Complex Polymeric Cations of Copper(I) with Graphite- and Diamond-Related Lattices: Crystal Structures of Poly-tris(μ-2,5-dimethylpyrazine)dicopper(I) Hexafluorophosphate and Poly-bis(μ-2,5-dimethylpyrazine)copper(I) Hexafluorophosphate

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Yellow crystals of composition $[Cu_2(2,5\text{-me}_2pyz)_3][PF_6]_2$, **1**, and orange-red ones of composition $[Cu(2,5\text{-me}_2pyz)_2][PF_6]$, **2**, were obtained from the reaction of $Cu(ClO_4)_2\cdot 6H_2O$, KPF_6, and 2,5-dimethylpyrazine in ethanol. Single-crystal X-ray diffraction studies on both are reported. Crystals of **1** are monoclinic, $a = 7.799(2)$ Å, $b = 15.862(1)$ Å, $c = 11.225(1)$ Å, $\beta = 96.11(1)°$, $Z = 2$, and space group $P2_1/n$. The structure was solved by the Patterson method and was refined by full-matrix least squares to $R = 0.038$ and $R_w = 0.044$ for 1442 reflections with $I > 3\sigma(I)$. The compound is a two-dimensional cationic polymer with a graphite-related lattice. PF_6^- ions occupy interlayer positions and weakly interact with the copper centers. **2** crystallizes in the tetragonal system, space group $P\bar{4}n2$, with $a = 13.209(2)$ Å, $c = 9.142(2)$ Å, and $Z = 4$. The structure was solved and refined as for **1** to $R = 0.034$ and $R_w = 0.033$ for 708 reflections with $I > 3\sigma(I)$. The compound is a three-dimensional cationic polymer with a diamond-like lattice. PF_6^- ions are noncoordinating and occupy positions in lattice cavities.

Introduction

Pyrazine (1,4-diazine) and substituted pyrazines have long been known to form linear bridges between metal ions generating oligomeric species[1–6] or polymeric arrays.[5–16] All crystal structure determinations that have been reported on the polymeric materials have revealed one of two basic structural types: (i) one-dimensional extended chain or (ii) two-dimensional square lattice. Our main interest in such materials has been in the correlation of magnetic properties with structure (see for example refs 16–20); hence the possibility of generating new structural types has been of primary concern to us. The counteranions present in the

materials studied to date typically constitute the ancillary ligands binding to metal centers in monodentate[10–14,16] bidentate chelating,[5,8,9] or bridging[15] modes. We reasoned that by utilizing noncoordinating anions as the counterions in the synthesis of pyrazine complexes it should be possible to obtain materials in which the metal ions are bonded only to bridging pyrazine ligands, thus generating new polymeric cationic lattices. Any such compounds with three-dimensional frameworks would fall into the class of "scaffolding-like materials" described by Hoskins and Robson.[21] Such materials would not only have potential utility in the areas of ion-exchange and catalysis as outlined in the previous work[21] but, where transition metal ions with paramagnetic ground states are incorporated into the structure, would also be of considerable interest to chemists and physicists studying magnetic exchange effects in extended systems.[22,23]

Initially we embarked on the investigation of complexes of copper(II) employing pyrazine and methyl-substituted pyrazines as the potentially bridging ligands and hexafluorophosphate and -arsenate as counteranions. These anions are commonly used to precipitate cationic species because of their very weak ligating abilities;[24–27] hence, they were selected for this study. Complexes with the desired structural features involving cationic arrays and containing copper in the +2 oxidation state have not been isolated in this work; however, two such complexes containing copper in the +1 state have. These compounds were isolated in crystalline form suitable for single-crystal X-ray diffraction studies, the results of which are described here. The compounds, $[Cu_2(2,5\text{-me}_2pyz)_3][PF_6]_2$, **1**, and $[Cu(2,5\text{-me}_2pyz)_2][PF_6]$, **2**, exhibit infinite cationic arrays with respectively graphite-related and

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diamond-related structures. One novel feature of the study is that the two complexes were isolated from the same reaction mixture.

While cationic polymers of copper(I) with chain,[28-31] sheet,[32,33] and three-dimensional lattice structures[21,34,35] are known, they are relatively rare. Scaffolding-like materials involving cationic diamond-like frameworks with anions in lattice cavities include the copper(I) systems Cu[4,4′,4″,4‴-tetracyanotetraphenylmethane]BF$_4$·xC$_6$H$_5$NO$_2$, described by Hoskins and Robson,[21] and [Cu(NC(CH$_2$)$_4$CN)$_2$]NO$_3$, described earlier by Kinoshita et al.[34] The potential of pyrazine and substituted pyrazine ligands to form such lattices is demonstrated by the structural characterization of **2** in the present work. We are aware of one other example of a three-dimensional cationic lattice involving a pyrazine derivative, that of the quinoxaline complex [Cu$_2$-(C$_8$N$_6$N$_2$)$_3$(ClO$_4$)](ClO$_4$).[35] In this compound, the copper(I) and quinoxaline entities form a two-dimensional array. Half of the perchlorates act as bridging ligands between the sheets to generate a three-dimensional array, while the other half of the perchlorate ions are noncoordinating and occupy lattice cavities.

Experimental Section

Synthesis. To 0.847 g (4.60 mmol) of potassium hexafluorophosphate was added 20 mL of ethanol containing 10% v/v 2,2-dimethoxypropane. The potassium salt did not fully dissolve in the solvent. To the solution was added 0.858 g (2.32 mmol) of copper(II) perchlorate hexahydrate dissolved in 5 mL of the same solvent, and the mixture was stirred for 0.25 h. The potassium perchlorate which formed, and any unreacted KPF$_6$, were removed by filtration. To remove any remaining ClO$_4^-$ ions more KPF$_6$ (0.430 g, 2.34 mmol) was added to the filtrate and the mixture stirred for an additional 1 h. KClO$_4$ and excess KPF$_6$ were again removed by filtration. 2,5-Dimethylpyrazine (0.50 mL, 4.58 mmol) was added dropwise to the [Cu(PF$_6$)$_2$] solution. The reaction vessel was continuously shaken during the addition. The blue color of the solution intensified, but no precipitate formed. The solution was pumped on briefly and then transferred to a nitrogen atmosphere glovebox. The reaction flask was covered with parafilm in which pinholes were made to allow for slow evaporation of the solvent. Within 4 days the color of the solution had changed from blue to green and a yellow crystalline material formed. After another 3 days a second product in the form of red-orange crystals also began to form. The yellow and red-orange materials were shown by X-ray crystallography to be [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ and [Cu(2,5-me$_2$pyz)$_2$][PF$_6$], respectively. A third product (blue in color) also precipitated out of the solution, about 2 weeks after the initial reaction, but not in a form suitable for single-crystal X-ray diffraction studies. The blue product is believed to be a copper(II) complex on the basis of its color. Although the reaction mixture was initially stored under a nitrogen atmosphere, the copper(I) complexes were found to be sufficiently air stable that no special precautions were taken during the X-ray structural analysis.

Infrared Spectroscopy. The infrared spectrum of **1** in the range 4000–250 cm^{-1} was recorded on a Perkin-Elmer Model 598 spectrometer using samples mulled in Nujol and hexachlorobutadiene and pressed between KRS-5 plates (Harshaw Chemical Co.). Calibration was achieved using polystyrene, and frequencies are considered accurate to ±3 cm^{-1}. Crystals of **2** are very small, and the product was obtained in such low yields that it was not possible to isolate sufficient sample for bulk studies from the mixture of products.

X-ray Crystallographic Analysis. Crystallographic data for [Cu$_2$(2,5-Me$_2$pyz)$_3$][PF$_6$]$_2$, **1**, and [Cu(2,5-Me$_2$pyz)$_2$][PF$_6$], **2**, appear in Table I.

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Table I. Crystallographic Data[a]

compd	[Cu$_2$(2,5-Me$_2$pyz)$_3$]-[PF$_6$]$_2$, **1**	[Cu(2,5-Me$_2$pyz)$_2$]-[PF$_6$], **2**
formula	C$_{18}$H$_{24}$Cu$_2$F$_{12}$N$_6$P$_2$	C$_{12}$H$_{16}$CuF$_6$N$_4$P
fw	741.45	424.80
cryst system	monoclinic	tetragonal
space group	$P2_1/n$	$P\bar{4}n2$
a, Å	7.799(2)	13.209(2)
b, Å	15.862(1)	13.209(2)
c, Å	11.225(1)	9.142(2)
β, deg	96.11(1)	90
V, Å^3	1380.6(6)	1595.1(5)
Z	2	4
ρ_{calc}, g/cm^3	1.783	1.769
T, °C	21	21
radiation	Mo	Cu
λ, Å	0.710 69	1.541 78
μ, cm^{-1}	17.58	35.40
transm factors (rel)	0.91–1.00	0.90–1.00
$R(F)$	0.038	0.033
$R_w(F)$	0.032	0.034
gof	1.66	2.61

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

The final unit-cell parameters were obtained by least squares on the setting angles of 25 reflections with $2\theta = 20.6$–$31.8°$ for **1** and 35.3–81.4° for **2**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, showed only small random fluctuations for both data sets. The data were processed[36] and corrected for Lorentz and polarization effects and for absorption (empirical, based on azimuthal scans for three reflections).

The structures were both solved by the Patterson method, the coordinates of the Cu and P atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The structure analysis of **2** was initiated in the noncentrosymmetric space group $P\bar{4}n2$ on the basis of the E-statistics and the Patterson function, this choice being confirmed by the subsequent successful solution and refinement of the structure.

The asymmetric unit of **1** contains one copper atom, 1.5 dimethylpyrazine ligands (one being situated about a crystallographic inversion center), and one hexafluorophosphate anion. In **2**, the asymmetric unit contains two Cu atoms in special positions (Cu(1) and Cu(2) occupy sites having S_4 and D_2 symmetries, respectively), one dimethylpyrazine ligand, and a hexafluorophosphate anion at a site having C_2 symmetry. The PF$_6^-$ anions are disordered in both structures. Two-fold rotational disorder (about F(1)–P–F(4) in **1** and about F(4)–P–F(4) in **2**) was modeled by split-atom refinement for both complexes, with the site occupancies adjusted (but not refined) as the refinements progressed to result in approximately equal average thermal parameters for the two components of the disordered models. Attempts at constrained refinement of the population parameters resulted in anomalous thermal parameters in both cases. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were fixed in idealized positions (methyl group orientations based on difference map peaks; C–H = 0.98 Å, B_H = 1.2$B_{bonded\ atom}$). A secondary extinction correction was applied for **2**, the final value of the extinction coefficient being 2.7(3) × 10^{-6}.

Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 37. A parallel refinement of the structure **2** having the opposite polarity gave significantly higher residuals, the R and R_w ratios being 1.065 and 1.088, respectively. Final atomic coordinates (non-hydrogen) and equivalent isotropic thermal parameters are given in Tables II and III for **1** and **2**, respectively. Selected bond lengths and bond angles for both compounds are given in Table IV.

Results and Discussion

Synthesis. In this work two copper(I) compounds, **1** and **2**, were obtained from an ethanolic solution of a copper(II) precursor,

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Table II. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for Non-Hydrogen Atoms in $[Cu_2(2,5\text{-me}_2pyz)_3][PF_6]_2{}^a$

atom	x	y	z	B_{eq}	occ
Cu(1)	0.32309(8)	0.19576(4)	0.55033(5)	3.28(3)	
P(1)	−0.0642(2)	0.0972(1)	0.7295(2)	4.13(8)	
F(1)	−0.2144(5)	0.1512(3)	0.6665(4)	10.2(3)	
F(2)	0.047(2)	0.1230(8)	0.633(1)	8.3(8)	0.65
F(2A)	0.078(3)	0.159(2)	0.699(3)	12(2)	0.35
F(3)	−0.009(2)	0.1781(6)	0.804(1)	10.7(8)	0.65
F(3A)	−0.101(3)	0.135(2)	0.835(1)	11(2)	0.35
F(4)	0.0891(5)	0.0459(3)	0.7935(4)	10.2(3)	
F(5)	−0.166(1)	0.0675(8)	0.839(1)	9.6(6)	0.65
F(5A)	−0.223(2)	0.037(1)	0.719(2)	8(1)	0.35
F(6)	−0.112(2)	0.0148(5)	0.669(1)	10.5(7)	0.65
F(6A)	−0.053(3)	0.065(2)	0.589(2)	12(1)	0.35
N(1)	0.1512(5)	0.2250(2)	0.4130(3)	2.6(2)	
N(2)	−0.0566(5)	0.2628(2)	0.2024(3)	2.8(2)	
N(3)	0.4295(5)	0.0793(2)	0.5132(3)	2.8(2)	
C(1)	0.0427(6)	0.2910(3)	0.4080(4)	2.9(2)	
C(2)	−0.0587(6)	0.3085(3)	0.3020(4)	3.2(2)	
C(3)	0.0487(6)	0.1956(3)	0.2085(4)	2.7(2)	
C(4)	0.1496(6)	0.1774(3)	0.3143(4)	2.8(2)	
C(5)	0.0413(8)	0.3466(4)	0.5169(5)	5.2(3)	
C(6)	0.0574(7)	0.1431(4)	0.0993(4)	4.6(3)	
C(7)	0.5625(7)	0.0684(3)	0.4474(4)	3.1(2)	
C(8)	0.3708(6)	0.0115(3)	0.5637(4)	3.1(2)	
C(9)	0.6353(7)	0.1434(3)	0.3895(5)	4.7(3)	

$^a B_{eq} = (8/3)\pi^2 \Sigma\Sigma U_{ij}a_i{}^*a_j{}^*(a_ia_j)$.

Table III. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for Non-Hydrogen Atoms in $[Cu(2,5\text{-me}_2pyz)_2][PF_6]^a$

atom	x	y	z	B_{eq}	occ
Cu(1)	0	0	0	3.43(4)	0.25
Cu(2)	$^1/_2$	0	$^1/_4$	2.57(3)	0.25
P(1)	0.3113(1)	0.1887	$^3/_4$	3.82(5)	0.50
F(1)	0.2294(8)	0.2706	$^3/_4$	12(1)	0.30
F(1A)	0.197(1)	0.199(2)	0.712(3)	11(1)	0.40
F(2)	0.3956(7)	0.1044	$^3/_4$	10.5(8)	0.30
F(2A)	0.422(1)	0.186(2)	0.790(3)	12(2)	0.40
F(3)	0.2329(9)	0.104(1)	0.737(2)	11.1(8)	0.60
F(4)	0.2930(4)	0.1734(4)	0.9197(5)	8.5(3)	
N(1)	0.1432(3)	−0.0040(3)	0.1060(5)	2.3(2)	
N(2)	0.3489(3)	0.0015(3)	0.1753(5)	2.3(2)	
C(1)	0.1759(4)	0.0451(4)	0.2262(6)	2.4(2)	
C(2)	0.2786(3)	0.0464(3)	0.2576(9)	2.4(2)	
C(3)	0.3156(4)	−0.0496(4)	0.0588(5)	2.3(2)	
C(4)	0.2134(4)	−0.0500(4)	0.0271(6)	2.4(2)	
C(5)	0.1029(4)	0.0946(5)	0.3269(5)	3.3(2)	
C(6)	0.3882(5)	−0.1055(6)	−0.0334(5)	3.5(3)	

$^a B_{eq} = (8/3)\pi^2 \Sigma\Sigma U_{ij}a_i{}^*a_j{}^*(a_ia_j)$.

[Cu(PF$_6$)$_2$], and 2,5-dimethylpyrazine with the solvent presumably acting as a reducing agent. Previously reported examples of this type of reaction include the preparation of dibromo-(tetramethylpyrazine)dicopper(I) by refluxing an ethanol solution of copper(II) bromide and the ligand[38] and the preparation of Cu(pyz)$_2$(CF$_3$SO$_3$) from a methanolic solution of Cu(CF$_3$SO$_3$)$_2$ and pyrazine.[10] As discussed previously for the trifluoromethanesulfonate compound,[10] the formation of insoluble polymers is no doubt important in stabilizing the +1 oxidation state in **1** and **2**.

Crystal Structure and Infrared Spectrum of [Cu$_2$(2,5-me$_2$pyz)$_3$]-[PF$_6$]$_2$, 1. The atom-labeling scheme for **1** is given in Figure 1, which also shows a stereoview of the geometry about the copper ions. A comparison of the structure of **1** with that of Cu(pyz)$_2$-(CF$_3$SO$_3$)[10] is useful. The pyrazine–triflate complex consists of zigzag chains of copper(I) ions linked by bidentate bridging pyrazine ligands. The tetrahedron around the copper ion is completed by coordination to a nitrogen atom from a monodentate terminal pyrazine ligand and an oxygen atom from a monodentate terminal trifluoromethanesulfonate group. Along the chain, the terminal ligands lie alternately above and below the plane of the

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Table IV. Bond Lengths (Å) and Bond Angles (deg) Involving the Copper Coordination Sphere in $[Cu_2(2,5\text{-me}_2pyz)_3][PF_6]_2$ and $[Cu(2,5\text{-me}_2pyz)_2][PF_6]^a$

$[Cu_2(2,5\text{-me}_2pyz)_3][PF_6]_2{}^b$		$[Cu(2,5\text{-me}_2pyz)_2][PF_6]^c$	
Bonds			
Cu(1)–F(2)	2.69(1)	Cu(1)–N(1)	2.126(4)
Cu(1)–F(2A)	2.73(3)	Cu(2)–N(2)	2.110(4)
Cu(1)–N(1)	1.987(4)		
Cu(1)–N(2)'	1.971(4)		
Cu(1)–N(3)	2.085(4)		
Angles			
N(1)–Cu(1)–N(2)'	144.5(2)	N(1)–Cu(1)–N(1)^1	125.7(2)
N(1)–Cu(1)–N(3)	107.6(2)	N(1)–Cu(1)–N(1)^2	102.0(1)
N(1)–Cu(1)–F(2)	82.6(3)	N(2)–Cu(2)–N(2)^3	95.0(2)
N(1)–Cu(1)–F(2A)	93.8(5)	N(2)–Cu(2)–N(2)^4	97.0(2)
N(2)'–Cu(1)–N(3)	107.8(1)	N(2)–Cu(2)–N(2)^5	142.2(2)
N(2)'–Cu(1)–F(2)	99.6(4)		
N(2)'–Cu(1)–F(2A)	80.8(6)		
N(3)–Cu(1)–F(2)	92.3(3)		
N(3)–Cu(1)–F(2A)	104.6(8)		

^{a} Estimated standard deviations in the least significant figure are given in parentheses. ^{b} The prime symbol ' refers to the symmetry operation $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$. ^{c} Supercripts refer to symmetry operations: (1) $-x, -y, z$; (2) $-y, x, -z$; (3) $^1/_2 - y, ^1/_2 - x, ^1/_2 - z$; (4) $^1/_2 + y, x - ^1/_2, ^1/_2 - z$; (5) $1 - x, -y, z$.

bridging pyrazine molecules. The structure of [Cu$_2$(2,5-me$_2$-pyz)$_3$][PF$_6$]$_2$ may be viewed as derived from that of the pyrazine complex with the very weakly interacting PF$_6^-$ anion occupying a position similar to that occupied by the triflate group in the latter complex. The position occupied by the terminal pyrazine in Cu(pyz)$_2$(CF$_3$SO$_3$) is now occupied by bridging 2,5-me$_2$pyz, thereby yielding a two-dimensional lattice. Thus, the structure of [Cu$_2$(2,5-me$_2$pyz)$_3$][PF$_6$]$_2$ is made up of parallel puckered layers of the cation [Cu$_2$(2,5-me$_2$pyz)$_3$]$^{2+}$ in which copper(I) ions are linked by 2,5-me$_2$pyz. PF$_6^-$ anions are located between the layers and interact very weakly with the copper(I) ions through one fluorine atom. Although the Cu(1)···F(2) distance of 2.69(1) Å is approximately 0.25 Å less than the estimated sum of the van der Waals radii of copper and fluorine atoms, it is considerably greater than the value of 1.89 Å for the sum of the ionic radii of the Cu$^+$ and F$^-$ ions.[39] Within each layer the copper ions, which are three coordinate, define hexagons. Thus, except for the puckering of the layers, the structure of **1** is akin to that of an intercalated graphite. The graphite-like structure of **1** is illustrated in Figure 2 in which 2,5-me$_2$pyz groups are represented by lines and the PF$_6^-$ ions are omitted for clarity.

The copper ions are three coordinate with Cu–N bond lengths of 1.987(4), 1.971(4), and 2.085(4) Å. The mean Cu–N bond length of 2.014 Å is the same as that found in Cu(2,5-me$_2$pyz)$_2$-(CF$_3$SO$_3$) (2.015 Å).[11] The dimethylpyrazine molecules are all planar within experimental error. Their internal bonding parameters are comparable to those found in Cu(2,5-me$_2$pyz)$_2$-(CF$_3$SO$_3$).

The PF$_6^-$ groups in **1** are disordered. The two alternative positions are interconvertible through rotation about the F(1)–P(1)–F(4) axis. The disorder, and possibly steric considerations as well, may account for the large deviations of the internal bonding parameters of this group from ideal values. For a large number of complexes containing the PF$_6^-$ anion, the bonding parameters have been found to lie in the following ranges:[24,26,40–44] *trans-*

(39) Huheey, J. E. *Inorganic Chemistry: Principles of Structures and Reactivity*, 2nd ed.; Harper and Row: New York, 1978.

(40) Prout, K.; Couldwell, M. C.; Forder, R. A. *Acta Crystallogr., Sect. B* **1977**, *33*, 218.

(41) Davies, B. W.; Payne, N. C. *Can. J. Chem.* **1973**, *51*, 3477.

(42) Prout, C. K.; Cameron, T. S.; Gent, A. R. *Acta Crystallogr., Sect. B* **1972**, *28*, 32.

(43) Allegra, G.; Benedetti, E.; Pedone, C.; Holt, S. L. *Inorg. Chem.* **1971**, *10*, 667.

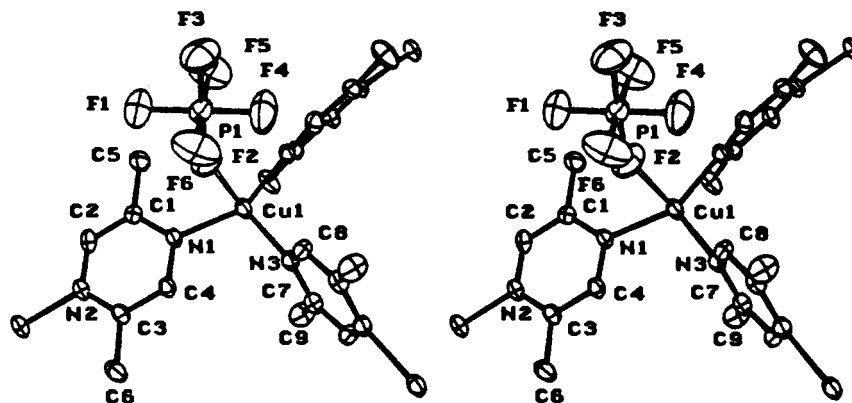(44) Davies, B. R.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 2768.

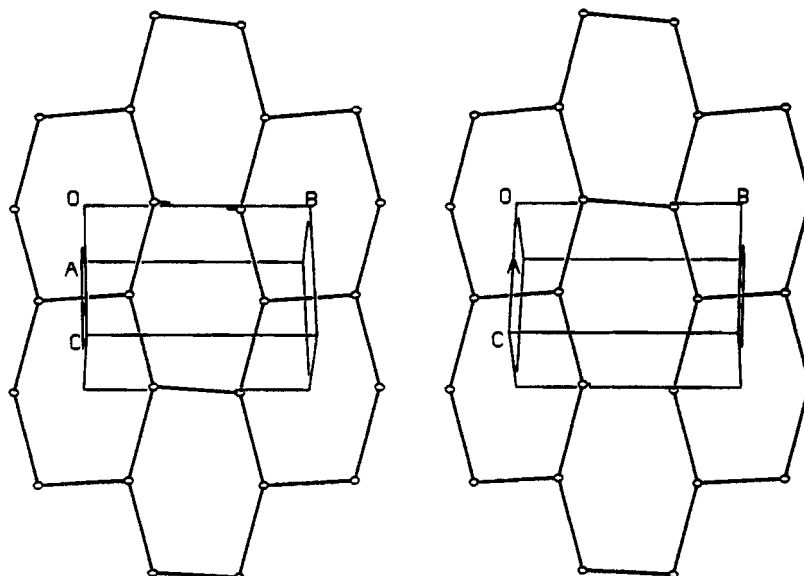**Figure 1.** Atom-labeling scheme and stereoview of the geometry about the copper ions in 1.

Figure 2. Stereoview of the structure of 1. The 2,5-me$_2$pyz groups are represented by lines, and the PF$_6^-$ ions are omitted for clarity.

F–P–F angles, 170–180°; *cis*-F–P–F angles, 85–95°; P–F bond lengths, 1.45–1.59 Å. In the compound reported here the *trans*- and *cis*-F–P–F angles lies in the ranges 160–178° and 75–106°, respectively. The P–F bond lengths also show a wide distribution with the shortest being 1.39(1) Å and the longest 1.67(2) Å.

The infrared spectrum of **1** exhibits bands that can be readily assigned to the PF$_6^-$ anions as follows:[27] 566 s (ν_4), 739 w (ν_1), 833 vs, br (ν_3) (all values are in cm^{-1}). This spectrum meets the criteria for noncoordinating PF$_6^-$ anions as described previously[27] and is consistent with the structure of **1**. The neutral ligand bands in **1** show good correspondence with published data.[11] In ref 11 attention was drawn to the potential diagnostic value of the band at 419 cm^{-1} in free 2,5-dimethylpyrazine in determining the denticity of this ligand in metal complexes. A band at 430 cm^{-1} was assigned to terminal, and bands at 451 and 461 cm^{-1} to bridging, 2,5-dimethylpyrazine in the spectra of Cu(2,5-me$_2$-pyz)$_2$(CF$_3$SO$_3$) and Cu(2,5-me$_2$pyz)(CF$_3$SO$_3$). In **1**, which contains only bridging 2,5-me$_2$pyz, the corresponding band is at 433 cm^{-1}, very close to the position of the band assigned previously to the terminal 2,5-dimethylpyrazine ligand. In spite of previous indications, one must conclude that this band cannot be used as a criterion of the bonding mode of the ligand.

Crystal Structure of [Cu(2,5-me$_2$pyz)$_2$][PF$_6$], 2. The atom-numbering scheme for **2** is shown in Figure 3, which also provides a stereoview of the geometry about the copper ions. The compound contains two crystallographically different copper(I) ions; Cu(1) and Cu(2) occupy sites having S_4 and D_2 symmetries, respectively. Both have angularly distorted CuN$_4$ chromophores which are related by a noncrystallographic C_2 axis coincident with the normal to the plane of the bridging 2,5-me$_2$pyz (Figure 3). It can also

be seen from Figure 3 that the 2,5-me$_2$pyz ligands which do not lie in the Cu(1)–Cu(2) axis are inclined upward about Cu(1) and downward about Cu(2). This feature is crucial in determining the overall three-dimensional structure of **2** as it leads to the crosslinking of a given layer with those immediately above and below it. Thus, the structure of **2** consists of a three-dimensional array of copper(I) ions linked by 2,5-me$_2$pyz molecules. PF$_6^-$ anions are located in cavities within the lattice. There is no conventional covalent bond between the cations and anions. Although the crystal system is tetragonal, the bonding is reminiscent of the diamond structure. This is illustrated in Figure 4 in which, for clarity, 2,5-me$_2$pyz and PF$_6^-$ groups are represented by lines and open circles, respectively.

The dimethylpyrazine groups in **2** are planar within experimental error, and their internal bonding parameters are very similar to those found in Cu(2,5-me$_2$pyz)$_2$(CF$_3$SO$_3$)[11] and **1**. The PF$_6^-$ groups are disordered. The two alternate orientations are interconvertible by a rotation about the F(4)–P(1) bond. The *trans*- and *cis*-F–P–F angles lie in the ranges 176–180° and 83–97°, respectively, while the P–F bond lengths lie between 1.51 and 1.58 Å. The deviations of the internal bonding parameters of the PF$_6^-$ anions in this complex from ideal values are significantly less compared to those in **1** and are in good agreement with literature values.[24,26,40–44]

Compounds **1** and **2** represent two new structural types for polymeric transition metal complexes containing pyrazine derivatives as the bridging ligands. It should be possible to synthesize compounds with these structures employing other metal(I) centers and other pyrazine derivatives. Complexes of metals in the +2 oxidation state will, of course, require twice as many counteranions
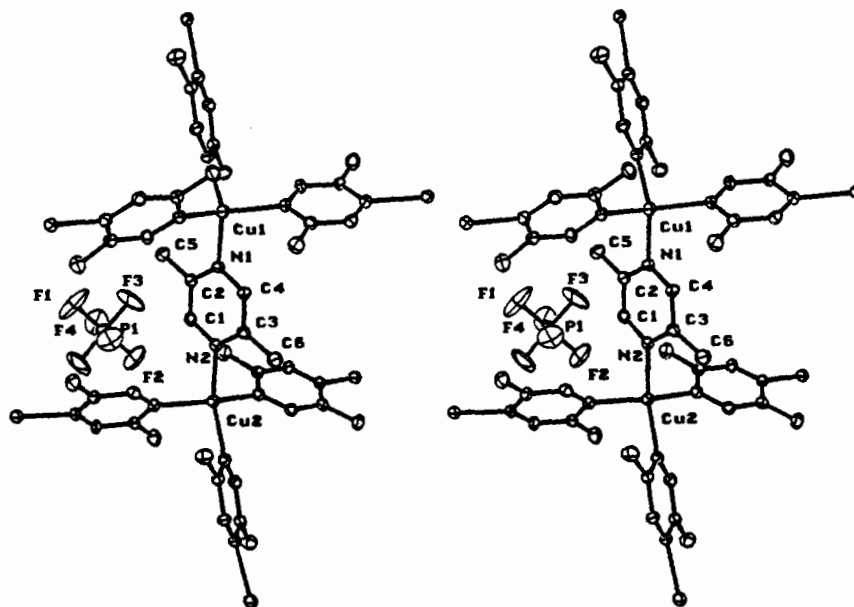
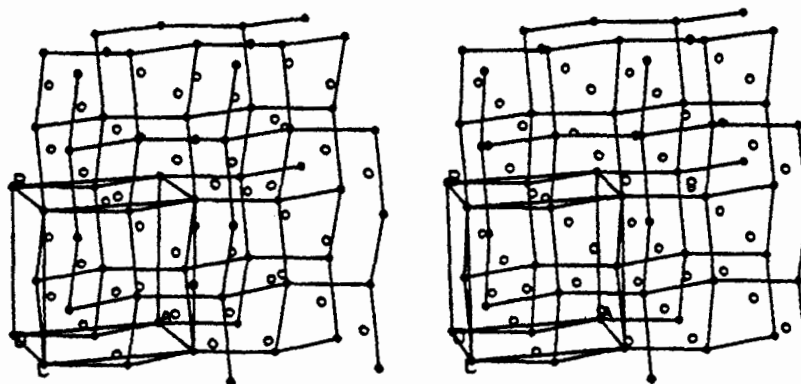**Figure 3.** Atom-labeling scheme and stereoview of the geometry about the copper ions in **2**.

Figure 4. Stereoview of the structure of **2**. For clarity, the 2,5-me$_2$pyz and PF$_6^-$ groups are represented by lines and open circles, respectively.

per metal (or anions of twice the charge). Presumably layer lattice structures, as in **1**, can accommodate additional anions between the layers and hence metal(II) complexes with this struture may not be too difficult to obtain. The synthesis of metal(II) complexes with diamond-related structures will present a greater challenge. In this type of structure the number of cavities equals the number of tetrahedral centers.[21] Hence in **2** all cavities contain one PF$_6^-$ ion. A metal(II) complex with this structure would require cavities large enough to contain two mononegative anions. Alternatively it may be possible to employ dinegative anions such as SiF$_6^{2-}$ or SnF$_6^{2-}$ (requiring only one anion per cavity) in assembling such structures. Work on these systems is continuing.

Supplementary Material Available: Tables giving crystal data and details of the structure determinations, bond lengths, bond angles, anisotropic thermal parameters, torsion angles, intermolecular contacts, least-squares planes, and hydrogen atom locations (22 pages). Ordering information is given on any current masthead page.