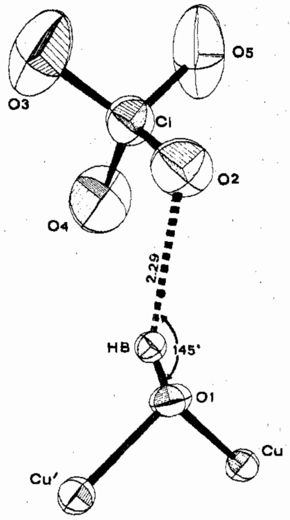

Figure 2. The approach of the perchlorate ion to the Cu-OH-Cu bridge in $[Cu(teen)OH]_2(ClO_4)_2$. The probable O-H· · ·O hydrogen bond is represented by the dashed bond.

Pauling[32] (2.80 Å) but slightly less than that of Bondi (3.04 Å).[33] Moreover, the O(2)· · ·HB separation of 2.30 Å is less than the sum of the reported van der Waals radii of H and O, and Hamilton and Ibers[34] have noted that the existence of two O-H separations which are less than this sum is a sufficient condition for hydrogen bonding, even if the O· · ·O distance exceeds the van der Waals radius sum. The O(1)-HB· · ·O(2) angle of 145° is in the range normally observed for weak hydrogen bonds.[28] Further support for this conclusion is found in an examination of the geometry of the perchlorate group (Tables III and IV). The three Cl-O distances not involving O(2) are 1.383 (7), 1.392 (5), and 1.392 (5) Å, with an average value of 1.389 (5) Å; the Cl-O(2) distance of 1.434 (5) Å is significantly longer than these three, as would be expected if O(2) were involved in hydrogen bonding to the bridge. A view of the perchlorate anion and its probable interaction with the bridge is shown in Figure 2.

The Cu-O-Cu bridging angle, ϕ, is 103.0 (2)°. The best unweighted least-squares line through the five available values of ϕ and $2J$ for di-μ-hydroxo-copper(II) dimers has an intercept of 7730 cm^{-1} and a slope of -79.1 cm^{-1} deg^{-1}. Using the published[4] value for $2J$ of -410 cm^{-1}, the predicted value of ϕ is 102.9 (1)°, which is in remarkable agreement with the observed angle. Evidently, therefore, the present structural data strongly support the hypothesis that, over the angular range $95° \leqslant \phi \leqslant 105°$, there is a linear relationship between ϕ and J. In the light of this observation, it should now be possible to predict J from ϕ or *vice versa* for this class of complexes.

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Registry No. $[Cu(teen)OH]_2(ClO_4)_2$, 51259-55-3.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1654.

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Structure of Tetrafluoroboratotris(triphenylphosphine)copper(I), $Cu(BF_4)(P(C_6H_5)_3)_3$. An Example of a Copper(I) Complex Containing a Weakly Coordinated Tetrafluoroborate Anion

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The structure of tetrafluoroboratotris(triphenylphosphine)copper(I), $Cu(BF_4)(P(C_6H_5)_3)_3$, has been determined from three-dimensional X-ray data collected by counter techniques. The material crystallizes in space group C_3^1-$P3$ of the trigonal system with three crystallographically independent molecules of the complex in the unit cell, each possessing imposed C_3 symmetry. Crystal data are $a = 18.749$ (3) Å, $c = 11.588$ (2) Å, $V = 3527.8$ Å^3, $\rho_{\text{measd}} = 1.34$ (2) g/cm^3, and $\rho_{\text{calcd}} = 1.32$ g/cm^3. The structure has been refined by a full-matrix least-squares procedure to a conventional R index of 0.050 for 2615 observations having $F_o^2 > 3\sigma(F_o^2)$. The absolute configuration has been assigned on the basis of statistical and experimental tests as *RSS*. The structural results reveal a molecular complex with the BF_4^- anion weakly coordinated to the copper atom through one of its terminal fluorine atoms. The coordination geometry about the copper atom may be described as trigonally distorted tetrahedral. The three independent molecules are roughly equivalent and the structure is discussed in terms of an averaged molecule. Averaged distances and angles of interest are as follows: Cu-P, 2.298 Å; Cu-F(coordinated), 2.31 Å; B-F(coordinated), 1.39 Å; B-F(terminal), 1.35 Å; P-Cu-P, 115.6°; P-Cu-F(coordinated), 102.2°. The infrared and Raman spectra of the complex have been recorded and the frequencies of the Cu-F stretch and the various modes of the BF_4^- group have been assigned. The nature of the Cu-FBF_3 interaction is discussed.

Introduction

Monodentate tertiary phosphine complexes of Cu(I) with a variety of monoanions exhibit a diversity of stoichiometries and structural types. Complexes with metal to phosphine ratios of 1:1, 1:2, 1:3, 1:4, and 2:3 have thus far been noted. The structural types represented by these stoichiometries involve Cu(I) in two-, three-, and four-coordinate environments with four-coordination predominant. The bonding in these systems may be rationalized in terms of sp (linear), sp^2 (trigonal), or sp^3 (tetrahedral) hybridization of the Cu(I) ion.

X-Ray studies of complexes of the 1:1 type have established the existence of two structural classes, monomeric and tetrameric species. *Pentahapto*cyclopentadienyl(triphenylphosphine)copper(I)[1] is an example of the monomeric class and the arrangement of the ligands suggests sp (linear) hybridization of the Cu(I) ion. The tetrameric species $[LCuX]_4$ (L = triphenylphosphine, X^- = chloro) consists of a tetrahedron of Cu atoms with triphenylphosphine groups coordinated at the apices and Cl atoms above each of the faces giving rise to tetrahedral coordination about each copper atom.[2] Structural studies of complexes of the 1:2 type, L_2CuX (L = tertiary phosphine, X = monoanion), have established three distinct structural classes depending on the nature of the monoanion. If the monoanion is capable of functioning as a bidentate ligand, *e.g.*, NO_3^- and BH_4^-, a monomeric tetrahedral species results.[3,4] When the monoanion is a pseudohalogen, *e.g.*, NCS^- and N_3^-, a dimeric complex containing two L_2Cu^+ (L = tertiary phosphine) moieties coordinatively linked by two monoanions results.[5,6] The environment about each copper atom in these complexes is tetrahedral. In the specific instance where L = triphenylphosphine and $X^- = Br^-$, a monomeric three-coordinate complex has been prepared and characterized structurally.[7] The coordination geometry about the copper atom is found to be trigonal planar, suggesting sp^2 hybridization of the Cu(I) ion. Complexes of the 2:3 type, $L_3Cu_2X_2$ (L = triphenylphosphine, $X^- = Cl^-, Br^-, I^-$), have been reported.[8] The structure determination of the chloro complex[9] revealed a chloro-bridged dimeric structure containing both three- and four-coordinate Cu(I). The bonding in this system has been described in terms of sp^2 and sp^3 hybridization, respectively, of the three- and four-coordinate Cu(I) ions.

To date, no structural characterizations of complexes of the 1:3 or 1:4 stoichiometries have appeared although several reports concerning the impending communication of structures of the 1:3 type have appeared.[9,10] The preparation of complexes of the 1:3 type, L_3CuX (L = triphenylphosphine, $X^- = Cl^-, Br^-, I^-, ClO_4^-, BF_4^-$), and 1:4 type, $[L_4Cu]X$ (L = triphenylphosphine, $X^- = ClO_4^-$), has been described.[8,11,12] A qualitative distinction, based on conductivity, molecular weight, and infrared data,[11] between complexes of the 1:3 type where $X^- = BF_4^-$ and ClO_4^- on the one hand and those of the 1:3 type where X^- = halide on the other may be drawn. When the monoanion is "noncoordinating," *e.g.*, BF_4^- and ClO_4^-, the complex is a 1:1 electrolyte in nitrobenzene whereas the halo complexes are not. Molecular weight determinations ($CHCl_3$) give values coincident with the monomer for noncoordinating anions while for the halide complexes values indicative of extensive dissociation are found. The nature of this dissociation has been described[13] in terms of a complex equilibrium involving the phosphine ligands. The solid-state infrared spectrum of L_3CuBF_4 (L = triphenylphosphine) in the B–F stretching region has been interpreted in terms of the C_{3v} point group,[11] suggesting some interaction, possibly coordination, between the BF_4^- group and the L_3Cu^+ moiety.

In order to establish firmly the nature of the 1:3 type complexes with noncoordinating anions, an X-ray structural investigation of $Cu(BF_4)(P(C_6H_5)_3)_3$ was undertaken. From the outset it was apparent that the complex involved either the trigonal-planar moiety $[Cu(P(C_6H_5)_3)_3]^+$ with the BF_4^- group uncoordinated or a pseudotetrahedral species involving a coordinated BF_4^- anion. The results of the study are reported here.

Experimental Section

X-Ray Data. Colorless crystals of $Cu(BF_4)(P(C_6H_5)_3)_3$ were prepared by the method of Cariati and Naldini[11] in which a suspension of $Cu(BH_4)(P(C_6H_5)_3)_2$[4] in ethanol is treated with ethanolic tetrafluoroboric acid. In a typical preparation, 0.69 g (1 mmol) of $Cu(BH_4)(P(C_6H_5)_3)_2$ was suspended in 25 ml of ethanol containing 0.79 g (3 mmol) of $P(C_6H_5)_3$. Ten millilieters of ~0.3 *N* HBF_4 was added over a period of 10 min with vigorous stirring. During the reaction, the evolution of a colorless gas, presumably B_2H_6, was observed. The colorless solution was stirred for an additional 30 min after gas evolution had ceased. The reaction mixture was then concentrated to approximately 10 ml on a rotary evaporator, followed by the addition of 5 volumes of diethyl ether. Well-formed crystals separated over a period of 24 hr from the solution maintained at 0°. The material melts at 220° in agreement with the results of other workers.[11] $Cu(BF_4)(P(C_6H_5)_3)_3$ is soluble in ethanol and is a conductor in nitrobenzene.[11]

On the basis of preliminary precession, Laue, and Weissenberg photography and observations on an optical goniometer, the crystals were assigned to Laue class $\bar{3}$ of the trigonal system. The lack of any systematic absences establishes the lattice as primtive and suggests C_3^1-$P3$ and C_{3i}^1-$P\bar{3}$ as possible space groups. The crystals give a negative piezoelectric test. The crystal selected for data collection shows 14 of the faces belonging to the forms {100}, {110}, {001}, and {101} and was carefully measured in anticipation of an absorption correction ($\mu = 20.39\ cm^{-1}$, Cu Kα). Its dimensions were 0.24 × 0.25 × 0.28 mm along the principal crystallographic directions with a calculated volume of 0.0114 mm^3. Lattice constants at 22° were determined from a least-squares refinement[14] of the setting angles of 12 reflections which had been centered on a Picker four-circle diffractometer using nickel-filtered Cu Kα_1 radiation (λ 1.54056 A) at a takeoff angle of 1.5°. They are $a = 18.749$ (3) Å and $c = 11.588$ (2) Å. The observed density, 1.34 (2) g/cm^3, determined by flotation in carbon tetrachloride–hexane, agrees well with that calculated (1.32 g/cm^3) for three formula units of $Cu(BF_4)(P(C_6H_5)_3)_3$ in the unit cell. With three formula units of the complex in the unit cell, no crystallographic symmetry is *a priori* imposed on the complex in space group $P3$ while in $P\bar{3}$, the complex must possess at least inversion symmetry. On the basis of the stoichiometry of the complex and $Z = 3$, $P\bar{3}$ can thus be rejected on chemical grounds except for the unlikely possibility that the structure is disordered. The probable space group ($P3$), the cell constants, and the number of formula units in the unit cell suggest that $Cu(BF_4)(P(C_6H_5)_3)_3$ is another member of a series of isomorphs of $Pt(CO)(P(C_6H_5)_3)_3$[15] which includes $CuX(P(C_6H_5)_3)_3$[10] ($X^- = Br^-, Cl^-$) and $Ir(NO)(P(C_6H_5)_3)_3$.[10] These complexes have been found to possess crystallographically imposed C_3 symmetry, being situated on the Wyckoff positions[16] a, b, and c of space group $P3$ rather than on general equipoints.

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The mosaic spread of the crystal was examined by open-counter, narrow-source ω scans[17] of several strong reflections. The average width at half-height is 0.05°, which is acceptably low.[17] Intensity data were collected by the θ–2θ scan technique[17] on a computer-controlled Picker FACS-1 automatic diffractometer with the c^* axis of the crystal purposely misset by approximately 7° from the diffractometer spindle axis to avoid multiple-diffraction effects.[18] Prefiltered (1-mil nickel foil) Cu Kα radiation was employed with a pulse height analyzer set to accept approximately 90% of the Cu Kα line. The takeoff angle was 2.2° at which the intensity is about 85% of the maximum available as a function of takeoff angle. A 4 mm × 4 mm aperture was positioned 31 cm from the crystal. An asymmetric scan range in 2θ was employed from 0.65° below the Kα_1 peak position to 0.75° above the Kα_2 peak position. The scan rate was 2°/min with stationary-crystal, stationary-counter background counts of 10-sec duration taken at the limits of the scan for each reflection. Copper-foil attenuators (ratio ~2.3) were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts/sec.

A total of 3145 reflections in the zones hkl and $h\overline{kl}$ ($|k| < h$) were recorded in the range $3° \leqslant 2\theta \leqslant 110°$. Beyond 110°, very few reflections of usable intensity are available. In anticipation of an attempt to determine the absolute configuration, 459 additional reflections in the zones $\overline{hkl}$ and $\bar{h}k\bar{l}$ ($|h| > k$) were gathered in the range $3° \leqslant 2\theta \leqslant 50°$. The intensities of six reflections in diverse regions of reciprocal space were monitored after every 100 reflections but no significant trends were noted and the variation in an individual standard was less than that expected from counting statistics.

All data processing was carried out as previously described.[14,19] The value of p was 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz, polarization, and absorption effects thereby yielding 2772 unique reflections and 447 Friedel pairs which were judged observed ($F_o^2 > 3\sigma(F_o^2)$). The transmission coefficients varied from 0.65 to 0.69. Of the 2772 unique reflections, 157 are of the type $0k0$ and $h\bar{k}0$ which are equivalent to $h00$ and $hk0$, respectively, in the absence of anomalous dispersion. These were omitted from the list and the resulting 2615 reflections were used as the basis for the subsequent refinement of the structure.

Infrared and Raman Data. The infrared spectra were recorded on a Beckman IR-9 infrared spectrophotometer over the range 400–1200 cm^{-1} as Nujol mulls between KBr plates. The resolution was 1.5 cm^{-1} and the estimated wave number accuracy was ±2 cm^{-1}. The Raman spectra of powdered samples in glass capillaries were obtained on a Spex 0.85 m double monochromator with sampling optics of local design, extensively modified Spex photon counting electronics, and a light-feedback stabilized Kr ion laser (Spectra Physics 164) for sample illumination (90°). A 6471-A excitation and a 1-cm^{-1} band pass were employed throughout the experiments. The spectral range covered was from 25 to 1200 cm^{-1}.

Solution and Refinement of the Structure

The structure was solved by standard heavy-atom techniques. Normalized structure factors were computed[20] and their statistical distribution suggested the acentric space group $P3$ (C_3^1) as the correct choice. On the basis of the assumption that the structure is isomorphous and isostructural with the platinum and iridium systems, *vide supra*, the three copper atoms were assigned to the Wyckoff positions a, b, and c of threefold symmetry in space group $P3$. The z coordinate of the copper atom occupying Wyckoff position a was conveniently taken as 0 to define the origin of the coordinate system for the polar space group and was held fixed during the subsequent refinement of the structure. The approximate z coordinates of the remaining copper atoms and trial positions for the three independent phosphorus atoms were derived from an analysis of a three-dimensional origin-removed Patterson function.[20] Two cycles of full-matrix least-squares refinement of an overall scale factor, the appropriate positional parameters, and isotropic thermal factors for each of the six atoms resulted in convergence. The remaining light atoms (excluding hydrogen) were located on two subsequent difference syntheses based on previously located atoms. The tetrafluoroborate anions were found to possess crystallographically imposed C_3 symmetry.

The trial structure was refined (on F) by a full-matrix least-squares procedure.[20] The function minimized is $\Sigma w(|F_o| - |F_c|)^2$ where the weights, w, are taken as $4F_o^2/\sigma^2(F_o^2)$ and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. The discrepancy indices, R_1 and R_2, are defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, respectively. The neutral atom scattering factors for Cu, P, F, C, and B were obtained from the tabulation of Cromer and Waber[21] while for hydrogen those of Stewart, *et al.*,[22] were used. The anomalous terms for Cu, P, and F were those reported by Cromer and Liberman[23] and were included in F_c.[24] During the refinement, the phenyl rings were treated as rigid groups possessing D_{6h} symmetry (C–C bond length 1.392 Å). A refinement of the complete trial structure with individual isotropic thermal parameters for each atom resulted in values of 0.089 and 0.109 for R_1 and R_2, respectively.

At this point the refinement was expanded to include an enantiomeric model B, related to the original choice A by inversion. A has the absolute configuration *RRS*[15] with the molecules situated about the Wyckoff b and c positions designated *R*, while the molecule situated about the Wyckoff a position is designated *S*. B has the opposite configuration *RSS*, *R*(Wyckoff a) and *S*(Wyckoff b, c).

In the next round of calculations parallel refinements of both enantiomeric models were performed. Prior to the refinements, the contributions to the calculated structure factors from the phenyl hydrogen atoms were computed for each model.[25] One cycle of refinement of each enantiomorph based on an anisotropic thermal model for the nongroup atoms and including the fixed hydrogen atom contributions resulted in a significant improvement in the discrepancy indices for both enantiomorphs. Inspection of the structure factor lists showed several strong reflections which appeared to be suffering from the effects of secondary extinction. The fixed hydrogen atom contributions were recomputed for each model and one additional cycle of least-squares refinement of the anisotropic thermal model based on 2615 observations with 190 variables including a correction for isotropic extinction resulted in final values of 0.0501 (R_1) and 0.0634 (R_2) for A and 0.0498 (R_1) and 0.0629 (R_2) for B. With the two weighted agreement factors as the basis for the Hamilton ratio test[26] and assuming only random errors in the data,[26] the hypothesis that the absolute configuration is *RRS*, model A, may be rejected at the 99.5% confidence level.

The largest parameter shifts in the final cycle (model B, *RSS*) were less than one-tenth of their estimated standard deviations. The standard deviation of an observation of unit weight is 1.90 e. A final difference Fourier map shows no peak 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 value of the isotropic extinction parameter is 2.1 (2) × 10^{-6} e^{-2}. Of the 373 reflections omitted from the refinement, nine had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$ and none had $|F_o^2 - F_c^2| > 5\sigma(F_o^2)$. A comparison of $\Sigma w(|F_o| - |F_c|)^2$ for various classes of reflections based on Miller indices, $|F_o|$, and setting angles shows no significant dependence on any of these quantities.

Since the validity of conclusions drawn from the Hamilton ratio test[26] is adversely affected by determinant errors in the data and in view of the similarity of the weighted discrepancy indices for the refinement of the two enantiomeric models,[15] we felt it was desirable to seek confirmation of the choice of the absolute configuration *via* a comparison of selected Friedel pairs. Because the values of $\Delta f''$

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(20) In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Johnson's ORTEP thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program, and Dewar's FAME normalized structure factor program. Our full-matrix least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program. Our absorption program, AGNOST, incorporates the Coppens–Leiserowitz–Rabinovich logic for gaussian integration.

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Table I. Positional and Thermal Parameters for the Nongroup Atoms of $Cu(BF_4)(P(C_6H_5)_3)_3$

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				Molecule 1					
Cu	0	0	0	26.6 (6)	26.6	57 (2)	13.3	0	0
P	−0.1281 (1)[a]	−0.1094 (1)	0.0407 (3)	23.8 (9)	25.0 (9)	62 (2)	10.6 (8)	0 (1)	−3 (1)
F(1)[c]	0	0	−0.2018 (8)	64 (3)	64	58 (9)	32	0	0
F(2)	−0.0737 (4)	−0.0105 (5)	−0.3599 (6)	64 (4)	101 (5)	119 (8)	45 (4)	−26 (4)	−12 (5)
B	0	0	−0.3213 (15)	54 (7)	54	15 (14)	27	0	0
				Molecule 2					
Cu	$-^2/_3$	$-^1/_3$	−0.2997 (3)	26.6 (5)	26.6	52 (2)	13.3	0	0
P	−0.7673 (1)	−0.3021 (1)	−0.2557 (3)	27.0 (9)	28.5 (9)	59 (2)	15.4 (8)	0 (1)	2 (1)
F(1)	$-^2/_3$	$-^1/_3$	−0.4949 (8)	94 (5)	94	38 (9)	47	0	0
F(2)	−0.6174 (6)	−0.3613 (7)	−0.6503 (7)	130 (7)	160 (8)	146 (9)	100 (6)	3 (6)	−30 (7)
B	$-^2/_3$	$-^1/_3$	−0.6125 (23)	58 (8)	58	119 (27)	29	0	0
				Molecule 3					
Cu	$-^1/_3$	$-^2/_3$	−0.5999 (2)	25.3 (5)	25.3	52 (2)	12.65	0	0
P	−0.4247 (1)	−0.6220 (1)	−0.6411 (3)	24.2 (9)	28.2 (9)	56 (2)	14.1 (8)	−1 (1)	−2 (1)
F(1)	$-^1/_3$	$-^2/_3$	−0.3998 (8)	89 (4)	89	28 (8)	44.5	0	0
F(2)	−0.3236 (6)	−0.5943 (5)	−0.2409 (7)	118 (6)	91 (5)	116 (8)	55 (5)	14 (5)	−25 (5)
B	$-^1/_3$	$-^2/_3$	−0.2769 (23)	70 (9)	70	80 (27)	35	0	0

[a] Estimated standard deviations of the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^4$. [c] The numbering system for the fluorine atoms is as follows: F(1) is bonded to the copper atom; F(2) is terminal.

for Cu Kα radiation are only 0.589 and 0.434 for copper and phosphorus, respectively, it was not possible to select any Friedel pairs from the Cu data which showed a difference in F_c for the two models that was greater than $\sigma(F_o)$. A structure factor calculation for each model was then performed using the anomalous terms for Mo Kα radiation ($\Delta f'' = 1.266$ for Cu; 0.095 for P). Comparison of the lists of F_c for the two models yielded 16 Friedel pairs for which the difference between $|F_c(hkl)|$ and $|F_c(\bar{h}\bar{k}\bar{l})|$ for each model ranged from 5 to 40% of $|F_c|$. $|F_c|$ for these 16 reflections ranged from 20 e to 100 e compared with the minimum observable, ~4 e. Accordingly, the data crystal was remounted on the diffractometer in the same orientation as that employed for the data collection. Two reflections, $10,\bar{3},1$ and 316, together with those equivalent under the Laue symmetry $(\bar{3})$,[27] were centered on the diffractometer using monochromatized Mo $K\alpha_1$ radiation (λ 0.70930 Å) at a takeoff angle of 1.5°. The setting angles for these 12 reflections served as the basis for a least-squares refinement of the orientation of the crystal.[14] Each of the six equivalent members of the form (under $\bar{3}$)[27] for each of the 16 reflections comprising the selected Friedel pairs was collected six times using monochromatized Mo Kα radiation. The takeoff angle was 1.5°. A 5.0 × 5.0 mm counter aperture was employed, positioned 31 cm from the crystal. The scan rate was 1°/min with background counts of 40-sec duration taken at the limits of the scan for each reflection. The scan ranged from 0.80° below the $K\alpha_1$ peak to 0.75° above the $K\alpha_2$ peak. The data were processed as described above[19] yielding 576 values of $F_o{}^2$ and $\sigma(F_o{}^2)$. The value of p was 0 in order that $\sigma(F_o{}^2)$ be based on counting statistics alone. Multiple observations were averaged and $\sigma(F_o{}^2)$ was taken as the larger of σ_{av} and σ_{range}.[14,19] The averaged data were corrected for absorption (μ(Mo Kα) = 6.12 cm^{-1}) as described above. The transmission coefficients varied from 0.88 to 0.89. Reflections which are equivalent under the point group $C3$[27] were then averaged with $\sigma(F_o{}^2)$ again taken as the larger of σ_{av} and σ_{range} yielding 16 Friedel pairs. Although the differences between $F_o(hkl)$ and $F_o(\bar{h}\bar{k}\bar{l})$ were not as large as expected, an unequivocal indication was obtained for enantiomorph B (*RSS*), consistent with the results of the Hamilton ratio test.

The parameters obtained from the final cycle of refinement of enantiomorph B are given in Tables I and II along with their estimated standard deviations as obtained from the inverse matrix.[28] The derived parameters for the group atoms are reported in Table III. The root-mean-square amplitudes of vibration of the 15 atoms refined anisotropically are given in Table IV.

Description of the Structure and Discussion

The Crystal Structure. The crystal structure consists of discrete molecules of $Cu(BF_4)(P(C_6H_5)_3)_3$ situated on axes of threefold symmetry in space group $P3$. The three crystallographically independent molecules in the unit cell are located about Wyckoff positions a, b, and c. For purposes of discussion, these will be referred to as molecules 1, 2, and 3, respectively. A stereoscopic view of the molecular arrangement is presented in Figure 1 and a stereoscopic view of a typical individual molecule, molecule 1, is shown in Figure 2. A perspective view of the inner coordination sphere of the molecule is given in Figure 3. The distances and angles quoted in Figure 3 refer to a chemically averaged molecule, *vide infra*.

The absolute configuration is *RSS*,[10] with molecule 1 having the conformation *R* and molecules 2 and 3 having the conformation *S*. This may be readily verified by reference to Figure 1 and use of the "steering wheel" convention[29] as adapted for the description of the chirality of $Pt(CO)(P(C_6H_5)_3)_3$[15] and $Ir(NO)(P(C_6H_5)_3)_3$.[10] Relative to the right-handed coordinate system defined by the unit cell vectors included in Figure 1, the Cu→FBF_3 vectors (coincident with the threefold axes) of molecules 1 and 2 are pointed in the negative z direction while that for molecule 3 is opposite.

The packing of the molecules in directions normal to the trigonal axes is dominated by interactions involving the bulky $P(C_6H_5)_3$ groups. There are no abnormally short contacts between phenyl rings on different molecules, the closest approach being 2.37 Å between R2H(2) and R2H(5) of molecules 1 and 3, respectively. The phenyl groups R3 and R1 of molecules 2 and 3, respectively, exhibit a quasigraphitic stacking of the rings which can best be described in terms of a van der Waals type interaction. The rings are almost parallel, the dihedral angle being 11.4°, and the mean separation of the planes is 3.69 Å. This value may be compared with 3.35 Å for the interplane distance in graphite[30] and with a value of 3.70 Å calculated as twice the estimated half-thickness of an aromatic ring.[30] The distance of closest approach for these two phenyl rings is 3.35 Å between R3H(5) and R1H(5). This arrangement is depicted in Figure 1 where the phenyl rings involved in the graphitic packing interaction have been darkened for clarity. The quasigraphitic stacking results in the stabilization of an infinite two-dimensional framework of *S* conformers, molecules 2

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(27) J. A. Ibers, *Acta Crystallogr.*, 22, 604 (1967).

(28) See paragraph at end of paper regarding supplementary material.

(29) R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, 12, 81 (1956).

(30) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley, New York, N. Y., 1972.

Table II. Rigid-Group Parameters for $Cu(BF_4)(P(C_6H_5)_3)_3$[a]

Group	x_c	y_c	z_c	δ	ϵ	η
			Molecule 1			
R1	−0.2124 (3)	−0.2652 (3)	−0.1290 (4)	−1.261 (6)	2.384 (4)	2.060 (6)
R2	−0.1025 (2)	−0.1685 (2)	0.2916 (4)	−3.055 (4)	2.703 (3)	−1.399 (4)
R3	−0.2706 (3)	−0.0614 (3)	0.0590 (4)	−0.753 (6)	2.151 (4)	−0.071 (7)
			Molecule 2			
R1	−0.8071 (3)	−0.1841 (3)	−0.4089 (4)	0.798 (7)	−2.258 (4)	1.976 (7)
R2	−0.7221 (2)	−0.2258 (2)	0.0021 (4)	2.681 (4)	−2.755 (3)	−1.444 (4)
R3	−0.9497 (3)	−0.4608 (3)	−0.2606 (4)	−2.624 (6)	2.132 (4)	3.003 (7)
			Molecule 3			
R1	−0.5823 (3)	−0.6717 (3)	−0.4780 (4)	0.423 (6)	2.373 (4)	−0.992 (6)
R2	−0.4895 (2)	−0.6901 (2)	−0.8952 (4)	−1.157 (4)	2.762 (3)	1.689 (4)
R3	−0.3428 (2)	−0.4249 (2)	−0.6433 (4)	1.099 (5)	2.201 (4)	−3.123 (6)

[a] x_c, y_c, and z_c are the fractional coordinates of the rigid-group centers. The angles δ, ϵ, and η (radians) have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 793 (1965).

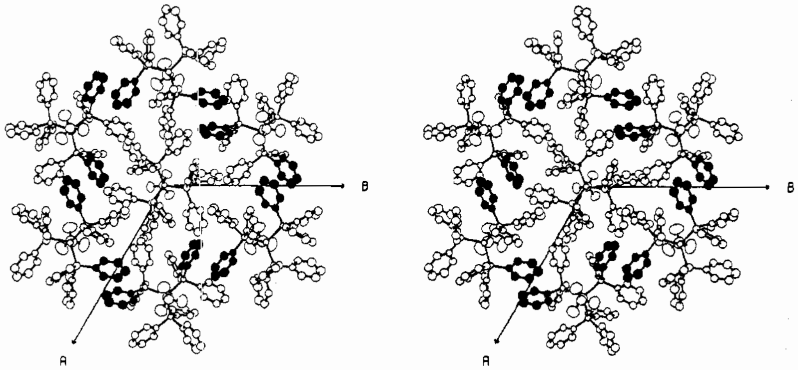

Figure 1. Stereoscopic packing diagram of $Cu(BF_4)(P(C_6H_5)_3)_3$ in its absolute configuration (*RSS*). The unit cell vectors are oriented as shown with the crystallographic *c* axis normal to the plane of the paper. The shapes of the atoms in this and following drawings represent 50% probability contours of thermal motion. The atoms of the phenyl groups involved in the graphitic packing arrangement have been darkened and the H atoms omitted for the sake of clarity.

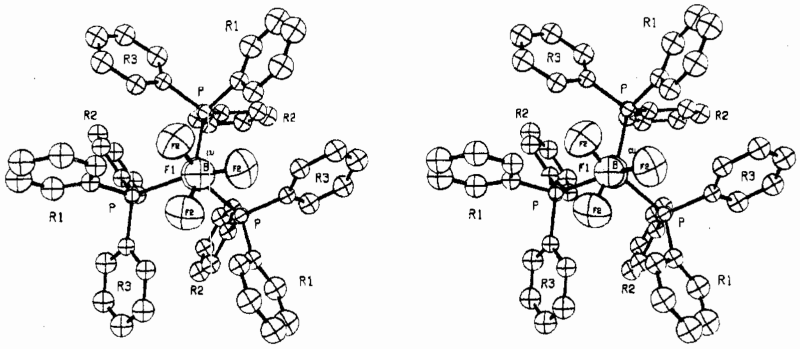

Figure 2. Stereoescopic view of a typical molecule of $Cu(BF_4)(P(C_6H_5)_3)_3$. The H atoms have been omitted for clarity.

and 3, with the voids in the network being partially filled by molecules of the *R* conformation. Because of the spatial restrictions imposed on the voids in the two-dimensional framework by the phenyl rings of molecules 2 and 3, molecules of type 1 cannot completely fill the voids. Rather, each molecule of type 1 occupies a position along the *z* axis roughly between successive layers of the two-dimensional framework. This arrangement results in each molecule of type 1 being sandwiched between two circular peripheries, each consisting of six *S* conformers stabilized by the graphitic stacking of phenyl rings and related to each other by unit translations along the *z* axis. Each periphery is composed of three molecules each of types 2 and 3 (Figure 1).

The packing in the *z* direction is controlled by intermolecular contacts involving certain phenyl protons associated with a given molecule and the terminal fluorine atoms of molecules related to it by unit translations along *z*. These distances are given in Table V. Several of the contacts are approximately equal to the sum of the van der Waals radii for hydrogen (1.2 Å) and fluorine (1.35 Å).[30] Because of the electronegativity difference between hydrogen and fluorine, we believe that these interactions are attractive and that they give rise to a stabilization of the packing in the *z* direction. Because of this stabilization and the disposition of molecules of type 1 (roughly between layers of the two-dimensional network) the crystals do not show a cleavage plane normal to [001].

Each molecule is in contact with 14 neighbors, two related to it by unit translations along the *z* axis and six each of the two remaining independent molecules, the latter being related to each other by appropriate unit translations along the *x*, *y*, and *z* axes. Only molecules of type 1, however, are surrounded by the stabilized circular peripheries described above. This can best be appreciated by reference to Figure 1 and consideration of the *z* coordinate of the center of the coordination sphere of each of the molecules. For purposes

Table III. Derived Parameters for Ring Carbon and Hydrogen Atoms of $Cu(BF_4)(P(C_6H_5)_3)_3$

Atom	x	y	z	B, Å^2
		Molecule 1		
R1C(1)[a]	−0.1752 (3)	−0.1996 (3)	−0.0520 (5)	3.0 (2)
R1C(2)	−0.1424 (3)	−0.1925 (3)	−0.1619 (5)	5.0 (2)
R1C(3)	−0.1796 (4)	−0.2580 (4)	−0.2390 (5)	6.1 (3)
R1C(4)	−0.2496 (4)	−0.3308 (4)	−0.2060 (6)	5.8 (3)
R1C(5)	−0.2823 (3)	−0.3379 (3)	−0.0961 (6)	5.5 (2)
R1C(6)	−0.2451 (4)	−0.2723 (4)	−0.0191 (4)	4.4 (2)
R2C(1)	−0.1202 (3)	−0.1476 (3)	0.1844 (4)	2.6 (1)
R2C(2)	−0.1055 (4)	−0.2131 (3)	0.1939 (4)	3.4 (2)
R2C(3)	−0.0878 (4)	−0.2341 (3)	0.3010 (5)	4.0 (2)
R2C(4)	−0.0847 (4)	−0.1895 (3)	0.3987 (4)	4.3 (2)
R2C(5)	−0.0994 (4)	−0.1239 (3)	0.3893 (4)	3.7 (2)
R2C(6)	−0.1171 (4)	−0.1030 (3)	0.2821 (5)	3.6 (2)
R3C(1)	−0.2117 (3)	−0.0858 (4)	0.0543 (5)	3.6 (2)
R3C(2)	−0.2133 (4)	−0.0340 (4)	−0.0303 (5)	4.5 (2)
R3C(3)	−0.2723 (4)	−0.0096 (4)	−0.0257 (6)	5.6 (2)
R3C(4)	−0.3295 (4)	−0.0370 (4)	0.0636 (6)	6.0 (3)
R3C(5)	−0.3279 (4)	−0.0888 (4)	0.1483 (5)	5.7 (2)
R3C(6)	−0.2689 (4)	−0.1132 (4)	0.1436 (5)	4.6 (2)
R1H(2)[b]	−0.095	−0.143	−0.184	c
R1H(3)	−0.158	−0.253	−0.314	
R1H(4)	−0.275	−0.376	−0.259	
R1H(5)	−0.330	−0.388	−0.074	
R1H(6)	−0.267	−0.277	−0.056	
R2H(2)	−0.108	−0.244	0.127	
R2H(3)	−0.078	−0.279	0.308	
R2H(4)	−0.073	−0.204	0.472	
R2H(5)	−0.097	−0.094	0.456	
R2H(6)	−0.127	−0.058	0.275	
R3H(2)	−0.174	−0.016	−0.091	
R3H(3)	−0.273	0.026	−0.084	
R3H(4)	−0.370	−0.020	0.066	
R3H(5)	−0.367	−0.107	0.209	
R3H(6)	−0.268	−0.148	0.201	
		Molecule 2		
R1C(1)	−0.7870 (3)	−0.2319 (4)	−0.3389 (5)	3.3 (2)
R1C(2)	−0.8308 (4)	−0.1964 (4)	−0.2935 (4)	4.3 (2)
R1C(3)	−0.8508 (3)	−0.1486 (4)	−0.3636 (6)	5.3 (2)
R1C(4)	−0.8271 (4)	−0.1364 (5)	−0.4790 (6)	6.9 (3)
R1C(5)	−0.7834 (4)	−0.1719 (5)	−0.5243 (4)	6.3 (3)
R1C(6)	−0.7633 (3)	−0.2196 (4)	−0.4543 (5)	4.6 (2)
R2C(1)	−0.7461 (3)	−0.2585 (3)	−0.1083 (4)	2.9 (2)
R2C(2)	−0.7646 (4)	−0.3107 (4)	−0.0139 (5)	3.9 (2)
R2C(3)	−0.7407 (4)	−0.2781 (4)	0.0965 (4)	4.7 (2)
R2C(4)	−0.6981 (4)	−0.1931 (4)	0.1125 (4)	4.8 (2)
R2C(5)	−0.6796 (4)	−0.1409 (4)	0.0181 (5)	4.4 (2)
R2C(6)	−0.7035 (4)	−0.1735 (4)	−0.0923 (4)	4.0 (2)
R3C(1)	−0.8710 (3)	−0.3926 (3)	−0.2518 (5)	3.4 (2)
R3C(2)	−0.8908 (3)	−0.4467 (4)	−0.3443 (5)	4.4 (2)
R3C(3)	−0.9696 (4)	−0.5149 (4)	−0.3531 (5)	6.0 (3)
R3C(4)	−1.0285 (3)	−0.5290 (4)	−0.2694 (7)	6.0 (3)
R3C(5)	−1.0087 (3)	−0.4750 (4)	−0.1770 (6)	5.4 (2)
R3C(6)	−0.9299 (4)	−0.4068 (4)	−0.1682 (5)	4.6 (2)
R1H(2)	−0.841	−0.205	−0.215	
R1H(3)	−0.881	−0.124	−0.333	
R1H(4)	−0.841	−0.104	−0.527	
R1H(5)	−0.767	−0.164	−0.603	
R1H(6)	−0.733	−0.244	−0.485	
R2H(2)	−0.794	−0.369	−0.025	
R2H(3)	−0.753	−0.313	0.161	
R2H(4)	−0.682	−0.171	0.188	
R2H(5)	−0.651	−0.083	0.029	
R2H(6)	−0.691	−0.138	−0.157	
R3H(2)	−0.850	−0.437	−0.401	
R3H(3)	−0.983	−0.552	−0.416	
R3H(4)	−1.082	−0.576	−0.276	
R3H(5)	−1.049	−0.485	−0.121	
R3H(6)	−0.916	−0.370	−0.105	
		Molecule 3		
R1C(1)	−0.5154 (3)	−0.6512 (4)	−0.5503 (5)	3.4 (2)
R1C(2)	−0.5788 (4)	−0.6382 (4)	−0.5865 (5)	5.2 (2)
R1C(3)	−0.6457 (4)	−0.6588 (5)	−0.5142 (6)	6.4 (3)
R1C(4)	−0.6491 (3)	−0.6922 (5)	−0.4058 (6)	5.9 (3)
R1C(5)	−0.5857 (4)	−0.7052 (4)	−0.3696 (5)	5.4 (2)
R1C(6)	−0.5189 (3)	−0.6846 (4)	−0.4418 (5)	3.9 (2)
R2C(1)	−0.4646 (3)	−0.6586 (3)	−0.7844 (4)	3.3 (2)
R2C(2)	−0.4139 (3)	−0.6188 (3)	−0.8784 (5)	3.5 (2)
R2C(3)	−0.4388 (3)	−0.6503 (3)	−0.9892 (4)	4.3 (2)
R2C(4)	−0.5143 (4)	−0.7215 (4)	−1.0060 (4)	4.3 (2)
R2C(5)	−0.5650 (3)	−0.7613 (3)	−0.9120 (5)	4.6 (2)
R2C(6)	−0.5401 (3)	−0.7299 (3)	−0.8012 (4)	3.8 (2)
R3C(1)	−0.3807 (3)	−0.5104 (2)	−0.6446 (5)	2.9 (2)
R3C(2)	−0.4007 (3)	−0.4699 (3)	−0.7280 (5)	4.6 (2)
R3C(3)	−0.3629 (4)	−0.3844 (4)	−0.7267 (5)	4.7 (2)
R3C(4)	−0.3050 (4)	−0.3393 (2)	−0.6420 (6)	5.1 (2)
R3C(5)	−0.2850 (3)	−0.3798 (3)	−0.5586 (5)	4.8 (2)
R3C(6)	−0.3228 (4)	−0.4654 (3)	−0.5599 (5)	3.7 (2)
R1H(2)	−0.576	−0.615	−0.661	
R1H(3)	−0.689	−0.650	−0.539	
R1H(4)	−0.695	−0.706	−0.357	
R1H(5)	−0.588	−0.728	−0.296	
R1H(6)	−0.476	−0.694	−0.418	
R2H(2)	−0.362	−0.570	−0.867	
R2H(3)	−0.404	−0.623	−1.054	
R2H(4)	−0.531	−0.743	−1.082	
R2H(5)	−0.616	−0.810	−0.924	
R2H(6)	−0.575	−0.757	−0.737	
R3H(2)	−0.440	−0.501	−0.786	
R3H(3)	−0.376	−0.357	−0.784	
R3H(4)	−0.279	−0.281	−0.642	
R3H(5)	−0.246	−0.349	−0.501	
R3H(6)	−0.309	−0.493	−0.503	

[a] C(1) is attached to P and the atoms of the ring are numbered sequentially with C(4) para to P. [b] The numbering system for the H atoms is analogous to that used for the C atoms with H(2) attached to C(2). [c] The thermal coefficients of the H atoms are taken as 1 Å^2 higher than the C atom to which they are attached.

of discussion, the center of the coordination sphere is taken as a point along the z axis midway between the terminal fluorine and phosphorus atoms of each molecule. These values are −0.1596, −0.4503, and −0.4410, expressed as fractions of the c-axis length, for molecules 1, 2, and 3, respectively. The centers of the coordination spheres of molecules 2 and 3 thus differ by only 0.11 Å along the z axis, reflecting the graphitic packing arrangement, while that for molecule 1 is 3.23 Å from the mean of molecules 2 and 3. Thus, the packing arrangement about molecule 1 is distinctly different from those about molecules 2 and 3. As a result of the alternation of the direction of the Cu→F vectors for molecules 2 and 3, the packing arrangements about these molecules are also distinctly different from each other. The 14 neighbors about molecule 2 consist of eight molecules whose Cu→F vectors are pointed in the negative z direction and six whose vectors are pointed in the positive z direction. The packing arrangement about molecule 3 consists of 12 neighbors whose Cu→F vectors are pointed in the negative z direction and two whose vectors are pointed in the positive z direction. Despite this dissimilarity in the packing arrangements about molecules 1, 2, and 3, the gross environments about molecules 1 and 3 are remarkably similar. This is reflected in the Cu-Cu distances for the 14 nearest neighbors about each copper atom as tabulated in Table VI. As can be seen from the table, the Cu-Cu nearest-neighbor distances

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

Atom	Min	Intermed	Max
	Molecule 1		
Cu	0.188 (2)	0.188 (2)	0.198 (3)
P	0.176 (3)	0.190 (3)	0.208 (3)
F(1)	0.199 (16)	0.292 (8)	0.292 (8)
F(2)	0.234 (9)	0.320 (9)	0.370 (9)
B	0.10 (5)	0.27 (2)	0.27 (2)
	Molecule 2		
Cu	0.188 (3)	0.189 (2)	0.189 (2)
P	0.179 (3)	0.195 (3)	0.203 (3)
F(1)	0.160 (18)	0.355 (9)	0.355 (9)
F(2)	0.275 (10)	0.365 (10)	0.477 (11)
B	0.28 (2)	0.28 (2)	0.28 (3)
	Molecule 3		
Cu	0.184 (2)	0.184 (2)	0.189 (3)
P	0.175 (4)	0.189 (3)	0.201 (3)
F(1)	0.139 (20)	0.344 (9)	0.344 (9)
F(2)	0.240 (10)	0.364 (10)	0.406 (10)
B	0.23 (4)	0.31 (2)	0.31 (2)

Table V. Intermolecular H· · ·F Contacts[a] between Molecules Related by Unit Translations along the *z* Axis in $Cu(BF_4)(P(C_6H_5)_3)_3$

Atom 1	Atom 2	Distance, Å	Molecule
F(2)	R2H(5)	2.55	1
F(2)	R2H(5)	2.79	1
F(2)	R2H(3)	2.59	2
F(2)	R2H(4)	2.83	2
F(2)	R2H(3)	2.87	2
F(2)	R2H(3)	2.55	3
F(2)	R2H(4)	2.90	3
F(2)	R2H(3)	2.94	3

[a] To 3.0 Å.

Table VI. Cu-Cu Nearest-Neighbor Distances in $Cu(BF_4)(P(C_6H_5)_3)_3$

Molecule	Distance, Å	No.	Molecule	Distance, Å	No.
		About Molecule 1			
2	11.368 (2)	3	3	12.865 (2)	3
1	11.588 (2)	2	2	13.529 (3)	3
3	11.776 (2)	3			
		About Molecule 2			
1	11.368 (2)	3	3	13.526 (3)	3
3	11.370 (2)	3	1	13.529 (3)	3
2	11.588 (2)	2			
		About Molecule 3			
2	11.370 (2)	3	1	12.865 (2)	3
3	11.588 (2)	2	2	13.526 (3)	3
1	11.776 (2)	3			

for molecules 1 and 3 are equal within experimental error while those for molecule 2 are distinctly different. Close inspection of Figure 1 reveals that molecules 1 and 3 approximately are inversion images of one another while molecule 2 bears no such relationship either to molecule 1 or to molecule 3. This identification of molecule 2 as being distinct from the other two is apparently related to the variation in the Cu-F distances, *vide infra.*

The Molecular Structure. Selected interatomic distances and angles are presented in Table VII. The coordination geometry about the Cu atoms is that of a slightly distorted tetrahedron. This may be verified by comparing the distances of the Cu atom from the bounding planes of the coordination polyhedron with those expected for an idealized ML_4 (L = generalized ligand) tetrahedron (Table VIII). The Cu-P distances range from 2.296 (2) to 2.303 (2) Å with a mean of 2.298 Å and are the longest yet found in $P(C_6H_5)_3$ complexes of Cu(I).[31] Several explanations have been advanced concerning the increase in the Cu-P bond lengths resulting from variations in coordination geometry[31] and the metal to phosphine ratio.[32] The P-C distances in the complex vary from 1.810 (5) to 1.850 (6) Å, mean 1.830 Å, and are within the usual range. There is a significant variation (7σ) in the Cu-F(1) distance of molecule 2 compared with the mean of the Cu-F(1) distances of molecules 1 and 3. The B-F(1) distances also show some variation that is not statistically significant. Variations on the order of 0.1 Å in the metal-axial ligand distances were found in the structures of the isomorphous $Ir(NO)(P(C_6H_5)_3)_3$[10] and $Pt(CO)(P(C_6H_5)_3)_3$[15] complexes. The least-squares refinement of the Ir complex was constrained with the three independent M-N and N-O distances set equal. The basis for this constraint was the appearance of a single, sharp N≡O absorption in the infrared spectrum of the complex, suggesting chemically equivalent Ir—N≡O interactions. The authors attributed the variation in the M-N and N-O distances found in an unconstrained refinement to "a quasi singularity in the least-squares matrix" or to "poor statistics in the intensity data." The variation cannot arise from a polar dispersion error[33] because a similar pattern of Cu-F(1) bond length variations was found by us during the refinement of the incorrect enantiomer of the present structure.

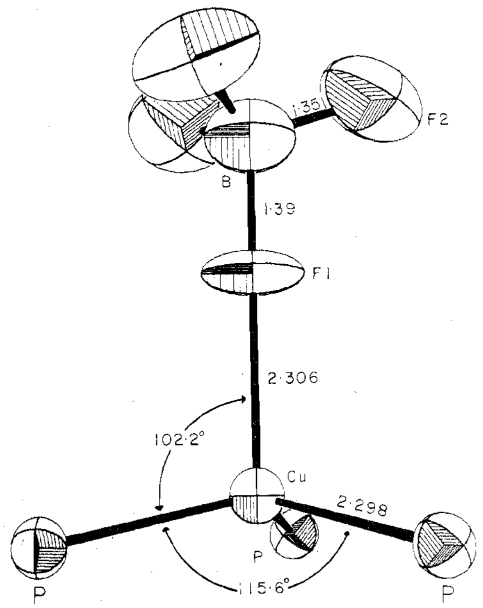

Figure 3. Perspective view of the inner coordination sphere of $Cu(BF_4)(P(C_6H_5)_3)_3$. The distances and angles given in the figure refer to a chemically averaged molecule (see text).

We emphasize that the arrangement of three independent molecules on three independent threefold axes in the space group does not *a priori* require that the metal-axial ligand interactions be identical. Rather, since molecule 2 has an environment different from the two other molecules, one might anticipate a different metal-axial ligand interaction for it. Indeed, this is the case. We therefore believe that these differences are real and do not arise from an ill-defined artifact in the data. Based on the magnitude of the variations in the distances, the differences are not chemically significant;

[31] S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, 10, 1322 (1971). See Table I therein for a tabulation of structural parameters for a series of copper-phosphine complexes.

[32] A. P. Gaughan, Jr., R. F. Ziolo, and Z. Dori, *Inorg. Chem.*, 10, 2776 (1971).

[33] D. W. J. Cruickshank and W. S. McDonald, *Acta Crystallogr.*, 23, 9 (1967).

Table VII. Interatomic Distances (Å) and Angles (deg) in $Cu(BF_4)(P(C_6H_5)_3)_3$

Atoms	Distance	Atoms	Angle
	Molecule 1		
Cu-P	2.296 (2)	P-Cu-P'	115.89 (5)
Cu-F(1)	2.339 (9)	P-Cu-F(1)	101.86 (8)
B-F(1)	1.384 (19)	F(1)-B-F(2)	109.1 (8)
B-F(2)	1.370 (8)	F(2)-B-F(2)'	109.9 (8)
P-R1C(1)	1.817 (6)	Cu-P-R1C(1)	120.9 (2)
P-R2C(1)	1.848 (6)	Cu-P-R2C(1)	106.3 (2)
P-R3C(1)	1.835 (8)	Cu-P-R3C(1)	116.1 (2)
P-P' ^{b}	3.892 (4)^a	R1C(1)-P-R2C(1)	105.5 (3)
P-F(1)	3.599 (8)^a	R1C(1)-P-R3C(1)	101.5 (3)
P-B	4.759 (15)^a	R2C(1)-P-R3C(1)	105.1 (3)
P-F(2)	4.913 (8)^a		
F(1)-F(2)	2.243 (10)^a		
F(2)-F(2)'	2.243 (12)^a		
Cu-B	3.723 (17)^a		
F(1)-R1H(2)	2.37^a		
F(2)-R1H(2)	2.71^a		
	Molecule 2		
Cu-P	2.296 (2)	P-Cu-P'	115.22 (6)
Cu-F(1)	2.261 (9)	P-Cu-F(1)	102.82 (8)
B-F(1)	1.364 (27)	F(1)-B-F(2)	109.0 (12)
B-F(2)	1.343 (11)	F(2)-B-F(2)'	109.9 (12)
P-R1C(1)	1.812 (8)	Cu-P-R1C(1)	124.0 (2)
P-R2C(1)	1.850 (6)	Cu-P-R2C(1)	107.2 (3)
P-R3C(1)	1.834 (4)	Cu-P-R3C(1)	113.3 (2)
P-P'	3.877 (4)^a	R1C(1)-P-R2C(1)	104.3 (3)
P-F(1)	3.562 (7)^a	R1C(1)-P-R3C(1)	100.3 (3)
P-B	4.702 (23)^a	R2C(1)-P-R3C(1)	106.3 (3)
P-F(2)	4.903 (9)^a		
F(1)-F(2)	2.204 (10)^a		
F(2)-F(2)'	2.199 (15)^a		
Cu-B	3.624 (26)^a		
F(1)-R1H(6)	2.55^a		
F(2)-R1H(6)	2.70^a		
	Molecule 3		
Cu-P	2.303 (2)	P-Cu-P'	115.80 (5)
Cu-F(1)	2.318 (9)	P-Cu-F(1)	101.99 (7)
B-F(1)	1.425 (27)	F(1)-B-F(2)	108.1 (11)
B-F(2)	1.342 (10)	F(2)-B-F(2)'	110.8 (11)
P-R1C(1)	1.835 (6)	Cu-P-R1C(1)	121.3 (3)
P-R2C(1)	1.810 (5)	Cu-P-R2C(1)	107.0 (3)
P-R3C(1)	1.825 (5)	Cu-P-R3C(1)	115.4 (2)
P-P'	3.902 (4)^a	R1C(1)-P-R2C(1)	105.6 (3)
P-F(1)	3.591 (7)^a	R1C(1)-P-R3C(1)	100.1 (3)
P-B	4.785 (23)^a	R2C(1)-P-R3C(1)	106.3 (3)
P-F(2)	4.939 (9)^a		
F(1)-F(2)	2.240 (10)^a		
F(2)-F(2)'	2.210 (14)^a		
Cu-B	3.743 (26)^a		
F(1)-R1H(6)	2.46^a		
F(2)-R1H(6)	2.69^a		
	Average		
Cu-P	2.298	P-Cu-P'	115.63
Cu-F(1)	2.306	P-Cu-F(1)	102.22
B-F(1)	1.391	F(1)-B-F(2)	108.7
B-F(2)	1.352	F(2)-B-F(2)'	110.2
P-R1C(1)	1.821	Cu-P-R1C(1)	122.1
P-R2C(1)	1.836	Cu-P-R2C(1)	106.8
P-R3C(1)	1.831	Cu-P-R3C(1)	114.9
		R1C(1)-P-R2C(1)	105.1
		R1C(1)-P-R3C(1)	100.6
		R2C(1)-P-R3C(1)	105.9

^{a} Nonbonded distance. ^{b} The primed symbols refer to symmetry-related atoms.

therefore the average (of three) will be used in ensuing discussions.

Of primary interest in this study is the nature of the Cu-FBF_3 interaction. The BF_4^- anion rarely coordinates to a metal. In those few complexes where a specific metal-BF_4^- interaction exists[34,35] the anion functions as a monodentate ligand. In the structure of $Cu(en)_2(BF_4)_2$[34] (en = ethylenediamine) the ligating F atoms of the "semicoordinated"[34] BF_4^- groups occupy the axial coordination sites in a tetragonally distorted octahedral arrangement at a distance of 2.56 Å from the metal. The Cu-FBF_3 distance in this complex is long compared with the Cu-F distances in CuF_2,[36] 1.93 Å (equatorial) and 2.27 Å (axial) in a tetragonally distorted octahedral arrangement, suggesting that the Cu-FBF_3 interaction is weak. By comparison the structure determination of $[Ni(en)_2(H_2O)(BF_4)][BF_4]$[35] reveals a coordinated BF_4^- group with an Ni-FBF_3 distance of 2.12 Å in a pseudooctahedral complex. The Ni-FBF_3 distance is only slightly longer than the Ni-F distance in NiF_2,[36] 1.97 Å (equatorial) and 2.02 Å (axial) again in a tetragonally distorted octahedral arrangement, which suggests that in $[Ni(en)_2(H_2O)(BF_4)]$-$[BF_4]$, the coordinated BF_4^- group functions as a normal ligand.[35] The chemically averaged Cu-F(1) distance in $Cu(BF_4)(P(C_6H_5)_3)_3$, 2.31 Å, is again long compared with the Cu-F distance in the corresponding Cu(I) halide, CuF (1.84 Å, tetrahedral coordination)[36] but is intermediate between those found in $Cu(en)_2(BF_4)_2$[34] and $[Ni(en)_2(H_2O)(BF_4)]$-$[BF_4]$.[35] Thus for the Cu-FBF_3 interaction in $Cu(BF_4)$-$(P(C_6H_5)_3)_3$ we suggest that the term "weakly coordinated" sufficiently describes the situation. We have chosen this terminology to avoid confusion with the "semicoordinated" BF_4^- groups in $Cu(en)_2(BF_4)_2$[34] because the long Cu-FBF_3 distances in that complex are presumably related to the expected tetragonal distortion in Cu(II) complexes.[37]

One may also consider the Cu-FBF_3 interaction in $Cu(BF_4)(P(C_6H_5)_3)_3$ to arise from the competition of two trigonal-planar Lewis acids, $Cu(P(C_6H_5)_3)_3^+$ [38,39] and BF_3, for the same Lewis base, F^-. The expected geometrical arrangement that will minimize steric interactions and maximize the σ donor-acceptor interaction is a linear Cu-F-B array with the F atoms of the BF_3 group staggered with respect to the P atoms of the CuP_3 group. Moreover, one expects some distortion of the trigonal-planar (sp^2) geometry of the acids toward a trigonal-pyramidal (sp^3) arrangement in response to this donor-acceptor interaction. The trend toward sp^3 hybridization would be expected to reflect the energy involved in reorganizing the planar acids to the pyramidal form.[40] However, nonbonded repulsions between the $P(C_6H_5)_3$ groups and the F atoms of the respective acids would also favor a tetrahedral arrangement for each acid-base pair. It is therefore of interest to examine the metrical details of the structure to see if they provide any information concerning the relative acceptor strengths of the two acids.

One naturally expects BF_3 to be a far stronger Lewis acid than $Cu(P(C_6H_5)_3)_3^+$ and, thus, to compete more effectively for the available electron density of the base. This would tend to favor a greater distortion toward tetrahedral geometry at the BF_3 terminus of the molecule. The angles about the B and Cu atoms (Table VII) seem to support such an explanation. However, because of the bulky nature of the Cu-

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(35) A. A. G. Tomlinson, M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J. Chem. Soc. A*, 1671 (1972).

(36) R. W. G. Wyckoff, "Crystal Structures," Vol. I, 2nd ed, Wiley, New York, N. Y., 1963.

(37) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.

(38) A. H. Lewin, R. J. Michl, P. Ganis, and U. Lepore, *J. Chem. Soc., Chem. Commun.*, 661 (1972).

(39) M. S. Weininger, G. W. Hunt, and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 1140 (1972).

(40) B. Swanson, D. F. Shriver, and J. A. Ibers, *Inorg. Chem.*, 8, 2182 (1969).

Table VIII

Distances (Å) of the Metal Atom from the Bounding Planes of the Coordination Polyhedron

Complex	Plane	Molecule 1	Molecule 2	Molecule 3	Av
$Cu(BF_4)(P(C_6H_5)_3)_3$	PP′P″ [a]	0.472 (3)	0.510 (3)	0.478 (3)	0.487
	PP′F(1)	0.868 (2)	0.847 (2)	0.866 (2)	0.860
ML_4 [b,c]	L1L2L3				0.767
$Ir(NO)(P(C_6H_5)_3)_3$ [d,e]	PP′P″	1.049 (4)	1.072 (5)	0.995 (5)	1.039
	PP′N	0.594 (5)	0.585 (4)	0.602 (5)	0.593
$Pt(CO)(P(C_6H_5)_3)_3$ [e-g]	PP′P″				0.922
	PP′C				0.673

Comparison of Bond Distances (Å) and Angles (deg)[h] in $Cu(BF_4)(P(C_6H_5)_3)_3$ and Its Trigonal Isomorphs

Complex	M–X	M–P	P–M–P	P–M–X
$Cu(BF_4)(P(C_6H_5)_3)_3$	2.31	2.30	115.6	102.2
$Ir(NO)(P(C_6H_5)_3)_3$ [d,e]	1.67	2.31	101.3	116.8
$Pt(CO)(P(C_6H_5)_3)_3$ [e,f,i]	1.84	2.36	105.7	113.0

[a] The primed symbols refer to symmetry-related atoms. [b] M = metal, X = axial ligand, P = $P(C_6H_5)_3$, L = generalized ligand. [c] Idealized polyhedron; M–L = 2.30 Å, L–M–L = 109.5°. [d] Reference 10. [e] M–X distance constrained. [f] Reference 15. [g] Atomic coordinates not supplied; distances deduced from parameters quoted in ref 10. [h] Averaged over three independent molecules. [i] Values quoted in ref 10.

$(P(C_6H_3)_3^+$ cation, it is conceivable that steric interactions between phenyl rings might limit the bending back of the $P(C_6H_5)_3$ groups. In this regard we note that one ring, R2 (Figure 2), of each $P(C_6H_5)_3$ group is disposed below the plane of the three P atoms and oriented such that one of its ortho protons lies directly above the plane of a symmetry-related ring at a distance of 2.63 Å. This distance is short compared with 3.05 Å calculated as the sum of the van der Waals radius of H and half the estimated thickness of an aromatic ring.[30] Any further bending back of the $P(C_6H_5)_3$ groups would most certainly lead to impossibly close contacts between these phenyl rings. Thus we conclude that steric interactions within the $Cu(P(C_6H_5)_3)_3^+$ cation are indeed present and that they are responsible for limiting the extent to which the cation distorts toward tetrahedral geometry.

The effects of this steric constraint on the geometry of the $Cu(P(C_6H_5)_3)_3^+$ cation are seen throughout the molecule, particularly in those structural parameters associated with the relative orientation of the two acids. Although, as expected, the Cu–F–B interaction is linear, the conformational angles about this line are not 60°, as would be required for perfectly staggered BF_3 and CuP_3 groups. Rather these conformational angles are 44.6, 52.2, and 45.5° for molecules 1, 2, and 3, respectively. This partially staggered conformation results, in part, from an intermolecular interaction involving the terminal F atoms and certain phenyl protons of the $P(C_6H_5)_3$ groups.[41] The phenyl ring designated R1 (Figure 2) is oriented such that one of its ortho protons lies close to the FBF_3^- group. These H atoms lie below the plane of the terminal F atoms at approximately the same level along the *z* axis as F(1). Their position relative to the BF_3 terminus suggests that H· · ·F(2) repulsion could inhibit the approach of the two acids to the base. The distances between these H atoms and the F atoms of the FBF_3^- group for molecules 1, 2, and 3 are given in Table VII along with the respective Cu–B distances. Although there are close contacts between the H atoms and F(1) for the three molecules, the H· · ·F(2) distances are all greater than the sum of the respective van der Waals' radii.[30] The H· · ·F(2) distances are also the same in each of the three molecules in spite of a variation of ~0.1 Å in the Cu–B distance of molecule 2 compared with the mean for molecules 1 and 3. The variation in the conformational angle over the three molecules (*vide supra*) suggests that the constant H· · ·F(2) distance results from rotation of the BF_3 terminus relative to the CuP_3 group. It also suggests that any increase in H· · ·F(2) repulsion resulting from the close approach of the two acids can, within limits, be alleviated by a rotation of the BF_3 group. Thus it seems that although steric interactions between the acids are important in determining their relative orientation, the interactions are not of sufficient magnitude to inhibit the approach of the acids to the base. It is, however, quite apparent that the Cu–F(1) interaction is weak and that in this complex, BF_3 functions as the stronger Lewis acid. With regard to the weakness of the Cu–FBF_3 interaction it can be argued that the steric constraints within the $Cu(P(C_6H_5)_3)_3^+$ cation effectively determine the "s" character of the acceptor orbital directed at the base and thus indirectly control the strength of the Cu–FBF_3 interaction.[42]

Vibrational Studies

The vibrational spectrum of the complex has been recorded in an effort to detect the small splitting that might be expected in the band arising from the Cu–F stretching motion and in the vibrational modes of the BF_4^- group as a result of variations in the Cu–F(1) distances. Both the infrared (400–1200 cm^{-1}) and Raman (25–1200 cm^{-1}) spectra of the complex were recorded at high resolution. To assist in the identification of the bands arising from the Cu–F and BF_4^- motions, the infrared and Raman spectra of the isomorphous complex $CuCl(P(C_6H_5)_3)_3$[10,11] were also recorded under identical conditions over the same spectral range. In the region 100–1200 cm^{-1},[43] bands attributable to motions of the BF_4^- group and to the Cu–F stretching motion, in addition to those arising from vibrations of the $Cu(P(C_6H_5)_3)_3^+$ group, are expected. The idealized BF_4^- anion possesses T_d symmetry and has four normal modes of vibration, two stretching motions ($\nu_1(A_1)$ and $\nu_3(F_2)$) and two deformation motions ($\nu_2(E)$ and $\nu_4(F_2)$). All four vibrations are Raman active while only ν_3 and ν_4 are infrared active. Frequency assignments for the four fundamental modes of both the $^{10}BF_4^-$ and $^{11}BF_4^-$ species, based on the infrared[44] and Raman[45] spectra of the alkali metal salts, are reproduced in

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(41) Intermolecular H· · ·F contacts between terminal F atoms of one molecule and certain phenyl protons on molecules related to it by unit translations along the *z* axis are also of importance in this regard (see Table V).

(42) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(43) The region below 100 cm^{-1} is not particularly useful because of the large number of lattice modes in this region.

(44) N. N. Greenwood, *J. Chem. Soc.*, 3811 (1959).

(45) J. Goubeau and W. Bues, *Z. Anorg. Allg. Chem.*, **268**, 221 (1952).

Table IX. Frequency Assignments[a] for Isotopically Substituted BF_4^- (cm^{-1})

Species	ν_1	ν_2	ν_3	ν_4
$^{11}BF_4^-$	769	353	984	524
$^{10}BF_4^-$	769	353	1016	529

[a] Reference 46.

Table IX.[46] Monodentate coordination of the BF_4^- group lowers the symmetry to C_{3v}, splitting each of the triply degenerate modes, ν_3 and ν_4, into two components ($F_2 \rightarrow A_1 + E$). The previously infrared-inactive modes, ν_1 and ν_2, are activated in the process.

The Raman spectra (100-1200 cm^{-1}) of the two complexes are almost perfectly superimposable with the exception of bands at 765 (w, s),[47] 355 (vw), and 176 cm^{-1} (m, s) in the spectrum of $Cu(BF_4)(P(C_6H_5)_3)_3$ and a somewhat equivocal band at ~220 cm^{-1} in the spectrum of $CuCl(P(C_6H_5)_3)_3$. The band at 765 cm^{-1} is assigned as the $\nu_1(A_1)$ mode of the BF_4^- group and the band at 355 cm^{-1} as the $\nu_2(E)$ deformation mode of the BF_4^- moiety. The band at 176 cm^{-1} is assigned to the Cu-F stretching vibration. None of the bands shows any splitting, indicating that the magnitude of the differences in the Cu-F(1) bond lengths is not sufficient to cause a detectable perturbation in the vibrational spectrum of the complex. The small shift in the ν_1 mode of the coordinated BF_4^- group relative to the value in the alkali metal salts (Table IX) and the relatively low energy of the Cu-F stretching mode suggest that the $Cu-FBF_3$ interaction is weak. This is also inferred from the length of the Cu-F(1) bond, *vide infra*.

The infrared spectra of the two complexes (400-1200 cm^{-1}) are also almost perfectly superimposable with the exception of bands at 765 (m, s), 970 (st, br), 1018 (m, br), 1088 (st, sh), and 1128 cm^{-1} (m, s) in the spectrum of $Cu(BF_4)(P(C_6H_5)_3)_3$. The band at 765 cm^{-1} is again assigned to the $\nu_1(A_1)$ mode of the coordinated BF_4^- group and the bands at 970 and 1018 cm^{-1} are assigned to the low-energy (A_1) components of the $\nu_3(A_1 + E)$ mode of coordinated $^{11}BF_4^-$ and $^{10}BF_4^-$, respectively. Similarly, the bands at 1088 and 1128 cm^{-1} are assigned to the high-energy (E) components of ν_3 for coordinated $^{11}BF_4^-$ and $^{10}BF_4^-$, respectively. The intensity ratios of the isotopically split components of $\nu_3(A_1)$ and $\nu_3(E)$ are roughly consistent with the natural abundance of ^{10}B (20%) and ^{11}B (80%) although quantitative estimates are difficult to obtain because of the large number of bands in this region of the spectrum. The isotopic splittings, 48 cm^{-1} for $\nu_3(A_1)$ and 40 cm^{-1} for $\nu_3(E)$, are as large as or slightly larger than expected for an ideal diatomic B-F oscillator. This suggests the presence of Fermi resonance between the various ν_3 components and the first overtone of ν_4.[44] The ν_4 mode, expected to be split in reduced symmetry ($A_1 + E$) and to show small isotopic splittings (Table IX), is not observed in the infrared spectrum of $Cu(BF_4)(P(C_6H_5)_3)_3$ because of the presence of strong bands in the region 500-525 cm^{-1}, attributable to $P(C_6H_5)_3$.[48] The infrared and Raman spectra are available.[28]

Comparison with Related Structures

Perhaps the most illuminating comparisons that can be made are those between $Cu(BF_4)(P(C_6H_5)_3)_3$ and its trigonal isomorphs $Ir(NO)(P(C_6H_5)_3)_3$[10] and $Pt(CO)(P(C_6H_5)_3)_3$.[15] These latter two complexes exhibit an extremely strong bonding interaction between the metal and the axial ligand. The strength of the axial interaction in these two complexes is reflected not only in the respective bond distances but also in the angles about the metal and in the distance of the metal atom from the plane of the three P atoms. The average deviation of the metal atom from the plane of the three P atoms is *ca.* 0.5 Å greater in $Ir(NO)(P(C_6H_5)_3)_3$ and $Pt(CO)(P(C_6H_5)_3)_3$ than in $Cu(BF_4)(P(C_6H_5)_3)_3$. These distances and angles are also given in Table VIII.

The angles about the metal atom in the Ir and Pt complexes are sufficiently different from those found in $Cu(BF_4)(P(C_6H_5)_3)_3$ to warrant further discussion. We have noted that the trend toward a tetrahedral arrangement for the $(P(C_6H_5)_3)_3Cu^+\cdots F^-$ pair is limited by steric constraints within the cation. Yet in the Ir and Pt complexes the bending back of the $P(C_6H_5)_3$ groups has occurred to an even greater extent than that required by tetrahedral geometry. An explanation for this apparent discrepancy is found in a comparison of the M-P-C(phenyl) angles in the Cu and Ir complexes.[49]

It is a general feature of $M-P(C_6H_5)_3$ complexes that the angles about the P atom deviate significantly from the tetrahedral value. The nature of this distortion is always such that the average of the three C-P-C angles is contracted by *ca.* 5° while the average of the three M-P-C angles is expanded to approximately the same degree relative to the tetrahedral value. Averaged M-P-C and C-P-C angles of 114.4 and 104.0°, respectively, are found over a representative sample of seven $M-P(C_6H_5)_3$ complexes exhibiting a diversity of coordination numbers and geometries.[1,7,50-54] Significant deviations in individual angles from the average are occasionally found but they generally occur in pairs, *i.e.*, one expansion and one contraction, such that the mean still conforms to the rule. The average M-P-C and C-P-C angles in $Cu(BF_4)(P(C_6H_5)_3)_3$, 114.6 and 103.9°, respectively, agree quite well with the expected values although individual pairs of M-P-C angles in the three independent molecules deviate considerably from the average (Table VII).

Because the Cu, Ir, and Pt complexes are isomorphous and very nearly isostructural they exhibit a similar orientation (Figure 2) of the phenyl rings of the $P(C_6H_5)_3$ ligands: (1) one ring, R1, whose geometric center lies above the plane of the three P atoms and is oriented such that it is in close contact with the axial ligand; (2) a second ring, R2, whose geometric center lies below the plane of the three P atoms and oriented such that it is roughly perpendicular to the plane of a symmetry related ring; (3) the third ring, R3, whose geometric center lies approximately in the plane of the three P atoms. The M-P-C angles involving the rings lying above (R1) and below (R2) the basal plane differ significantly between the Cu and Ir complexes. In $Cu(BF_4)(P(C_6H_5)_3)_3$ the rings above the basal plane, R1, are bent away from the axial ligand (average Cu-P-C angle 122.1°) because of the

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(46) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970.

(47) Abbreviations used: vw, very weak; w, weak; m, medium; st, strong; s, sharp; b, broad; sh, shoulder.

(48) It would seem possible to put forth arguments concerning the strength of the $Cu-FBF_3$ interaction based on the magnitude of the splitting of the A_1 and E components of ν_3 for each isotopic species (118 and 110 cm^{-1} for $^{11}BF_4^-$ and $^{10}BF_4^-$, respectively). However, in view of the possibility of Fermi resonance between the various components of ν_3 and the first overtone of ν_4 and the fact that ν_4 is unobserved, such arguments would be mere speculation.

(49) These particular structural parameters are not reported for $Pt(CO)(P(C_6H_5)_3)_3$.[15]

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steric bulk of the BF_4^- group while the rings below the basal plane, R2, are bent inward (average Cu-P-C angle 106.8°). This distortion is responsible for the close inter-ring contacts below the basal plane and in turn for limiting the extent to which the bending back of the $P(C_6H_5)_3$ groups occurs. In $Ir(NO)(P(C_6H_5)_3)_3$, however, the Ir-P-C angle of the rings lying above the basal plane is normal (average Ir-P-C angle 114.1°) while that involving the rings lying below the basal plane is large (average Ir-P-C angle 121.2°). It is the expansion in this angle that allows for the greater bending back of the $P(C_6H_5)_3$ groups in $Ir(NO)(P(C_6H_5)_3)_3$. If one envisions a lever and fulcrum arrangement with the P atom as the fulcrum and R1 and R2 (Figure 2) on the lever arms, then it is the steric bulk of the axial ligand in $Cu(BF_4)(P(C_6H_5)_3)_3$ which is ultimately responsible for limiting the extent to which the bending back of the $P(C_6H_5)_3$ groups occurs.

The averaged structure of $Cu(BF_4)(P(C_6H_5)_3)_3$ and its comparison with its trigonal isomorphs also provide further support for our contention that the variation in the Cu-F(1) bond length is real. We note that molecule 2 which has the shortest Cu-F(1) distance (1) has the largest P-Cu-F(1) angle, (2) shows the largest deviation of the Cu atom from the plane of the three P atoms, (3) exhibits the largest conformational angle for the BF_3 group relative to the CuP_3 moiety, and (4) shows the largest fulcrum effect at the P atom.

In conclusion we have shown that the BF_4^- group in $Cu(BF_4)(P(C_6H_5)_3)_3$ is definitely coordinated, albeit weakly. But the factors responsible for the coordination of the BF_4^- group are not clear to us. Thus the related complex with tetramethylthiourea replacing the $P(C_6H_5)_3$ ligands, $[Cu(SC(N(CH_2)_2)_2)_3][BF_4]$,[45] contains a trigonal-planar Cu(I) cation and an uncoordinated BF_4^- anion. We believe that the trigonal-planar $Cu(P(C_6H_5)_3)_3^+$ cation should be isolable under the appropriate conditions since its isoelectronic analogs, $Pt(P(C_6H_5)_3)_3$[55] and CuL_3^+ (L = ethylenethiourea,[45] tetramethylthiourea,[45] and 2-picoline[44]), have been isolated and their structures determined. Perhaps the $Cu(P(C_6H_5)_3)_3^+$ cation exists as a discrete entity in $Cu(P(C_6H_5)_3)_3{\cdot}B(C_6H_5)_4$. A structure determination of this complex is clearly in order.

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Supplementary Material Available. A listing of structure factor amplitudes and reproductions of the infrared and Raman spectra of $Cu(BF_4)(P(C_6H_5)_3)_3$ and $CuCl(P(C_6H_5)_3)_3$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1657.

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Structure of a Transition Metal Complex with a Terminal Dicyanovinylidene Ligand, $MoCl(\pi\text{-}C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$

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The structure of (dicyanovinylidene)(π-cyclopentadienyl)-*trans*-bis(trimethyl phosphite)chloromolybdenum(II), $MoCl(\pi\text{-}C_5H_5)[C{=}C(CN)_2][P(OCH_3)_3]_2$, has been determined from three-dimensional X-ray data collected by counter methods. The clear orange compound crystallizes in space group $C_{2h}^5\text{-}P2_1/n$ of the monoclinic system with four molecules in a unit cell of dimensions $a = 9.127$ (2) Å, $b = 18.515$ (2) Å, $c = 12.923$ (2) Å, and $\beta = 91.56$ (1)°. The observed and calculated densities are 1.51 (2) and 1.58 g cm^{-3}, respectively. Full-matrix least-squares refinement led to a final value of the conventional R index (on F) of 0.043 for the 3037 reflections having $F^2 > 3\sigma(F^2)$. The structure consists of discrete monomers. The coordination geometry about the metal is distorted square pyramidal. The π-cyclopentadienyl ligand occupies the apical position while the dicyanovinylidene, chloro, and trimethyl phosphite ligands occupy the basal plane. The molybdenum atom is located 0.779 (3) Å from the basal plane. The trans trimethyl phosphite ligands are disordered. Some important bond distances (in Å) are as follows: Mo-C(dicyanovinylidene), 1.833 (6); Mo-P(1), 2.461 (2); Mo-P(2), 2.470 (2); Mo-Cl, 2.467 (1). An interesting feature of the structure is that the nearly planar dicyanovinylidene ligand is bent (Mo-C(1)-C(2) = 166.6 (4)°) toward the apical cyclopentadienyl ring which, in its own right, is tilted toward the dicyanovinylidene ligand. These structural features are consistent with an attractive "through-space" ligand-ligand interaction, as well as with an asymmetric metal-ligand π-back-bonding interaction.

Introduction

The binding of cyanocarbon ligands to transition metals has begun to be extensively studied because of the potential for stabilizing unstable and even unisolable hydrocarbon derivatives by replacement of hydrogen atoms with the cyano group.[2] Another feature of cyanocarbon chemistry is the close relationship between many compounds containing a dicyanomethylene [:C(CN)$_2$] group and the corresponding compound containing an oxygen atom in place of the dicyanomethylene group.[3] In particular the dicyanovinylidene lig-

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