2C_2$	0.0601 (6)	0.0859 (6)	0.0084 (5)	3.1
$P_1R_2C_3$	0.0189 (4)	0.1207 (12)	0.0489 (7)	3.9
$P_1R_2C_4$	0.0347 (4)	0.173 (8)	0.1019 (6)	2.2
$P_1R_2C_5$	0.0916 (6)	0.1908 (6)	0.1142 (5)	2.0
$P_1R_2C_6$	0.1328 (4)	0.1560 (11)	0.0737 (7)	1.5
$P_2R_1C_1$	0.3326 (3)	0.3483 (8)	0.3263 (6)	3.2
$P_2R_1C_2$	0.3607 (6)	0.4023 (5)	0.3678 (6)	5.1
$P_2R_1C_3$	0.4194 (6)	0.3997 (6)	0.3784 (5)	4.5
$P_2R_1C_4$	0.4499 (3)	0.3431 (8)	0.3475 (6)	3.3
$P_2R_1C_5$	0.4217 (5)	0.2891 (5)	0.3060 (6)	2.8
$P_2R_1C_6$	0.3630 (5)	0.2917 (6)	0.2954 (5)	1.7
$P_2R_2C_1$	0.3958 (7)	0.2299 (6)	0.1277 (8)	2.6
$P_2R_2C_2$	0.4359 (5)	0.2007 (8)	0.0813 (6)	4.7
$P_2R_2C_3$	0.4546 (6)	0.1295 (10)	0.0921 (7)	7.5
$P_2R_2C_4$	0.4332 (8)	0.0875 (6)	0.1492 (9)	8.1
$P_2R_2C_5$	0.3931 (5)	0.1168 (8)	0.1956 (7)	5.9
$P_2R_2C_6$	0.3744 (5)	0.1880 (9)	0.1849 (6)	2.4
$P_3R_1C_1$	0.1487 (6)	0.2292 (7)	0.4452 (8)	5.0
$P_3R_1C_2$	0.1128 (5)	0.2699 (9)	0.4887 (4)	4.3
$P_3R_1C_3$	0.0809 (7)	0.3263 (10)	0.4566 (8)	4.6
$P_3R_1C_4$	0.0849 (6)	0.3420 (7)	0.3809 (9)	6.4
$P_3R_1C_5$	0.1208 (5)	0.3014 (9)	0.3374 (4)	4.3
$P_3R_1C_6$	0.1527 (7)	0.2450 (10)	0.3695 (7)	2.2
$P_3R_2C_1$	0.1870 (3)	0.0366 (9)	0.3221 (5)	2.4
$P_3R_2C_2$	0.1565 (6)	−0.0292 (6)	0.3248 (5)	2.3
$P_3R_2C_3$	0.0977 (6)	−0.0271 (6)	0.3169 (6)	2.5
$P_3R_2C_4$	0.0693 (3)	0.388 (9)	0.3063 (6)	5.5
$P_3R_2C_5$	0.0998 (6)	0.1035 (6)	0.3036 (6)	3.4
$P_3R_2C_6$	0.1587 (6)	0.1024 (6)	0.3115 (6)	1.9

Group	X_0[e]	Y_0	Z_0	ϕ[f]	θ	ρ	B, Å^2
CF_3	0.0622 (3)	0.4667 (4)	0.1272 (5)	2.741 (9)	2.900 (12)	1.387 (10)	5.9 (3)
P_1R_1	0.2707 (2)	0.0293 (4)	0.0606 (4)	−2.643 (8)	2.487 (10)	−1.739 (8)	3.0 (2)
P_1R_2	0.0758 (3)	0.1383 (3)	0.0613 (3)	−2.784 (13)	2.360 (6)	−3.312 (11)	2.7 (2)
P_2R_1	0.3912 (3)	0.3457 (4)	0.3369 (3)	1.093 (9)	3.328 (8)	−2.591 (6)	2.5 (2)
P_2R_2	0.4145 (3)	0.1587 (5)	0.1385 (4)	0.030 (11)	2.612 (10)	2.334 (8)	2.7 (2)
P_3R_1	0.1168 (3)	0.2856 (4)	0.4131 (4)	−2.680 (11)	−2.231 (11)	−1.882 (11)	2.5 (2)
P_3R_2	0.1282 (3)	0.0377 (4)	0.3142 (3)	−2.109 (10)	−3.038 (6)	3.197 (6)	2.9 (2)

Atom	β_{11}[g,h]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	24.0 (6)	27.1 (11)	27.4 (8)	1.0 (8)	3.0 (6)	0.6 (9)
P_1	14.06 (13)	36.8 (25)	25.9 (21)	−1.4 (16)	0.2 (12)	0.5 (20)
P_2	18.7 (13)	33.1 (27)	33.4 (22)	4.1 (15)	3.3 (14)	1.9 (19)
P_3	22.1 (14)	35.0 (25)	19.6 (21)	−2.0 (17)	4.0 (13)	−3.2 (19)

[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 atoms are derived from an analysis of the rigid-group positional and orientational parameters. [c] The thermal parameters of the rigid-group atoms should be regarded as estimates only since they were varied early on the refinement and fixed throughout the final stages of refinement. The quantity refined is the group thermal parameter. [d] F_4, F_5, and F_6 are the positions with occupancy factor 0.25 in the disordered model for the fluorine atoms of the trifluoromethyl group. [e] X_0, Y_0, Z_0 are the fractional coordinates of the origin of the rigid-group coordinate system. For the phenyl rings, the origin is chosen as the center of gravity of the ring. For the trifluoromethyl group, the origin is chosen as the geometric center of the 3(6) fluorine atoms. [f] The rigid-group orientational parameters, ϕ, θ, and ρ are given in radians. ϕ, θ, and ρ correspond to δ, ϵ, and η, respectively, as defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965). [g] The form of the anisotropic thermal ellipsoid is $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [h] The quantities given in the table are the thermal coefficients $\times 10^4$.

were probably incorrect and they were reassigned giving occupancy factors of 0.75 and 0.25 to the three original and three remaining positions, respectively. The contribution of the phenyl hydrogens to the calculated structure factors were then computed and included as fixed contributions in all further calculations. Examination of the structure factor table showed nine reflections with large discrepancies between $|F_o|$ and $|F_c|$ and these were excluded from the list.[22] Three additional cycles of refinement with 1436 reflections above 2σ and 117 variables converged to final values of 0.068 and 0.046 for R and R', respectively.[23] The largest parameter shifts on the final cycle were less than 0.1 of their estimated standard deviations and the standard deviation of an observation of unit weight was 1.17. A final difference Fourier map showed no peaks higher than 0.3 e/Å^3 whereas the average electron density of a carbon atom in this structure is 2.5 e/Å^3. The parameters obtained from this refinement are taken as the final parameters for 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 angles will be found in

TABLE II

ANALYSIS OF THE AGREEMENT BETWEEN OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES FOR $Cu_2(CF_3CN_4)_2((CH_2P(C_6H_5)_2)_2)_3$[a]

Range of $(\sin \theta)/\lambda$	No. within Range	R	R'
0.000–0.136	64	0.033	0.031
0.136–0.204	147	0.045	0.037
0.204–0.272	258	0.062	0.052
0.272–0.340	362	0.075	0.065
0.340–0.408	340	0.101	0.099
0.408–0.481	264	0.103	0.155
All	1436	0.068	0.046

[a] The value of $F(000)$ is 3288. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume 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, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

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(22) Five reflections were found photographically to be affected by streaking and four were obviously misset in the collection of the data.

(23) Three cycles of refinement in which the atoms of the tetrazole ring were also allowed to vibrate according to an anisotropic thermal model converged to R and R' values of 0.066 and 0.045, respectively. This slight improvement is insignificant according to the Hamilton test: W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

TABLE III

SIGNIFICANT INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG) FOR $Cu_2(CF_3CN_4)_2((CH_2P(C_6H_5)_2)_2)_3$

Atoms	Distance	Atoms	Angle
$Cu-P_1$	2.277 (5)	P_1-Cu-P_2	116.1 (2)
$Cu-P_2$	2.298 (5)	P_1-Cu-P_3	119.0 (2)
$Cu-P_3$	2.338 (5)	P_1-Cu-N_2	102.4 (4)
$Cu-N_2$	2.009 (13)	P_2-Cu-P_3	89.9 (2)
P_1-C_1	1.911 (14)	P_2-Cu-N_2	117.9 (5)
$P_1-P_1R_1C_6$	1.821 (10)	P_3-Cu-N_2	112.3 (4)
$P_1-P_1R_2C_6$	1.837 (13)	$Cu-P_1-C_1$	115.3 (5)
C_1-C_1'	1.604 (23)	$Cu-P_1-P_1R_1C_6$	115.4 (5)
P_2-C_2	1.884 (14)	$Cu-P_1-P_1R_2C_6$	114.9 (4)
$P_2-P_2R_1C_6$	1.824 (11)	$C_1-P_1-P_1R_1C_6$	104.2 (6)
$P_2-P_2R_2C_6$	1.783 (14)	$C_1-P_1-P_1R_2C_6$	100.0 (8)
C_2-C_3	1.542 (16)	$P_1R_1C_6-P_1-P_1R_2C_6$	105.3 (7)
P_2-C_3	1.919 (13)	$Cu-P_2-C_2$	100.3 (5)
$P_3-P_3R_1C_6$	1.833 (11)	$Cu-P_2-P_2R_1C_6$	125.2 (7)
$P_3-P_3R_2C_6$	1.850 (15)	$Cu-P_2-P_2R_2C_6$	120.0 (6)
N_2-N_3	1.119 (17)	$C_2-P_2-P_2R_1C_6$	101.5 (5)
N_2-N_1	1.425 (17)	$C_2-P_2-P_2R_2C_6$	107.1 (8)
N_1-C_4	1.372 (24)	$P_2R_1C_6-P_2-P_2R_2C_6$	100.2 (7)
N_3-N_4	1.482 (20)	$Cu-P_3-C_3$	104.3 (4)
N_4-C_4	1.413 (22)	$Cu-P_3-P_3R_1C_6$	121.6 (5)
C_4-C_5	1.426 (21)	$Cu-P_3-P_3R_2C_6$	122.5 (7)
		$C_3-P_3-P_3R_1C_6$	101.2 (7)
		$C_3-P_3-P_3R_2C_6$	104.2 (6)
		$P_3R_1C_6-P_3-P_3R_2C_6$	100.1 (5)
		$P_1-C_1-C_1'$	106.0 (1)
		$P_2-C_2-C_3$	112.0 (1)
		$P_3-C_3-C_2$	106.0 (1)
		$Cu-N_2-N_3$	133.0 (2)
		$Cu-N_2-N_1$	116.0 (1)
		$N_2-N_3-N_4$	119.0 (2)
		$N_3-N_4-C_4$	97.0 (2)
		$N_4-C_4-N_1$	110.0 (2)
		$C_4-N_1-N_2$	106.0 (2)
		$N_1-N_2-N_3$	107.0 (2)
		$N_1-C_4-C_5$	132.0 (2)
		$N_4-C_4-C_5$	118.0 (1)

Table III. The root-mean-square amplitude of vibration along the principal ellipsoid axes of the four atoms refined anisotropically, the dihedral angle between planes about the copper atom, and the equation of the least-squares plane through the atoms of the tetrazole ring are given in Table IV.

TABLE IV

Root-Mean-Square Amplitudes of Vibration along Principal Ellipsoid Axes (Å)

Atom	Min	Intermed	Max
Cu	0.207 (4)	0.216 (5)	0.262 (3)
P_1	0.201 (9)	0.206 (8)	0.252 (9)
P_2	0.212 (9)	0.228 (8)	0.257 (9)
P_3	0.172 (10)	0.238 (9)	0.260 (9)

Dihedral Angle between Planes of Three Atoms about Copper

Plane 1	Plane 2	Angle, deg
Cu,P_1,P_2	Cu,P_3,N_2	74.1 (3)
Cu,P_2,P_3	Cu,P_1,N_2	86.5 (3)
Cu,P_2,N_2	Cu,P_1,P_3	77.5 (2)

Least-Squares Plane for Tetrazole Ring[a]

Best Plane Equation through Atoms N_1, N_2, N_3, N_4, C_4

$$10.24X + 4.46Y - 15.83Z - 0.76 = 0$$

Distances of Atoms (Å) from Plane

N_1	−0.01 (2)	N_3	−0.04 (2)	C_4	−0.01 (2)	Cu[b]	0.46
N_2	0.02 (1)	N_4	0.03 (2)	C_5[b]	0.00		

[a] The equation of the plane is given in terms of monoclinic coordinates. [b] Given zero weight in the determination of the plane equation.

Description of the Structure and Discussion

With the exception of the coordination position occupied by the 5-perfluoromethyltetrazolate ion, hereafter abbreviated as 5-PFMT, $Cu_2(CF_3CN_4)_2(diphos)_3$ is very nearly isostructural with $Cu_2(N_3)_2(diphos)_3$,[7] hereafter referred to as "the azido complex." Minor differences in the coordination geometry about the copper atom, in the conformation of the Cu–diphos–Cu chain, and in the conformation of the five-membered chelate ring formed by the copper and the bidentate diphos ligand are noted (*vide infra*). As in the case of the azido complex, the molecule as a whole is centrosymmetric with the center of symmetry located between the methylene carbons of a bridging diphos ligand. A stereoscopic view of the coordination geometry and salient skeletal features of the molecule is presented in Figure 1 and a perspective view of the entire molecule is shown in Figure 2.

The Coordination Geometry.—In the complex, each copper atom is in a distorted tetrahedral environment consisting of one nitrogen and three phosphorus atoms (Figure 1). The distortions from idealized tetrahedral geometry are similar to those observed in the structure of the azido complex[7] and can be attributed, at least in part, to the "bite" of the bidentate diphos ligand. The angle of the "bite," *i.e.*, the P_2-Cu-P_3 angle, is 89.9 (2)° and agrees with experimental error with that observed in the azido complex. The remaining angles about the copper are in qualitative agreement with those of the azido complex. The dihedral angles between planes about the copper atom (Table IV) in the two complexes are in good agreement. The distances of the copper atom from the bounding planes of the tetrahedron (0.79 Å from P_1, P_2, P_3; 0.62 Å from P_1, P_2, N_2; 0.66 Å from P_1, P_3, N_2; 0.81 Å from P_2, P_3, N_2) in this structure are in close agreement with those of the azido complex indicating that although minor differences in bond angles and distances exist, *vide infra*, the overall geometry of the coordination spheres of the present molecule and the azido complex are very similar.

It is interesting to note that the similarity of the coordination geometries is maintained in spite of the additional bulk of the 5-PFMT ion relative to the azide ion. Inspection of a molecular model shows that there is no crowding of the coordination sphere resulting from steric interactions involving the 5-PFMT ion. In fact, the ion is oriented in such a way as to make N_1 and N_3 equidistant from the copper (2.90 Å), a distance which is only 0.10 Å less than the Cu-β-N distance observed in the azido complex.

The $Cu-N_2$ bond distance, 2.009 (13) Å, is marginally shorter than the Cu-α-N bond length, 2.040 (13) Å, observed in the azido complex indicating that the σ-donor properties of the 5-PFMT ion and the monodentate azide ion[7] are similar. Harris, *et al.*,[24] as the result of a series of spectroscopic studies on complexes of Fe(II), Co(II), Ni(II), and Cu(II) containing this anion concluded that the 5-PFMT ion functioned as a strong σ-donor ligand and placed it near bipyridyl and *o*-phenanthroline in the spectrochemical series.

The pattern of long Cu-P bond lengths observed in the structure of the azido complex is repeated in this structure (Table III) although minor differences are noted. The $Cu-P_1$ bond length of 2.277 (5) Å is shorter than that observed in the azido complex (2.317 (6) Å) but is longer than that generally observed for

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[24] A. D. Harris, H. B. Jonassen, and R. D. Archer, *Inorg. Chem.*, **4**, 147 (1965).

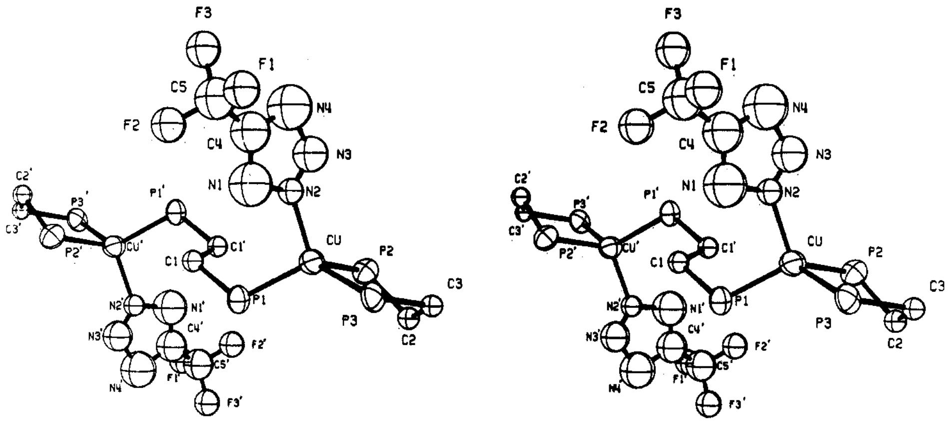

Figure 1.—Stereoscopic view of the coordination geometry of $Cu_2(CF_3CN_4)_2((CH_2P(C_6H_5)_2)_2)_3$. The phenyl rings are omitted for clarity. In Figures 1 and 2, the primed symbols refer to the centrosymmetrically equivalent atoms.

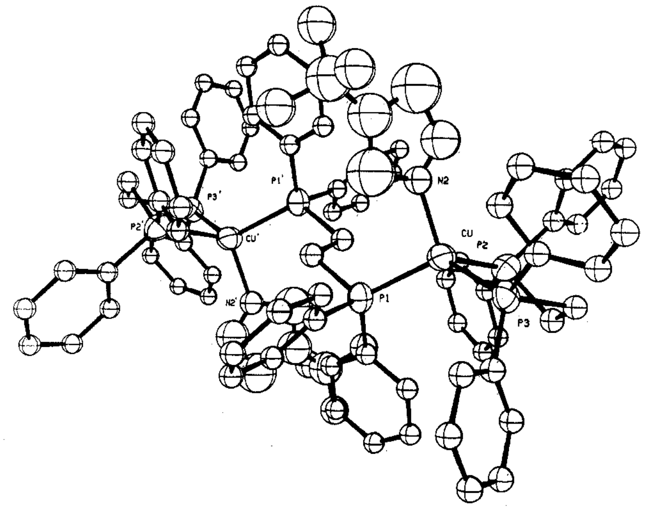

Figure 2.—Perspective view of the molecular structure of $Cu_2(CF_3CN_4)_2((CH_2P(C_6H_5)_2)_2)_3$.

monodentate tertiary phosphine complexes of copper(I)[8,25–27] except in the case of a borohydride[28] and an octahydrotriborato complex[29] where the bond lengths are approximately the same. The Cu–P_2 bond length, 2.298 (5) Å, agrees (perhaps fortuitously) with that of the azido complex while the Cu–P_3 bond length, 2.338 (5) Å, is about 0.02 Å longer than the corresponding distance in the azido complex. The discrepancy between the Cu–P_2 and Cu–P_3 bond lengths in these two complexes is not unique; rather, it appears to be a fairly common feature of transition metal complexes containing diphos and other five-membered chelate rings[30–33] and has been commented on by one author[30] although no explanation was offered.

The Monodentate diphos Ligand.—As in the case of the azido complex,[7] the presence of the crystallographic center of symmetry constrains the P_1–C_1–C_1'–P_1' chain to the trans configuration. The C_1–C_1' bond length, 1.604 (23) Å, is somewhat longer than that expected for a C–C single bond distance (1.537 (5) Å).[34] The P_1–phenyl carbon distances, mean 1.829 Å, and the P_1–alkyl carbon distance of 1.911 (14) Å are in excellent agreement with those observed in other transition metal complexes containing diphos,[7,31,35] triphenylphosphine,[8,25,29] and methyldiphenylphosphine.[26] The C–P_1–C bond angles range from 100.0 (8) to 105.3(7)°, mean 103.2°, and, as expected, are significantly lower than the tetrahedral value of 109.5°, and are in essential agreement with those of the azido complex. The Cu–P_1–C angles, mean 115.2°, are greater than the tetrahedral value. The contraction of the C–P_1–C angles and the expansion of the Cu–P_1–C angles has been noted previously.[7] The P_1–C_1–C_1' bond angle, 106 (1)°, is slightly less than the corresponding angle in the azido complex.

As was noted in the report on the structure of the azido complex,[7] the conformation of the Cu–diphos–Cu chain is a significant factor in determining the overall configuration of the molecule. As defined in that report, δ, the rotation angle about the C_1–P_1 (C_1'–P_1') bonds, provides a convenient basis for discussing the conformation of the chain. Analysis of the conformations corresponding to several of the possible values of δ indicated that the Cu–Cu′ distance[36] and the distance of the copper atom from the plane defined by P_1', C_1', C_1, P_1 were correlated with the value of δ and therefore characteristic of the conformation of the chain. The value of δ for the azido complex (62°) represents a rotation of 62° about the C_1–P_1 bond from a conformation which places the copper atom in the plane of P_1', C_1', C_1, P_1 at a minimum distance from its centrosymmetric equivalent toward the conformation which displaces the copper atom a maximum distance from the P_1', C_1', C_1, P_1 plane.

Quite surprisingly, it is found that the value of δ for this molecule (59°) is slightly lower than that of the azido complex, *vide supra*. It had been expected that replacement of the azide function by the bulkier 5-PFMT ligand would cause δ to assume larger values in order to minimize intramolecular nonbonded interactions. This appears not to be the case; rather, minimi-

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(25) G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, **8**, 2750 (1969).

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

(27) P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, **21**, 957 (1966).

(28) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967).

(29) S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969).

(30) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

(31) M. C. Hall, B. T. Kilbourn, and K. A. Taylor, *J. Chem. Soc. A*, 2539 (1970).

(32) S. D. Ibekwe, B. T. Kilbourn, and U. A. Raeburn, *Chem. Commun.*, 433 (1969).

(33) B. R. Davis and J. A. Ibers, *Inorg. Chem.*, **9**, 2768 (1970).

(34) *Chem. Soc., Spec. Publ.*, **No. 18**, S14s (1965).

(35) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 206 (1970).

(36) This is the centrosymmetric Cu–Cu′ vector observed in the Patterson synthesis.

zation of nonbonded interactions is achieved *via* an increase in the rotation angle about the P_1–Cu bond from a value of 28° for the azido complex to a value of 37.4° for the 5-PFMT complex. The Cu–Cu′ distance in the present structure is found to be 7.17 Å compared to 7.31 Å for the azido complex and reflects the lower value of δ although the smaller Cu–P_1 distance and C–P_1–Cu angle (Table III) certainly contribute to the lowering of the value. The distance of the copper atom from the P_1', C_1', C_1, P_1 plane is 1.77 Å and is only slightly less than that of the azido complex. The conformation adopted by the Cu–diphos–Cu chain is therefore very similar to that of the azido complex and indicates that the factors influencing the overall geometry of the molecules are similar. Examination of the environment surrounding the molecules in the two complexes shows that the packing in the two structures is almost identical, *vide infra*.

The Bidentate diphos Ligand.—The conformation of the five-membered chelate ring formed by the copper atom and the bidentate diphos ligand is slightly different from that observed in the azido complex. C_2 and C_3 (Figure 1) are displaced by 0.65 and 0.14 Å above and below the plane defined by P_2, Cu, P_3 while the corresponding distances for the azido complex are 0.50 and 0.30 Å, respectively. The disortions in the endocyclic P–C and C–C bond lengths observed in the azido complex[7] are absent in the present structure, all bond distances being within range of accepted values.[31,34,35] The phosphorus–phenyl carbon distances, mean 1.825 Å, and the Cu–P–phenyl carbon angles, mean 122.3°, are very similar to those observed in the azido complex[7] and in good agreement with those found in other structures containing diphos chelate rings.[30,31,35] The exocyclic C–P–C bond angles, mean 102.6°, show the expected contraction relative to the tetrahedral value. The internal angles of the chelate ring are in quantitative agreement with those of the azido complex although it is noted that the P_2–C_2–C_3 angle of the 5-PFMT complex is equal to the P_3–C_3–C_2 angle of the azido complex and *vice versa*. The dihedral between the P_2–Cu–P_3 and C_2–Cu–C_3 planes is 32° in both complexes.

Theoretical calculations of Gollogly and Hawkins[37] on the conformational energies of five-membered diamine chelate rings have shown that in the absence of significant van der Waals interactions, the total conformational energy of a given ring system may be decomposed into a sum of two terms, E_t and E_θ, which arise from variations in the torsional (E_t) and interbond (E_θ) angles of the ring. The authors found that E_t is essentially independent of the actual conformation of the ring, as defined by the interbond angles and the displacement of the two carbon atoms from the N–M–N plane, and strongly dependent on ω, the torsional angle about the C–C bond. This was taken to imply that if the displacements of the two carbon atoms from the N–M–N plane are varied while maintaining ω (and therefore, E_t) constant, any increase in the torsional energy of one N–C bond (*i.e.*, any change in the torsional angle about the bond which results in a higher E_t) arising from these variations must be accompanied by a corresponding decrease in the torsional energy of the other N–C bond. Further, it was found that E_θ depends strongly on the interbond angles and ω but is independent of the displacement of the two carbon atoms from the N–M–N plane. The authors therefore concluded that the total conformational energy of the ring ($E_t + E_\theta$) is independent of the displacement of the two carbon atoms from the N–M–N plane. These results have been extended to other five-membered chelate rings by Hall, *et al.*,[31] who used them as a basis for comparing the results of structural investigations on a number of metal complexes involving bidentate diphos ligands.

Using these theoretical considerations as a basis for comparing the conformations of the diphos chelate rings in the present structure and the azido complex, it is concluded that the conformational energies of the two ring systems are essentially the same. The value of ω for the 5-PFMT complex, 58 (1)°, agrees within experimental error with the corresponding value for the azido complex, 57 (1)°, and there is quantitative agreement (as noted above) between the internal angles of the two ring systems.

Accompanying the variations in the displacement of C_2 and C_3 from the P_2, Cu, P_3 plane in going from the azido to the 5-PFMT complex, *vide supra*, are variations in the torsional angles about the remaining bonds of the two chelate rings. The torsional angle about the P_2–C_2 bond rises from a value of 42° in the azido complex to a value of 51° in the 5-PFMT complex while the torsional angle about the P_3–C_3 bond falls from a value of 44° in the azido complex to a value of 35° in the 5-PFMT complex. This is exactly the result predicted by the theoretical considerations noted above and provides justification for discussing the conformation of diphos chelate rings in terms of a theoretical analysis developed for diamine chelate rings. The torsional angle about the Cu–P_2 bond increases from 14.9° in the azido complex to a value of 20.5° in the 5-PFMT complex and the torsional angle about the Cu–P_3 bond decreases from 8.8° in the azido complex to 4.5° in the 5-PFMT complex. These variations in the torsional angles about the Cu–P bonds in the two structures are correlated with variations in the displacements of the two carbon atoms from the P_2, Cu, P_3 plane[31] and, in light of the theoretical considerations presented above, cause no change in the conformational energy of the two ring systems.

The 5-Perfluoromethyltetrazolate Anion.—The five-membered heterocyclic ring substituted in the 2(Cu) and 5(CF_3) positions exhibits an irregular pentagonal structure and is essentially planar (Table IV). The endocyclic C–N distances of 1.37 (2) and 1.41 (2) Å are equivalent in the limit of experimental error and are significantly shorter than the C–N single-bond distance of 1.472 Å[38] indicating partial double-bond character. They are however longer than the C–N distances found in other tetrazole structures.[38,39,40] Although the difference in these two bond lengths is probably not significant in view of the estimated uncertainties, it is interesting to note that a difference of this magnitude in the C–N bond lengths has been observed in the structure of 2-methyl-5-aminotetrazole[41] where the difference appears to be the result of the unsymmetrical 2,5-

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[37] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969).

[38] *Chem. Soc., Spec. Publ.*, **No. 11**, S16 (1958).

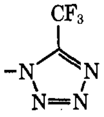
[39] K. Britts and J. L. Karle, *ibid.*, **22**, 308 (1967).

[40] Y. Kushi and Q. Fernando, *J. Amer. Chem. Soc.*, **92**, 1965 (1970).

[41] J. H. Bryden, *Acta Crystallogr.*, **9**, 874 (1956).

substitution pattern. This behavior is in contrast to that noted for the more symmetrically substituted tetrazoles (5-substituted and 2,3-di-5-monosubstituted) which have been found to exhibit *mm*[42] and twofold[39,40] symmetry.[43] The N–N bond lengths between the 1,2 and 3,4 positions on the ring, 1.43 (2) and 1.48 (2) Å, respectively, are significantly longer than the corresponding lengths observed in other tetrazole structures[39,40,42] and are in fair agreement with the value for the N–N single bond length in hydrazine, 1.451 Å.[44] As in the case of the C–N bonds, *vide supra*, it is difficult to say whether the difference in the two N–N bond lengths is significant.

The N_2–N_3 distance is very short, 1.12 (2) Å, compared to a N–N double-bond length of 1.23 Å observed in *trans*-azobenzene[45] and suggests a considerable localization of π-electron density in the bond. A similar localization of π-electron density, *albeit* not to the same degree, has been observed in the structures of 5-aminotetrazole monohydrate[39] and the hydrazene salt of 5-aminotetrazole[46] where the N_2–N_3 distances are 1.255 (15) and 1.295 (7) Å, respectively. This is in contrast to the behavior of sodium tetrazole monohydrate[42] and anhydro-5-mercapto-2,3-diphenyltetrazolium hydroxide[40] where the π systems are essentially delocalized over the entire ring. The internal angles of the ring system are in fair agreement with those of other tetrazole structures[39,40,42] and the pattern of distortions is similar to that observed in the structure of 2-methyl-5-aminotetrazole.[41] The dimensions found for the tetrazole ring are therefore taken to indicate a localization of π-electron density in the N_2–N_3 bond and a delocalization of the negative charge over the N_1–C_4–N_4 part of the ring suggesting that the resonance forms contributing significantly to the electronic structure of the ground state are I and II.



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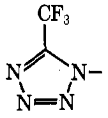
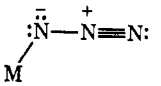


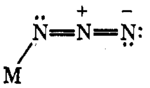
II

The exocyclic C–C distance, 1.43 (2) Å, is reasonable in view of the presence of the electronegative fluorine atoms and the fact that the bond is formed between $sp^3(C_5)$ and $sp^2(C_4)$ hybridized carbon atoms.[47] It is interesting to note that C_5 lines in the plane of the tetrazole ring (Table IV) although the rigid-group treatment in the refinement, *vide supra*, does not require this to be the case and thus provides some justification for including C_5 in the group. The Cu–N_2–N_3 angle, 133 (2)°, is significantly larger than the Cu–N_2–N_1 angle, 116 (1)°. The difference may be attributed to the greater repulsion between the electron density localized in adjacent single-bond (Cu–N_2) and multiple-bond (N_2–N_3) orbitals relative to the repulsion between two adjacent single-bond orbitals (Cu–N_2 and N_2–N_1).[48]

Of particular interest in the present structure is the mode of addition of the trifluoroacetonitrile molecule to the coordinated azide. X-Ray structural determinations of metal complexes containing coordinated azide functions[7,33,49,50] have shown that the two dominant canonical forms in describing the electronic structure of the ground state of the azide ion are III and IV, indicating that both the α and γ nitrogens



III



IV

possess some nucleophilic character. If one envisions the first step in the cycloaddition reaction as a nucleophilic attack on the relatively electropositive carbon atom of the CF_3CN nitrile function, two possible routes can be proposed. The first of these possibilities involves a nucleophilic attack by the γ nitrogen atom leading directly to the observed structure. The second involves attack by the α nitrogen leading to the formation of the tetrazole ring in which the ring carbon atom is ortho to the coordinated nitrogen. This possibility appears to be inconsistent with the present structural results; however, nucleophilic attack by the α nitrogen cannot be ruled out in view of the results found by Nelson, *et al.*[4] (*vide supra*), and in light of the 1,3-cycloaddition reaction between trimethylsilyl azide and substituted acetylenes in which triazole ring formation is followed by migration of the $Si(CH_3)_3$ group to the β nitrogen of the original azide function.[51]

The Crystal Structure.—The structure consists of the packing of discrete units of $Cu_2(CF_3CN_4)_2((CH_2P(C_6H_5)_2)_2)_3$ oriented about the 4(c) positions of $\bar{1}$ symmetry. The Cu–Cu′ vector (Figure 1) exhibits angles of 82.4, 86.5, and 5.9° with respect to the crystallographic *a*, *b*, and *c* directions. There are no abnormal intermolecular contacts. The shortest intermolecular contact is 2.4 Å between the calculated positions of several of the phenyl hydrogens. The large cavity surrounding the anion coordination position noted in the azido complex is present in this structure and appears to have enlarged somewhat. The shortest contact involving the atoms of the anion is 2.5 Å and occurs between the fluorines and several of the phenyl hydrogens. The large empty space is undoubtedly responsible for the high thermal parameters found for the atoms of the 5-PFMT anion.

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Appendix

The complete set of atomic positions (exclusive of the azide nitrogens) for $Cu_2(N_3)_2(diphos)_3$,[7] in fractional coordinates (*i.e.*, fractions of a cell edge), $x_j{}^i$,[52] were reexpressed in terms of a right-handed orthogonal co-

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[42] G. J. Palenik, *Acta Crystallogr.*, **16**, 596 (1963).

[43] The structure reported in ref 39 exhibits only approximate twofold symmetry.

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[52] The index *j* runs from 1 to 43 representing each atom. The index *i* runs from 1 to 3 representing the three coordinates for each atom.

ordinate system ($\vec{X}^i$) defined by suitable cross products of the unit cell vectors $\vec{a}$, $\vec{b}$, $\vec{c}$

$$\begin{aligned}\vec{X}^2 &\equiv \| \vec{b} \\ \vec{X}^1 &\equiv \| \vec{b} \times \vec{c} \\ \vec{X}^3 &\equiv \| \vec{X}^1 \times \vec{X}^2\end{aligned} \qquad (1)$$

such that

$$(X_j) = (\Upsilon^a)(x_j) \qquad 1 \leq j \leq 43 \qquad (2)$$

where Υ^a is the (3×3) transformation matrix based on the cross-product definitions given in (1) and evaluated by determining the components of the unit cell vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ in the coordinate system $\vec{X}^i$, and $X_j{}^i$ are the coordinates of each atom in this system.

The origin of this coordinate system was then shifted to the copper atom ($X_1{}^i$) and the coordinates, $X'_j{}^i$, of all atoms were recalculated with respect to the new origin

$$X'_j{}^i = X_j{}^i - X_1{}^i \qquad 1 \leq i \leq 3,\ 1 \leq j \leq 43 \quad (3)$$

An internal right-handed orthogonal coordinate system ($\vec{R}^i$) was defined in terms of suitable cross products of the three $\overrightarrow{\mathrm{Cu{-}P}}$ vectors

$$\begin{aligned}\vec{R}^2 &\equiv \| \overrightarrow{\mathrm{Cu{-}P_2}} \\ \vec{R}^1 &\equiv \| \overrightarrow{\mathrm{Cu{-}P_2}} \times \overrightarrow{\mathrm{Cu{-}P_3}} \\ \vec{R}^3 &\equiv \| \vec{R}^1 \times \vec{R}^2\end{aligned} \qquad (4)$$

and the coordinates $R_j{}^i$ of Cu (origin), P$_1$, P$_2$, and P$_3$ in this coordinate system were evaluated. The elements (τ_{ik}) of the transformation matrix Υ^b required to take $\vec{X}^i$ into $\vec{R}^i$ were determined by solving the set of simultaneous equations relating P$_1$, P$_2$, and P$_3$ in the two coordinate systems

$$R_j{}^i = \sum_{k=1}^{3} X'_j{}^k \epsilon \tau_{ik} \qquad 1 \leq i \leq 3,\ 2 \leq j \leq 4 \quad (5)$$

Using the matrix Υ^b, the coordinates of all atoms were expressed in the coordinate system $\vec{R}^i$

$$(R_j) = (\Upsilon^b)(X'_j) \qquad 1 \leq j \leq 43 \qquad (6)$$

The net result of these transformations is a set of atomic coordinates, $R_j{}^i$, for Cu$_2$(N$_3$)$_2$(diphos)$_3$ which is *independent* of the *lattice*-based coordinate system for the structure.

The fractional coordinates of the copper and three phosphorus atoms, $y_j{}^i$, corresponding to one of the image solutions for Cu$_2$(CF$_3$CN$_4$)$_2$(diphos)$_3$ were then transformed by a series of steps identical with (1) and (2) (*vide supra*) yielding a transformation matrix Υ^c, analogous to Υ^a and a set of positions $Y_j{}^i$ for Cu, P$_1$, P$_2$, and P$_3$. The origin of the coordinate system $\vec{Y}^i$ was then shifted to the copper atom ($Y_1{}^i$) and the coordinates of Cu, P$_1$, P$_2$, and P$_3$ were recalculated in a manner identical with (3) to yield a set of atomic coordinates $Y'_j{}^i$ analogous to $X'_j{}^i$.

The origin of the coordinate system $\vec{R}^i$ was formally made coincident with the origin of the coordinate system $\vec{Y}^i$ and the transformation matrix Υ^d required to superimpose the corresponding phosphorus atoms in the two coordinate systems was evaluated in a manner similar to (5). Using the matrix Υ^d, the coordinates of all atoms of Cu$_2$(N$_3$)$_2$(diphos)$_3$ on the internal coordinate system $\vec{R}^i$ were evaluated in the *lattice*-based coordinate system, $\vec{Y}^i$, of Cu$_2$(CF$_3$CN$_4$)$_2$(diphos)$_3$

$$(Y'_j) = (\Upsilon^d)(R_j) \qquad 1 \leq j \leq 43 \qquad (7)$$

The origin of this coordinate system was then shifted to the standard origin for the space group (*C*2/*c*, 000) and the fractional coordinates of all atoms were calculated by applying the inverse of the transformation matrix Υ^c

$$(Y_j) = (\Upsilon^c)^{-1}(Y_j) \qquad 1 \leq j \leq 43 \qquad (8)$$

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The Crystal Structure of [BrF$_4{}^+$][Sb$_2$F$_{11}{}^-$]

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Crystals of the 1:2 adduct formed by BrF$_5$ and SbF$_5$ consist of infinite chains of discrete BrF$_4{}^+$ and Sb$_2$F$_{11}{}^-$ ions coupled by relatively weak fluorine bridges and, accordingly, should be formulated as [BrF$_4{}^+$][Sb$_2$F$_{11}{}^-$]. This is the first direct evidence for the existence of the BrF$_4{}^+$ ion. The crystals are monoclinic with the most probable space group P2$_1$/*a*, lattice constants $a = 14.19 \pm 0.03$, $b = 14.50 \pm 0.03$, $c = 5.27 \pm 0.01$ Å, $\beta = 90.6 \pm 0.1°$, and four formula units per unit cell; the calculated density is 3.72 g cm^{-3}. The structural parameters were refined by the method of least-squares with visually estimated Weissenberg photographic intensity data. The final value of the conventional agreement index R was 0.14 for 773 reflections having $|F_o|$ greater than $\sigma(|F_o|)$.

Introduction

Previous investigations of solid halogen fluoride adducts have provided evidence that some are predominantly ionic[1-4] and others are predominantly covalent.[5-7] Infrared and Raman spectroscopic studies[4] of the 1:2 adduct[8] formed by BrF$_5$ and SbF$_5$ yielded

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